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Photochemistry of Iron and Ruthenium Carbonyl Complexes: Evidence for Light-Induced Loss of Carbon Monoxide and Reductive Elimination of Triethylsilane from *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$

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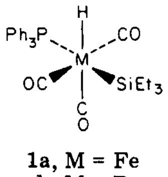
The near-UV photochemistry of $M(CO)_4PPh_3$ and $HM(SiEt_3)(CO)_3(PPh_3)$ (M = Fe, Ru) has been investigated. The $HM(SiEt_3)(CO)_3(PPh_3)$ complexes have a meridional structure with the H cis to both PPh_3 and the $SiEt_3$ and are referred to as the *cis-mer* isomer. In low-temperature (~100 K) rigid organic glasses the $M(CO)_4PPh_3$ undergoes dissociative loss of CO to form the 16-electron $M(CO)_3PPh_3$, $M(CO)_3(PPh_3)(2\text{-MeTHF})$, $M(CO)_3(PPh_3)(1\text{-}C_5H_{10})$, or *cis-mer-* and *fac*-$HM(SiEt_3)(CO)_3(PPh_3)$ complex when the organic glass is an alkane, 2-MeTHF, 1-C_5H_{10}, or Et_3SiH, respectively. The *fac*-$HM(SiEt_3)(CO)_3(PPh_3)$ complexes undergo thermal isomerization to the *cis-mer* isomer upon warmup to 298 K. Near-UV excitation of *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ at ~100 K in an organic glass gives evidence for both the loss of CO and reductive elimination of Et_3SiH. Photochemistry of the complexes at 298 K in fluid solution accords well with photoreactions observed at ~100 K in rigid media. Irradiation of *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ in a hydrocarbon solution of Ph_3SiH at 298 K results in the formation of *cis-mer*-$HM(SiPh_3)(CO)_3(PPh_3)$ and Et_3SiH with a 313-nm quantum yield of ~0.6. The process is photochemically reversed if the *cis-mer*-$HM(SiPh_3)(CO)_3(PPh_3)$ is irradiated in the presence of excess Et_3SiH. Irradiation of *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ in a hydrocarbon solution at 298 K in the presence of ^{13}CO yields both ^{13}CO-enriched $M(CO)_4PPh_3$ and ^{13}CO-enriched *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$. Irradiation of *cis-mer*-$HM(SiR_3)(CO)_3(PPh_3)$ (R = OMe, OEt) or *cis-mer*-$HRu(SiMeCl_2)(CO)_3(PPh_3)$ at 298 K in the presence of Et_3SiH yields *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$, establishing the light-induced reductive elimination of R_3SiH to occur for a wide range of R groups for these complexes.

Photoexcitation of organometallic molecules can yield reactive fragments via excited-state chemistry involving dissociative processes including extrusion of two-electron donor ligands, metal–metal bond cleavage, and reductive elimination of small molecules such as H_2 from a cis dihydride.[1] Information concerning the relative importance of such excited-state processes is necessary to develop catalytic applications of organometallic photochemistry. In this article we wish to report on the low-temperature (~100 K) photochemistry of $M(CO)_4PPh_3$ and *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ (M = Fe, Ru), **1a** and **1b**. The



1a, M = Fe
b, M = Ru

new finding is that reductive elimination of a silicon–hydride can be a quantum-efficient process that can occur competitively with loss of two-electron donor ligands even in low-temperature organic glasses. The reductive elimination of H_2 from cis dihydride is a well-known photoreaction,[2] but reductive elimination of a bulky molecule such as Et_3SiH is somewhat surprising in view of the large cage effect expected for a rigid organic glass. The photochemistry of the systems represented here is of importance in understanding the photocatalyzed hydrosilation of alkenes that can be effected by the irradiation of $M(CO)_4PPh_3$ in the presence of R_3SiH/alkene mixtures.[3]

Experimental Section

Instruments. UV–vis absorption spectra were recorded on a Cary 17 or Hewlett-Packard 8451A diode array spectrophotometer. IR absorption spectra were recorded with a Perkin-Elmer 180 grating or Nicolet 7199 Fourier transform spectrometer.

(1) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(2) Geoffroy, G. L. *Prog. Inorg. Chem.* **1980**, *27*, 123.

(3) Sanner, R. D.; Austin, R. G.; Wrighton, M. S.; Honnick, W. D.; Pittman, C. U., Jr. *Inorg. Chem.* **1979**, *18*, 928.

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Table I. IR and UV-vis Spectroscopic Data for Relevant Compounds

compd	medium (T, K)	IR ν_{CO}, cm^{-1} (rel OD)	UV-vis λ_{max}, nm (ϵ)
$Fe(CO)_4PPh_3$	3-methylpentane (100)	2052 (1.8), 1979 (1.0), 1946 (3.3)	274, 266, 260[a]
	2-MeTHF (100)	2046 (1.6), 1966 (1.0), 1938 (3.2)	
$Fe(CO)_3PPh_3$	3-methylpentane (100)	2004 (1.7), 1918 (1.0), 1884 (1.5)	
$Fe(CO)_3(PPh_3)$(2-MeTHF)	2-MeTHF (100)	1977 (1.1), 1888 (1.0), 1859 (1.6)	
$Fe(CO)_2(PPh_3)(2\text{-MeTHF})_2$	2-MeTHF (100)	1903 (1.0), 1816 (1.7)	
$Fe(CO)_3(PPh_3)_2$	3-methylpentane (298)	1895	
$Fe(CO)_3(PPh_3)(P(OCH_2)_3CEt)$	2-MeTHF (298)	1909	
$Fe(CO)_3(PPh_3)(1\text{-}C_5H_{10})$	$1\text{-}C_5H_{10}$ (100)	2013 (2.9), 1951 (1.0), 1916 (2.7)	
cis-mer-$HFe(SiEt_3)(CO)_3(PPh_3)$	3-methylpentane (298)	2032 (1.0), 1980 (6.7), 1961 (16.0)	275, 260
fac-$HFe(SiEt_3)(CO)_3(PPh_3)$	Et_3SiH (100)	2035 (1.4), 1971 (1.0)	
trans-mer-$HFe(SiEt_3)(CO)_3(PPh_3)$	3-methylpentane (298)	2061 (1.0), 1999 (2.4)	
cis-mer-$HFe(SiPh_3)(CO)_3(PPh_3)$	2-MeTHF (298)	2040 (1.0), 1985 (sh), 1972 (23.0)	280, 240
cis-mer-$HFe[Si(OMe)_3](CO)_3(PPh_3)$	3-methylpentane (298)	2052 (1.0), 1994 (sh), 1982 (~20)	
cis-mer-$HFe[Si(OEt)_3](CO)_3(PPh_3)$	3-methylpentane (298)	2051 (1.0), 1994 (sh), 1980 (~17)	
$Ru(CO)_4PPh_3$	methylcyclohexane (100)	2060 (2.2), 1984 (1.0), 1951 (3.8)	268 (sh), 259 (9400)[a]
	2-MeTHF (100)	2055 (1.8), 1978 (1.0), 1948 (3.2)	
$Ru(CO)_3PPh_3$	methylcyclohexane (100)	2027 (1.0), 1908 (1.3)	425, 342
$Ru(CO)_3(PPh_3)$(2-MeTHF)	2-MeTHF (100)	1999 (1.0), 1902 (1.1), 1871 (1.5)	
$Ru(CO)_3(PPh_3)_2$	methylcyclohexane (298)	1908	
$Ru(CO)_3(PPh_3)(P(OCH_2)_3CEt)$	methylcyclohexane (298)	1932	
$Ru(CO)_3(PPh_3)(1\text{-}C_5H_{10})$	$1\text{-}C_5H_{10}$ (100)	2035 (1.5), 1967 (1.3), 1935 (1.0)	
cis-mer-$HRu(SiEt_3)(CO)_3(PPh_3)$	methylcyclohexane (298)	2066 (1.0), 2009 (9.0), 1992 (17.5)	270 (sh), 228 (sh)
fac-$HRu(SiEt_3)(CO)_3(PPh_3)$	Et_3SiH (100)	2065 (1.0), 2003 (1.1)	
cis-mer-$HRu(SiPh_3)(CO)_3(PPh_3)$	methylcyclohexane (298)	2071 (1.0), 2022 (3.6), 2007 (9.0)	
cis-mer-$HRu(SiMeCl_2)(CO)_3(PPh_3)$	*n*-hexane (298)	2098 (1.0), 2042 (5.5), 2021 (11.0)	
cis-mer-$HRu[Si(OMe)_3](CO)_3(PPh_3)$	methylcyclohexane (298)	2086 (1.0), 2032 (4.7), 2006 (9.6)	
cis-mer-$HRu[Si(OEt)_3](CO)_3(PPh_3)$	methylcyclohexane (298)	2090 (1.0), 2025 (4.3), 2008 (9.7)	
$HRu(SiEt_3)(CO)_2(PPh_3)(P(OCH_2)_3CEt)$	methylcyclohexane (298)	1974	

[a] Temperature for these measurements was 298 K.

Low-temperature IR spectra were obtained by using a Precision Cell, Inc., Model P/N 21,000 variable-temperature cell with CaF_2 outer windows, using liquid N_2 as coolant. Care was taken to ensure that low-temperature IR results were unaffected by the source of the spectrometer. This was established by showing that spectra of intermediates could be reproduced after prolonged exposure to the interrogating beam of the spectrometer. NMR spectra were recorded with a JEOL FX90Q Fourier transform or Bruker 250- or 270-MHz Fourier transform spectrometer.

Irradiations. Photochemical reactions were carried out by using a Bausch and Lomb SP200 200-W high-pressure Hg lamp with a Pyrex water filter or a Hanovia 550-W medium-pressure Hg lamp unless otherwise noted. Quantum yields at 313 nm were measured in a merry-go-round[4] using $\sim 10^{-3}$ M *cis-mer*-$HM(SiR_3)(CO)_3(PPh_3)$ (M = Fe, R = Ph; M = Ru, R = Et) with appropriate ligand concentrations. The 3.0-mL samples in 13 × 100 nm test tubes were freeze–pump–thaw degassed prior to irradiation. The light source was a 500-W Hanovia medium-pressure Hg lamp equipped with a chemical (K_2CO_3/K_2CrO_4 solution) and glass (Corning no. 7-54) filter system to isolate the 313-nm Hg emission. Ferrioxalate actinometry[5] was used to determine light intensity, which was typically $\sim 10^{-8}$ einstein/min.

Materials. All manipulations of air-sensitive materials were carried out in a N_2-filled Vacuum Atmospheres He-63-P Dri-Lab glovebox with an attached He-493 Dri-Train or under Ar by using conventional Schlenk techniques. Methylcyclohexane (99%, Aldrich), 3-methylpentane (99+%, Aldrich), and 1-pentene (99+%, Phillips) were passed through grade 1 alumina (neutral, Woelm) and degassed prior to use. 2-Methyltetrahydrofuran (Aldrich) was freshly distilled from Na under N_2. Triphenylphosphine (Aldrich) was recrystallized three times from absolute EtOH prior to use. $Fe(CO)_5$ and $Ru_3(CO)_{12}$ were obtained from Strem Chemicals and used as received. Triethylsilane was obtained from Petrarch and used without further purification. Triphenylsilane (Aldrich) was recrystallized from hexane before use. Et_3SiD was prepared by using procedures previously described.[6] ^{13}CO (90% ^{13}C) was obtained from Cambridge Isotope Laboratories.

Literature procedures[7] were used to synthesize $M(CO)_4PPh_3$ (M = Fe, Ru). The *cis-mer*-$HM(SiR_3)(CO)_3PPh_3$ (M = Fe, Ru; R = Et, Ph) complexes were prepared by the irradiation of an

(4) Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.

(5) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(6) Seyferth, D.; Damrauer, R.; Mui, J. Y. P.; Theodore, F. J. *J. Am. Chem. Soc.* **1968**, *90*, 2344.

(7) (a) Condor, H. L.; Darensbourg, M. Y. *J. Organomet. Chem.* **1974**, *63*, 93 and references therein. (b) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *Ibid.* **1974**, *67*, C75; *J. Chem. Soc., Dalton Trans.* **1976**, 1876. (c) Albers, M. D.; Coville, N. J. *J. Organomet. Chem.* **1981**, *217*, 385.

Table II. NMR Data for Relevant Compounds[a]

compound	^{1}H,[b] δ	^{13}C,[b] δ
$Fe(CO)_4PPh_3$[c]	PPh_3, 7.38 (m)	CO, 213.9 [$^2J_{P-C}$ = 19 Hz] PPh_3, 134
cis-mer-$HFe(SiEt_3)(CO)_3(PPh_3)$[d]	PPh_3, 7.35 (m, 15) Si-Et_3, 2.50 (m, 15) Fe-H, −9.13 (d, 1) [$^2J_{P-H}$ = 25 Hz]	CO, 212.9 [$^2J_{P-C}$ = 10 Hz] PPh_3, 132.5 $SiCH_2CH_3$, 11.9 $SiCH_2CH_3$, 9.6
cis-mer-$HFe(SiPh_3)(CO)_3(PPh_3)$[d]	$SiPh_3$, 7.67 (m, 15) PPh_3, 7.32 (m, 15) Fe-H, −8.44 (d, 1) [$^2J_{P-H}$ = 25 Hz]	CO, 212.1 [$^2J_{P-C}$ = 12 Hz]
$Ru(CO)_4PPh_3$	PPh_3, 7.24 (m)	CO, 204.7 [$^2J_{P-C}$ = 5 Hz] PPh_3, 134.0
cis-mer-$HRu(SiEt_3)(CO)_3(PPh_3)$	PPh_3, 7.23 (m, 15) $SiCH_2CH_3$, 1.29 (t, 9) $SiCH_2CH_3$, 1.19 (q, 6) Ru-H, −6.89 (d, 1) [$^2J_{P-H}$ = 16 Hz]	CO, 201.7 [$^2J_{P-C}$ = 8 Hz], 199.8 br PPh_3, 133.5 $SiCH_2CH_3$, 12.2 $SiCH_2CH_3$, 9.3
cis-mer-$HRu(SiPh_3)(CO)_3(PPh_3)$	$SiPh_3$, 7.64 (m, 15) PPh_3, 7.26 (m, 15) Ru-H, −6.24 (d, 1) [$^2J_{P-H}$ = 16 Hz]	CO, 200.3 [$^2J_{P-C}$ = 10 Hz], 199.0 br

[a] All data are for benzene-d_6 solutions at 298 K unless otherwise noted. [b] Chemical shifts vs. $Si(CH_3)_4$; peak multiplicity (d = doublet, t = triplet, q = quartet, m = multiplet) and integration are given in parentheses for ^{1}H NMR. ^{13}C spectra are ^{1}H decoupled. [c] Measured as cyclohexane-d_{12} solution at 298 K. [d] The ^{1}H and ^{13}C NMR indicate that this compound is fluxional at 298 K.

alkane or toluene solution of $M(CO)_4PPh_3$ containing excess $HSiR_3$ under Ar at 298 K. Removal of excess R_3SiH and solvent left a brownish yellow oil for M = Fe and R = Et and a greenish yellow solid for M = Fe and R = Ph. In the case of M = Ru, an orange solid was isolated for both R = Et and Ph that could then be purified by recrystallization from hexane. The compound *cis*-$HFe(SiEt_3)(CO)_4$ was reacted with PPh_3 in hexane as reported by Cardaci[8] to give a second isomer of $HFe(SiEt_3)(CO)_3(PPh_3)$, a meridional isomer where the H is trans to the PPh_3. UV–vis, IR, and ^{1}H and ^{13}C NMR spectroscopies were used to characterize these compounds, and the results are listed in Tables I and II. The *cis-mer*-$HM(SiR_3)(CO)_3(PPh_3)$ (M = Fe, Ru; R = OMe, OEt) and *cis-mer*-$HRu(SiMeCl_2)(CO)_3(PPh_3)$ complexes were prepared by irradiating $M(CO)_4PPh_3$ in the presence of the R_3SiH or $MeCl_2SiH$ in alkane solvent followed by removal of solvent and excess silane under vacuum. Samples were then taken up in alkane containing Et_3SiH to study the light-induced conversion to *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$.

Results and Discussion

Photochemistry of $M(CO)_4PPh_3$. Previous studies[9,10] of $M(CO)_4$(P-donor) (M = Fe, Ru) have led to the conclusion that CO loss, not P-donor loss, dominates the excited-state chemistry of $M(CO)_4$(P-donor). In the present work we have examined the IR spectral changes accompanying near-UV irradiation of $M(CO)_4PPh_3$ in various organic glasses at ~100 K to monitor the loss of CO and to determine the nature of the photoproduct when the glass is, or contains, a two-electron donor or an oxidative addition substrate (Figures 1–3 and Tables I and II).

All data are consistent with loss of CO upon photoexcitation of $M(CO)_4PPh_3$. In alkane media the metal-containing product is a 16-electron species as indicated in eq 1.[10b] Initially, <15% conversion, the loss of one CO

$$M(CO)_4PPh_3 \xrightarrow[\sim 100\ K]{h\nu} M(CO)_3PPh_3 + CO \qquad (1)$$

(±15%) per $M(CO)_4PPh_3$ consumed is established by a quantitative comparison of the growth of the 2132 cm^{-1} absorption assigned to the free CO and the decline of absorptions due to $M(CO)_4PPh_3$.[11] In no case do we observe loss of PPh_3, since IR spectral features for the $M(CO)_4$[12] that would accompany PPh_3 loss are not observed.

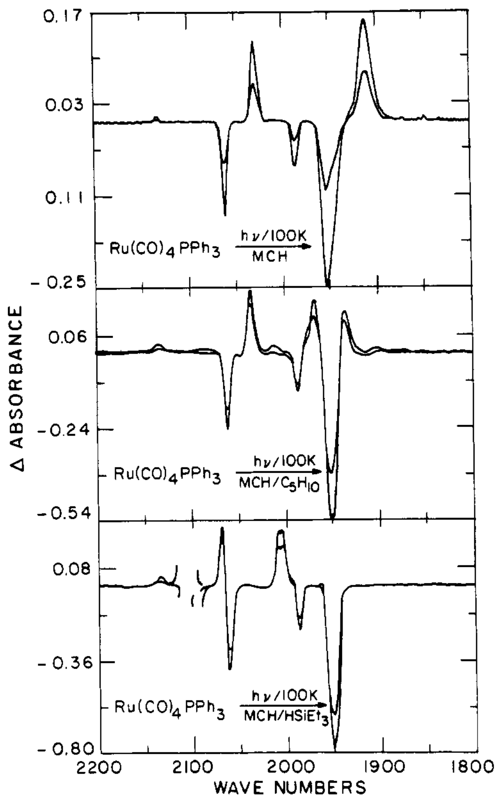


Figure 1. IR difference spectra accompanying near-UV photolysis of $Ru(CO)_4PPh_3$ at 100 K in methylcyclohexane to yield $Ru(CO)_3PPh_3$ (top), in 1-C_5H_{10} to yield $Ru(CO)_3(PPh_3)(1\text{-}C_5H_{10})$ (middle), and in methylcyclohexane/Et_3SiH (1/1) to yield *cis-mer*- and *fac*-$HRu(SiEt_3)(CO)_3(PPh_3)$.

(8) Bellachionna, G.; Cardaci, G. *Inorg. Chem.* **1982**, *21*, 3233.
(9) (a) Graff, J. L.; Sanner, R. D.; Wrighton, M. S. *Organometallics* **1982**, *1*, 837; *J. Am. Chem. Soc.* **1979**, *101*, 273.
(10) (a) Liu, D. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 898. (b) Liu, D. K.; Wrighton, M. S.; McKay, D. R.; Maciel, G. R. *Inorg. Chem.* **1984**, *23*, 212.
(11) The molar absorptivity of CO in organic glasses is ~350 ± 20% M^{-1} cm^{-1}. These data will be reported elsewhere.
(12) (a) Poliakoff, M. *J. Chem. Soc., Dalton Trans.* **1974**, 210. (b) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 93.

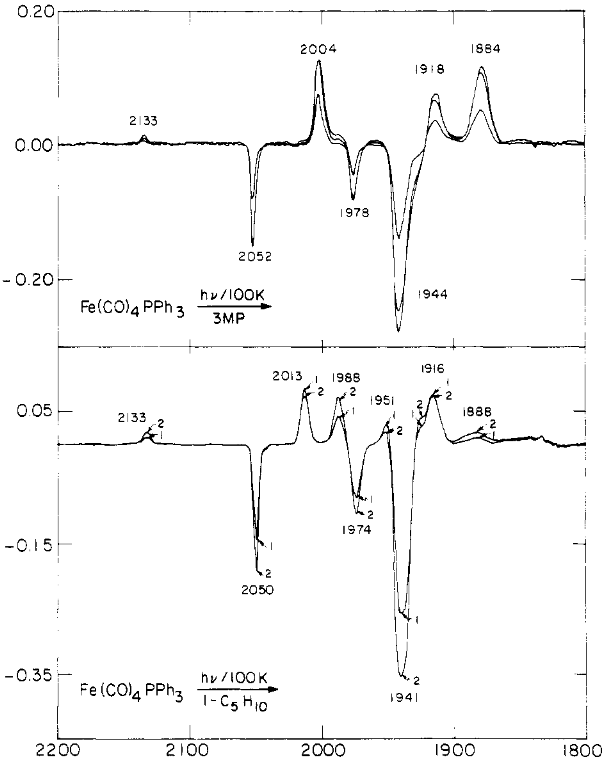


Figure 2. Top: irradiation of $Fe(CO)_4PPh_3$ in 3-methylpentane at 100 K. The negative peaks at 2052, 1978, and 1944 cm^{-1} are $Fe(CO)_4PPh_3$. The positive peaks at 2004, 1918, and 1884 cm^{-1} are $Fe(CO)_3PPh_3$, and the peak at 2133 cm^{-1} is due to free CO. Bottom: irradiation of $Fe(CO)_4PPh_3$ in 1-pentene at 100 K. The negative peaks at 2050, 1974, and 1941 are $Fe(CO)_4PPh_3$. The positive peak at 2133 cm^{-1} is due to free CO; the positive peaks at 2013, 1951, and 1916 cm^{-1} are $Fe(CO)_3(1\text{-}C_5H_{10})(PPh_3)$. The peaks at 1988 and 1888 cm^{-1} are secondary photoproducts.

The lack of a strong interaction of the $M(CO)_3PPh_3$ fragments with the alkane glasses is deduced from the relatively low energy IR absorptions in the CO stretching region compared to $M(CO)_4PPh_3$ or $HM(SiEt_3)(CO)_3(PPh_3)$ (Table I). It is also noteworthy that $Ru(CO)_3PPh_3$ shows significantly lower energy UV–vis absorption maxima than $Ru(CO)_4PPh_3$, consistent with the expected stabilization of the LUMO upon converting $Ru(CO)_4PPh_3$ to $Ru(CO)_3PPh_3$.[10b] The two-band IR spectrum for $Ru(CO)_3PPh_3$ (Figure 1) signals a C_{3v} geometry whereas $Fe(CO)_3PPh_3$ (Figure 2) appears to have a C_s symmetry, since a three-band spectrum is found in the CO stretching region. Similar differences in the geometry of other 16-electron $M(CO)_3L$ fragments have been observed.[13] Warmup of $M(CO)_3PPh_3$ in the absence of added ligands yields regeneration of $M(CO)_4PPh_3$. However, warmup of a ~100 K alkane glass containing photogenerated $M(CO)_3PPh_3$ and PPh_3 yields $M(CO)_3(PPh_3)_2$ consistent with the unsaturated nature of the $M(CO)_3PPh_3$.

In a 2-MeTHF or $1\text{-}C_5H_{10}$ glass, irradiation of $M(CO)_4PPh_3$ yields $M(CO)_3(PPh_3)(2\text{-MeTHF})$ or $M(CO)_3(PPh_3)(1\text{-}C_5H_{10})$, respectively, as evidenced by the very different IR spectral changes compared to those in the alkane glasses. For M = Fe or Ru, the differences in the IR spectral changes accompanying irradiation in an alkane compared to $1\text{-}C_5H_{10}$ are shown in Figures 1 and 2. The similarity of the pattern of absorption in the CO stretching region for the Fe and Ru complexes indicates similar structures. The 2-MeTHF is a sterically encumbered,

(13) Boxhoorn, G.; Cerfontain, M. B.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1336.

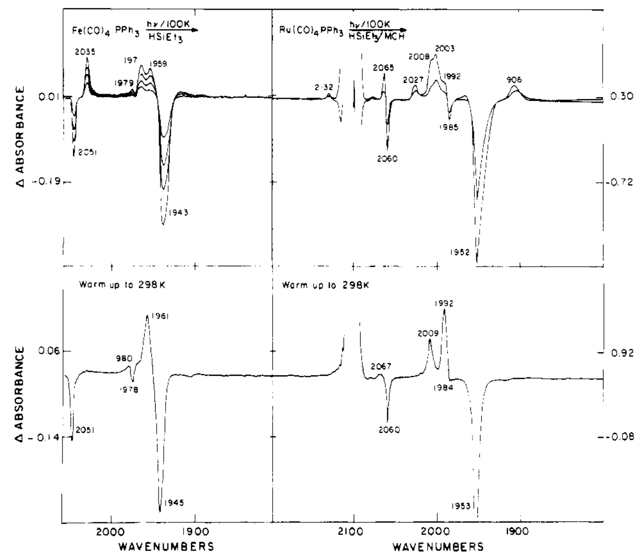
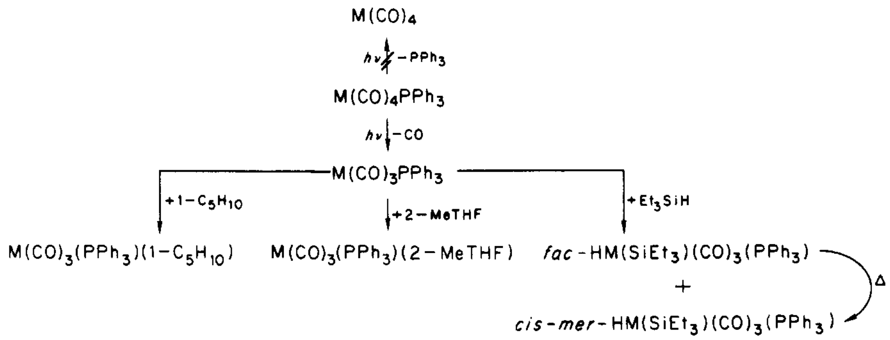


Figure 3. Left top: IR difference spectral changes accompanying UV irradiation of $Fe(CO)_4(PPh_3)$ in a $HSiEt_3$ matrix at 100 K. The negative peaks at 2051 and 1943 cm^{-1} are associated with the disappearance of $Fe(CO)_4PPh_3$. The positive peaks at 2035 and 1971 cm^{-1} are attributed to *fac*-$HFe(SiEt_3)(CO)_3(PPh_3)$ and those at 1979 and 1959 cm^{-1} are attributed to *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$, **1a**. Left bottom: warmup to 298 K yields only the *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$ isomer at 1980 and 1961 cm^{-1}. Right top: FTIR spectral changes accompanying UV irradiation of $Ru(CO)_4PPh_3$ in a $HSiEt_3$/methylcyclohexane matrix at 100 K. The negative peaks at 2060, 1985, and 1952 cm^{-1} are associated with the disappearance of $Ru(CO)_4PPh_3$. The positive peak at 2132 cm^{-1} is attributed to free CO. Other positive peaks include 2065 and 2003 cm^{-1} attributed to *fac*-$HRu(SiEt_3)(CO)_3(PPh_3)$, 2008 and 1992 cm^{-1} attributed to *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$, **1b**, and 2027 and 1906 cm^{-1} assigned to $Ru(CO)_3PPh_3$. Right bottom: warmup to 298 K yields only the *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$ isomer at 2067, 2009, and 1992 cm^{-1}. In all cases the feature at ~1980 cm^{-1} due to $M(CO)_4PPh_3$ overlaps with product peaks.

σ-donor only ligand that should form a substitution labile complex. The significantly lower energy of IR absorptions for the photoproduct in 2-MeTHF compared to the photoproduct in the alkene glass is consistent with the fact that 2-MeTHF is not a π-bonding ligand. The $M(CO)_4PPh_3$ complexes do show slightly lower energy (~6–8 cm^{-1}) absorptions in 2-MeTHF than in the alkane solvent, but the ~30 cm^{-1} lower energy absorptions for $M(CO)_3(PPh_3)(2\text{-MeTHF})$ in 2-MeTHF compared to $M(CO)_3PPh_3$ in an alkane is too great a difference to attribute to a solvent effect on the spectrum of the $M(CO)_3PPh_3$. Though the oxygen donor 2-MeTHF is a weakly bound ligand, it is probably best viewed as such toward the $M(CO)_3PPh_3$ fragment, and the species in 2-MeTHF should not be regarded as 16-electron complexes. The $M(CO)_3(PPh_3)(L)$ (L = 2-MeTHF, $1\text{-}C_5H_{10}$) complexes, and especially the Fe complexes, undergo very rapid secondary photoreaction to yield $M(CO)_2(PPh_3)L_2$ as evidenced by the appearance of additional CO absorption (2132 cm^{-1}) and new metal carbonyl absorptions.

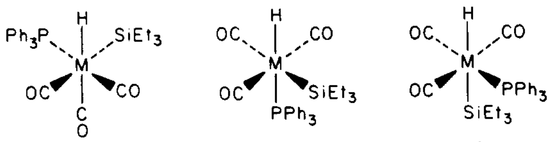
Irradiation of $M(CO)_4PPh_3$ in a low-temperature (~100 K) Et_3SiH matrix or an alkane matrix containing Et_3SiH results in reaction to form what appears to be one stable and one unstable isomer of $HM(SiEt_3)(CO)_3(PPh_3)$ (Figures 1–3). The fact that one of the products is unstable is established by warming the sample to 298 K. For both the Fe and Ru systems the warming of the photoproduct mixture to 298 K results in IR spectral changes revealing the formation of more of the stable product at the expense of the unstable product. The stable product is the same product that results upon irradiating $M(CO)_4PPh_3$ at 298

Scheme I. Photochemistry of $M(CO)_4PPh_3$ (M = Fe, Ru)



K in the presence of Et_3SiH. Cooling the 298 K product to at least 100 K in the dark does not regenerate the low-temperature photoproduct. The IR spectral changes that occur upon irradiation of $M(CO)_4PPh_3$ at ~100 K in Et_3SiH are very different from those in an alkane matrix, establishing that the $M(CO)_3PPh_3$ does react with the Et_3SiH at low temperature. As shown in Figure 3, the use of a small amount of Et_3SiH (~10% by volume) in an alkane matrix allows detection of both $Ru(CO)_3PPh_3$ and two isomers of $HRu(SiEt_3)(CO)_3(PPh_3)$. Warmup results in loss of $Ru(CO)_3PPh_3$ and growth of additional $HRu(SiEt_3)(CO)_3(PPh_3)$. Photolysis of $Ru(CO)_4PPh_3$ in an alkane/Et_3SiH (1/1) matrix yields only $HRu(SiEt_3)(CO)_3(PPh_3)$ (Figure 1). A recent report on the oxidative addition of Et_3SiH to photogenerated $Et_3SiCo(CO)_3$ at low temperature[14] and low-temperature oxidative addition of H_2[15] to $Fe(CO)_4$ or to $HCo(CO)_3$ provide precedent for the 100 K oxidative addition chemistry reported here. Interestingly, we have found that lowering the temperature by ~5 K in the case of $Fe(CO)_4PPh_3$ shows that $Fe(CO)_3PPh_3$ can be formed in neat Et_3SiH; warmup yields $HFe(SiEt_3)(CO)_3(PPh_3)$. A study to detail the thermal parameters for addition of Et_3SiH to $Fe(CO)_3PPh_3$ is underway in this laboratory.

There are several possible structures for the $HM(SiEt_3)(CO)_3(PPh_3)$ complexes as shown in **1**–**4**. Structure



2 **3** **4**

3 was recently assigned to the *thermal* product from reaction of PPh_3 with *cis*-$HFe(SiPh_3)(CO)_4$.[8] The IR bands in the CO region were found[8] to be at 2065 (s), 2000 (s), 1975 (sh) cm^{-1} in hexane with a hydride signal in the ^1H NMR showing a $^2J_{P-H}$ coupling of 47 Hz in Et_2O. Our data for the *photoproduct* from irradiation of $Fe(CO)_4PPh_3$ in the presence of Ph_3SiH is very different (Tables I and II) and at least shows that the structure of $HFe(SiPh_3)(CO)_3(PPh_3)$ formed photochemically is not that reported in ref 8. We have found the IR bands at 2061 and 1999 cm^{-1} in alkane when *cis*-$HFe(SiPh_3)(CO)_4$ is reacted thermally with PPh_3 at −20 °C in accord with data in ref 8. The IR spectra and $^2J_{P-H}$ coupling constants for $HFe(SiPh_3)(CO)_3(PPh_3)$ and $HFe(SiEt_3)(CO)_3(PPh_3)$ formed photochemically at 298 K are quite similar, and the values of $^2J_{P-H}$ for all $HM(SiR_3)(CO)_3(PPh_3)$ complexes at 298 K are most consistent with a cis disposition of the PPh_3 and the H.[16] The IR spectra in the CO region for the $HM(SiR_3)(CO)_3(PPh_3)$ complexes at 298 K are very similar to those for $HRu(SiR_3)(CO)_3(PPh_3)$ complexes characterized previously[17] as having structure **1**. We thus adopt structure **1** for $HM(SiR_3)(CO)_3(PPh_3)$ complexes formed via irradiation of $M(CO)_4PPh_3$ in the presence of R_3SiH at 298 K.

The other low-temperature photoproduct $HM(SiR_3)(CO)_3(PPh_3)$ is assigned structure **2**. The IR data are inconsistent with structure **1**[17] or **3**,[8] and we rule out **4**, since the H and SiR_3 would most likely be cis to each other upon oxidative addition in a rigid matrix. This leaves the facial isomer **2** as the other low-temperature photoproduct. The two-band IR pattern in the CO region at low temperature is consistent with the facial arrangement. To summarize, Scheme I illustrates the photochemistry of $M(CO)_4PPh_3$; all photoproducts arise from the loss of CO, not PPh_3. The quantum yield for loss of CO has been determined to exceed 10^{-1} at 298 K.[9,10]

Low-Temperature Photochemistry of 1a and 1b. The consequences of near-UV irradiation of **1** have been investigated over a wide temperature range and in a variety of media. The conclusion is that loss of CO and R_3SiH are competitive processes from the lowest excited state. The low-temperature experiments supporting this conclusion will now be detailed.

Spectral changes accompanying irradiation of **1** at 100 K provide direct evidence that light-induced loss of CO and Et_3SiH do occur (Figures 4 and 5). Two key absorptions grow as the starting material is consumed. The feature at 2132 cm^{-1} is characteristic of uncomplexed CO and the broader band at 2104 cm^{-1} is associated with the Si–H stretch of Et_3SiH. The uncomplexed CO and the Et_3SiH appear as photoproducts when the matrix is alkane, 1-C_5H_{10}, or 2-MeTHF. Both CO and Et_3SiH are detected at the lowest extent conversions measurable, and their ratio is constant at the initial stages (<15% conversion) of the reaction. Interestingly, the Ru complex appears to undergo photoisomerization from structure **1** to **2** at 100 K in an alkane matrix (Figure 5). However, irradiation of the Ru complex in the 1-C_5H_{10} (or 2-MeTHF, not shown) matrix suppresses the isomerization and there appears to be more free Et_3SiH relative to CO. These results suggest that the photoisomerization proceeds via loss of Et_3SiH from **1b** followed by back-reaction to give the same product derived from light-induced CO loss from $Ru(CO)_4PPh_3$ at low temperature. The donor matrix molecules, 1-C_5H_{10} or 2-MeTHF, presumably can saturate the $Ru(CO)_3PPh_3$ prior to reaction with the Et_3SiH to give the facial isomer of $HRu(SiEt_3)(CO)_3(PPh_3)$. The Fe complex does not show detectable isomerization in an alkane matrix, but irradi-

(14) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995.
(15) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410; **1982**, *104*, 3739.
(16) (a) Muetterties, E. L., Ed. "Transition Metal Hydrides"; Marcel Dekker: New York, 1971; p 119. (b) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1407.
(17) Pomeroy, R. K.; Hu, X. *Can. J. Chem.* **1982**, *60*, 1279.

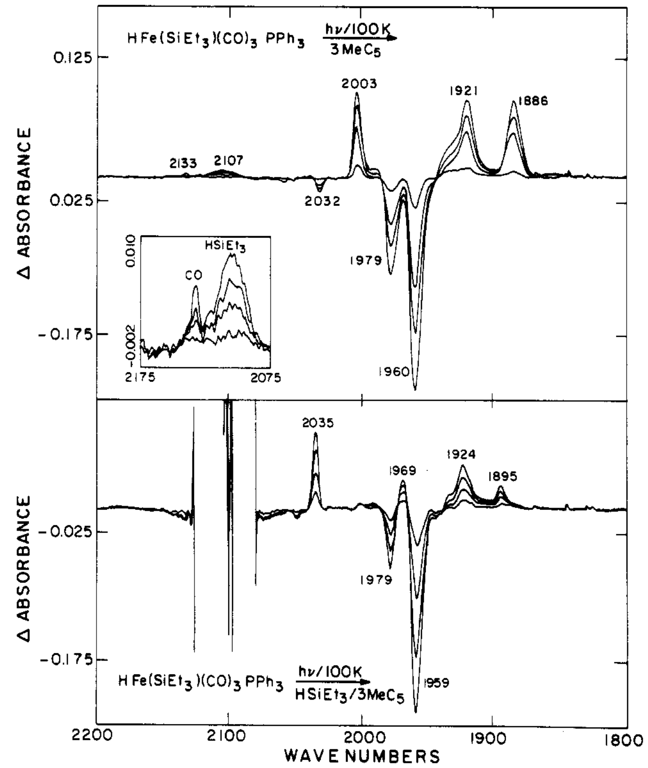


Figure 4. Top: IR difference spectral changes accompanying UV irradiation of *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$ in a 3-methylpentane matrix at 100 K. The negative peaks at 2032, 1979, and 1960 cm^{-1} are associated with loss of *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$. The positive peaks at 2133 and 2107 cm^{-1} are due to free CO and $HSiEt_3$, respectively, while those at 2003, 1921, and 1886 cm^{-1} are attributed to the 16-valence-electron $Fe(CO)_3PPh_3$. The inset shows the expansion of the free CO and $HSiEt_3$ region. Bottom: IR difference spectral changes accompanying UV irradiation of *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$ in a 1:1 mixture of $HSiEt_3$ and 3-methylpentane at 100 K. The negative peaks are associated with the disappearance of *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$, and the positive peaks at 2035 and 1969 cm^{-1} are attributed to *fac*-$HFe(SiEt_3)(CO)_3(PPh_3)$. The peaks appearing at 1924 and 1895 cm^{-1} may be due to $HFe(SiEt_3)(CO)_2(PPh_3)$, cf. text.

ation in the presence of Et_3SiH at low temperature does yield the isomer of structure **2** (Figure 4). There are clearly some subtle differences in the photochemistry of **1a** and **1b**, but establishing the reasons will be difficult. The species $Ru(CO)_3PPh_3$ and $Fe(CO)_3PPh_3$ have different structures and the orientation of the 16-electron fragment relative to the extruded Et_3SiH may be different as well. An important quantitative conclusion can be made from the appearance of Et_3SiH and CO upon photolysis of **1**. When isomerization of **1** to **2** is unimportant, the appearance of CO and Et_3SiH accounts for all of the **1** consumed in the photoreaction, within an experimental error of ±20%. This means that other possible primary photoreactions are relatively unimportant. Thus, homolysis of M–H, M–$SiEt_3$, and loss of PPh_3 are ruled out as important photoprocesses. Equation 2 appears to represent the photochemistry of **1** at ~100 K.

$$\textit{cis-mer-}HM(SiEt_3)(CO)_3(PPh_3) \xrightarrow[\sim 100\ K]{h\nu} xEt_3SiH + (1-x)CO + xM(CO)_3PPh_3 + (1-x)HM(SiEt_3)(CO)_2(PPh_3) \quad (2)$$

$$M = Fe,\ x = 0.60 \pm 0.12;\ M = Ru,\ x = 0.60 \pm 0.12$$

The light-induced appearance of Et_3SiH from **1** at low temperature is accompanied by the appearance of the metal carbonyl product expected, assuming that the resulting $M(CO)_3PPh_3$ has the same structure as produced upon irradiation of $M(CO)_4PPh_3$. In an alkane $M(CO)_3PPh_3$ is produced; in 1-C_5H_{10} $M(CO)_3(PPh_3)(1\text{-}C_5H_{10})$ is produced; and in 2-MeTHF $M(CO)_3(PPh_3)$(2-MeTHF) is formed. The formation of structure **2** upon irradiation in the presence of Et_3SiH also accords well with the formation of $M(CO)_3PPh_3$ via loss of Et_3SiH from photoexcited **1**.

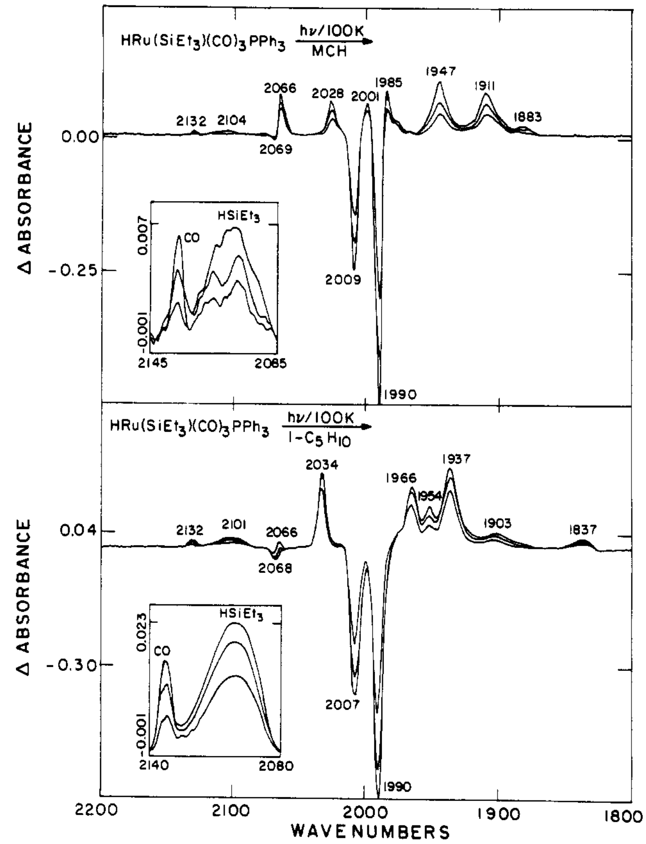


Figure 5. Top: IR difference spectral changes accompanying UV irradiation of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$ in a methylcyclohexane matrix at 100 K. The negative peaks at 2069, 2009, and 1990 cm^{-1} are associated with the disappearance of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$. The positive peaks at 2132 and 2104 cm^{-1} are due to free CO and $HSiEt_3$, respectively. Other positive peaks include 2066 and 2001 cm^{-1} attributed to *fac*-$HRu(SiEt_3)(CO)_3(PPh_3)$ and 2028 and 1911 cm^{-1} attributed mainly to the 16-valence-electron $Ru(CO)_3PPh_3$ of C_{3v} symmetry. The peaks at 1985 and 1947 cm^{-1} may be due to $HRu(SiEt_3)(CO)_2(PPh_3)$, cf. text. Inset shows the expansion of the free CO and $HSiEt_3$ region. Bottom: IR difference spectral changes accompanying UV irradiation of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$ in a 1-C_5H_{10} matrix. The negative peaks are associated with loss of *mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$. The positive peaks at 2132 and 2101 cm^{-1} are due to free CO and $HSiEt_3$, respectively. Other positive peaks include 2066 cm^{-1} attributed to *fac*-$HRu(SiEt_3)(CO)_3(PPh_3)$ and 2034, 1966 and 1937 cm^{-1} attributed to $Ru(CO)_3(PPh_3)(1\text{-}C_5H_{10})$. The peak at 1954 cm^{-1} may be due to $HRu(SiEt_3)(CO)_2(1\text{-}C_5H_{10})(PPh_3)$ or to secondary photolysis products, cf. text. Inset shows the expansion of the free CO and $HSiEt_3$ region.

Identification of the metal-containing product from loss of Et_3SiH from **1** in the various media is possible because all of the products can be made independently by irradiation of $M(CO)_4PPh_3$. The loss of CO from **1** should yield $HM(SiEt_3)(CO)_2(PPh_3)$ in unreactive matrices or $HM(SiEt_3)(CO)_2(PPh_3)(L)$ in donor (L) matrices. The IR spectral changes do show product absorptions that are not attributable to *fac*-$HM(SiEt_3)(CO)_3(PPh_3)$ or to the $M(CO)_3PPh_3$ or $M(CO)_3(PPh_3)(L)$ from the loss of Et_3SiH. For example, in Figure 4 the features that grow in at 1924 and 1895 cm^{-1} for the irradiation of **1a** in the Et_3SiH/3-methylpentane glass could be attributed to $HFe(SiEt_3)$-

$(CO)_2(PPh_3)$. The same features might, in fact, be present in the pure 3-methylpentane matrix, but strong features at 1921 and 1886 cm^{-1} due to $Fe(CO)_3PPh_3$ (Figure 2) obscure the region. The 1921 cm^{-1} feature does show a shoulder on the high-energy side, and the absorbance at 1921 cm^{-1} relative to the absorbance for the 2003 cm^{-1} band of $Fe(CO)_3PPh_3$ is higher than for $Fe(CO)_3PPh_3$ generated from $Fe(CO)_4PPh_3$. Thus, it is logical to assume that the Fe-containing product from CO loss from **1a** absorbs at $\sim$1920 cm^{-1}. The lack of higher energy absorptions for the CO loss product from **1a** in Et_3SiH vs. an alkane matrix suggests that the Et_3SiH does not oxidatively add to the coordinatively unsaturated metal.

The IR spectral changes accompanying the irradiation of **1b** at 100 K also show product features in the CO stretching region that can be attributed to the Ru-containing products derived from CO loss. For example, in Figure 5, the prominent band at 1947 cm^{-1} and that at $\sim$1985 cm^{-1} in the alkane matrix are not due to $Ru(CO)_3PPh_3$ (Figure 1) and are logically associated with the $HRu(SiEt_3)(CO)_2(PPh_3)$ species. In the $1\text{-}C_5H_{10}$ matrix the 1947 cm^{-1} feature is absent, consistent with chemistry resulting from interaction of the 16-electron $HRu(SiEt_3)(CO)_2(PPh_3)$ with the donor matrix. However, the product may not be merely a $1\text{-}C_5H_{10}$ complex, since there is the possibility of chemistry associated with the interaction of the 16-electron hydride species with the olefin. This issue requires further study. Irradiation of **1b** in a Et_3SiH matrix yields the *fac*-$HRu(SiEt_3)(CO)_3(PPh_3)$. There are features in the metal carbonyl region of the IR that indicate that at least one other product is formed, consistent with CO loss from **1b**. However, the prominent band at 1947 cm^{-1} in the alkane matrix is not present, indicating that the Et_3SiH may oxidatively add to the photogenerated $HRu(SiEt_3)(CO)_2(PPh_3)$.

Photochemistry of 1 at 298 K in Fluid Solution. The photochemistry of 1 in 298 K solution accords well with findings from the irradiation of 1 in organic glasses at $\sim$100 K. Irradiation of 1 has been carried out in the presence of various species in solution to establish the importance of reductive elimination of R_3SiH in fluid solution.

Figure 6 shows results relating to the photochemistry represented by eq 3 and 4. As the IR and ^1H NMR

$$\textit{cis-mer-}HM(SiEt_3)(CO)_3(PPh_3) + Ph_3SiH \underset{}{\overset{h\nu}{\rightleftharpoons}} \textit{cis-mer-}HM(SiPh_3)(CO)_3(PPh_3) + Et_3SiH \quad (3)$$

$$\textit{cis-mer-}HM(SiR_3)(CO)_3(PPh_3) + PPh_3 \xrightarrow{h\nu} M(CO)_3(PPh_3)_2 + R_3SiH \quad (4)$$

spectral changes show, the irradiation of 1 in the presence of Ph_3SiH results in the exchange process given in eq 3. The photochemical exchange process can be effected essentially quantitatively starting either with 1 or with the $SiPh_3$ analogue in the presence of excess Ph_3SiH or Et_3SiH, respectively. Typical photoreaction conditions were 1–5 mM of the metal complexes irradiated with near-UV excitation in hydrocarbon (alkane or C_6D_6) solution containing 10–50 mM of R_3SiH. The ^1H NMR in the hydride region establishes that total hydride concentration is conserved in the photoreaction, and IR spectral changes, especially those in the Si–H stretching region, are also consistent with quantitative exchange processes. The irradiation of 1 or the $SiPh_3$ analogues under the same conditions except in the presence of 10–50 mM PPh_3 instead of R_3SiH results in clean conversion to $M(CO)_3(PPh_3)_2$. The reactions represented by eq 3 and 4 occur with a 313-nm quantum yield of 0.6 ± 0.1 for both the Fe

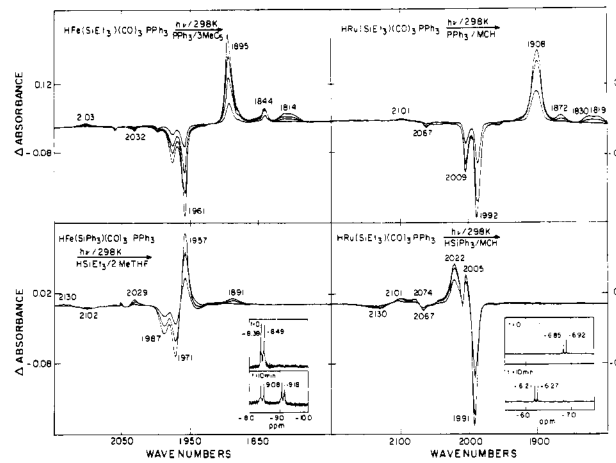


Figure 6. Left top: IR difference spectral changes upon irradiation of *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$ in the presence of excess PPh_3 in 3-methylpentane solution at 298 K. The negative peaks are associated with the loss of *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$. The positive peak at 2103 cm^{-1} is attributed to $HSiEt_3$ and that at 1895 cm^{-1} is due to $Fe(CO)_3(PPh_3)_2$. The peaks at 1844 and 1814 cm^{-1} are due to secondary photoproducts. Left bottom: IR difference spectral changes upon irradiation of *cis-mer*-$HFe(SiPh_3)(CO)_3(PPh_3)$ in the presence of excess $HSiEt_3$ in 2-MeTHF solution at 298 K. The negative peak at 2102 cm^{-1} is due to disappearance of $HSiEt_3$ and those at 1987 and 1971 cm^{-1} are due to disappearance of *cis-mer*-$HFe(SiPh_3)(CO)_3(PPh_3)$. The positive peak at 2130 cm^{-1} is attributed to $HSiPh_3$ and those at 2029 and 1957 cm^{-1} are attributed to *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$. The inset shows the ^1H NMR spectrum of *cis-mer*-$HFe(SiPh_3)(CO)_3(PPh_3)$ in $HSiEt_3/C_6D_6$ at 298 K before and after 10-min irradiation, showing only the upfield metal–hydride region. The doublet at −8.39 and −8.49 ppm is the Fe–H resonance of *cis-mer*-$HFe(SiPh_3)(CO)_3(PPh_3)$, and the new doublet at −9.08 and −9.18 ppm is attributed to the Fe–H resonance of *cis-mer*-$HFe(SiEt_3)(CO)_3(PPh_3)$. Right top: IR difference spectral changes upon irradiation of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$ in the presence of excess PPh_3 in methylcyclohexane solution at 298 K. The negative peaks are associated with the loss of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$. The positive peak at 2101 cm^{-1} is attributed to $HSiEt_3$ and that at 1908 cm^{-1} is due to $Ru(CO)_3(PPh_3)_2$. The peaks at 1872, 1830, and 1819 cm^{-1} are due to secondary photoproducts. Right bottom: IR difference spectral changes upon irradiation of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$ in the presence of excess $HSiPh_3$ in methylcyclohexane solution at 298 K. The negative peak at 2130 cm^{-1} is due to disappearance of $HSiPh_3$ and those at 2067 and 1991 cm^{-1} are due to disappearance of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$. The positive peak at 2101 cm^{-1} is attributed to $HSiEt_3$ and those at 2074, 2022, and 2005 cm^{-1} are attributed to *cis-mer*-$HRu(SiPh_3)(CO)_3(PPh_3)$. The inset shows the ^1H NMR spectrum of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$ in $HSiPh_3/C_6D_6$ at 298 K before and after 10-min irradiation, showing only the upfield metal–hydride region. The doublet at −6.85 and −6.92 ppm is the Ru–H resonance of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$, and the new doublet at −6.21 and −6.27 ppm is attributed to the Ru–H resonance of *cis-mer*-$HRu(SiPh_3)(CO)_3(PPh_3)$.

and Ru species. Thus, the chemistry not only is clean but also occurs with high quantum efficiency. Though the reactions have not been studied in detail, we note that *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ is the photoproduct from near-UV irradiation of *cis-mer*-$HM(SiR_3)(CO)_3(PPh_3)$ (M = Fe, Ru; R = OMe, OEt) or *cis-mer*-$HRu(SiMeCl_2)(CO)_3(PPh_3)$ in 298 K alkane solutions containing Et_3SiH. These examples lend credence to the conclusion that light-induced reductive elimination of R_3SiH could be important for a wide range of R.

The photochemistry represented by both eq 3 and 4 is consistent with clean and quantum efficient reductive elimination of R_3SiH from 1 and the Ph_3Si analogues in fluid solution. These data do not reveal whether there is any role for loss of CO from 1 in fluid solution. However,

Table III. Product Distribution of the Reaction of $Ru(CO)_4PPh_3$ or 1b with Different Ratios of $Ph_3SiH/P(OCH_2)_3CEt$ and Ph_3SiH/PPh_3[a]

reactant	$[Ph_3SiH]$, mM	$[P(OCH_2)_3CEt]$, mM	product ratio $HRu(SiPh_3)(CO)_3(PPh_3)$/ $Ru(CO)_3(PPh_3)(P(OCH_2)_3CEt)$[b]
$Ru(CO)_4PPh_3$	20	20	1.4
	100	20	2.5
cis-mer-$HRu(SiEt_3)(CO)_3(PPh_3)$	20	20	1.3
	100	20	2.3

reactant	$[Ph_3SiH]$, mM	$[PPh_3]$, mM	product ratio $HRu(SiPh_3)(CO)_3(PPh_3)$/ $Ru(CO)_3(PPh_3)_2$
$Ru(CO)_4PPh_3$	20	20	0.9
	100	20	2.6
cis-mer-$HRu(SiEt_3)(CO)_3(PPh_3)$	20	20	0.7
	100	20	1.8

[a] Irradiations were carried out at 298 K by using ~1-5 mM metal carbonyl complex and excess Ph_3SiH/P-donor in methylcyclohexane. Product ratios given are ±10%. [b] There is a band at 1974 cm^{-1} attributed to $HRu(SiEt_3)(CO)_2(PPh_3)(P(OCH_2)_3CEt)$, cf. text.

several experiments have been done that do show that CO loss is a process that competes with reductive elimination of R_3SiH from photoexcited 1. Direct evidence for loss of CO from 1 comes from the initial product distribution from irradiation of **1b** in the presence of ^{13}CO in toluene solution. Both ^{13}CO-enriched $Ru(CO)_4PPh_3$ and ^{13}CO-enriched **1b** are formed as products at ~10% conversion as evidenced by ^{13}C NMR. Irradiation of *cis-mer*-$HFe(SiPh_3)(CO)_3(PPh_3)$ under the same conditions gives ^{13}CO-enriched $Fe(CO)_4PPh_3$ and *cis-mer*-$HFe(SiPh_3)(CO)_3(PPh_3)$, but the lowest extent conversion where the ^{13}C NMR could be recorded was ~30%. The data indicate that CO loss is competitive with R_3SiH loss, but the relative importance could not be measured by ^{13}C NMR due to low signal-to-noise at low extent conversions. However, the ^{13}CO exchange results do accord well with the low-temperature photolysis of 1 where CO is detected directly by IR.

A puzzling finding in view of the ^{13}CO exchange results is that the photolysis of 1 in the presence of PPh_3 does not yield any detectable products other than $M(CO)_3(PPh_3)_2$. It is possible that the CO substitution product $HM(SiEt_3)(CO)_2(PPh_3)_2$ is very labile with respect to thermal elimination of Et_3SiH, owing to steric crowding. Thus, primary loss of CO from 1 would be a route to $M(CO)_3(PPh_3)_2$ via the sequence represented by eq 5–8. Of course,

$$cis\text{-}mer\text{-}HM(SiR_3)(CO)_3(PPh_3) \underset{\Delta,\ +CO}{\overset{h\nu,\ -CO}{\rightleftarrows}} HM(SiR_3)(CO)_2(PPh_3) \quad (5)$$

$$HM(SiR_3)(CO)_2(PPh_3) + PPh_3 \overset{\Delta}{\rightleftarrows} HM(SiR_3)(CO)_2(PPh_3)_2 \quad (6)$$

$$HM(SiR_3)(CO)_2(PPh_3)_2 \overset{\Delta}{\rightleftarrows} M(CO)_2(PPh_3)_2 + R_3SiH \quad (7)$$

$$M(CO)_2(PPh_3)_2 + CO \rightarrow M(CO)_3(PPh_3)_2 \quad (8)$$

$M(CO)_3(PPh_3)_2$ formation occurs, at least in part, via prompt reductive elimination of R_3SiH from 1 to form $M(CO)_3PPh_3$ that can be scavenged by PPh_3. It is possible that $HM(SiR_3)(CO)_2(PPh_3)_2$ does not occur because PPh_3 is incapable of capturing $HM(SiR_3)(CO)_2(PPh_3)$ (eq 6) in competition with back-reaction with the photoejected CO. Irradiation of **1b** in the presence of a less sterically demanding P-donor, $P(OCH_2)_3CEt$, yields $Ru(CO)_3(PPh_3)(P(OCH_2)_3CEt)$ and apparently substitution of a CO. A band is observed in the IR at ~1974 cm^{-1} that we assign to $HRu(SiEt_3)(CO)_2(PPh_3)(P(OCH_2)_3CEt)$. The ^1H NMR in the hydride region shows new products when **1b** is irradiated in the presence of $P(OCH_2)_3CEt$, but the spectrum is complicated, suggesting several isomers and secondary photoproducts are formed. While the $P(OCH_2)_3CEt$ photosubstitution products have not been fully characterized, the irradiation at **1b** in the presence of $P(OCH_2)_3CEt$ does at least confirm a role for CO loss from photoexcited **1b**.

The light-induced incorporation of ^{13}CO into 1 and the CO photosubstitution by $P(OCH_2)_3CEt$ raises the issue of whether loss of CO from 1 can play a role in the R_3SiH exchange chemistry represented by eq 3. The point is that CO loss from 1 in the presence of Ph_3SiH could yield exchange via an oxidative addition/reductive elimination mechanism as indicated in eq 9 and 10 followed by uptake

$$HM(SiEt_3)(CO)_2(PPh_3) + Ph_3SiH \rightleftarrows H_2M(SiEt_3)(SiPh_3)(CO)_2(PPh_3) \quad (9)$$

$$H_2M(SiEt_3)(SiPh_3)(CO)_2(PPh_3) \rightleftarrows HM(SiPh_3)(CO)_2(PPh_3) + Et_3SiH \quad (10)$$

of CO released in the primary step to complete the exchange chemistry (eq 11). We do find that irradiation of

$$HM(SiPh_3)(CO)_2(PPh_3) + CO \rightarrow cis\text{-}mer\text{-}HM(SiPh_3)(CO)_3(PPh_3) \quad (11)$$

cis-mer-$HM(SiPh_3)(CO)_3(PPh_3)$ in the presence of Et_3SiD does *not* give a quantitative yield of Ph_3SiH and the *cis-mer*-$DM(SiEt_3)(CO)_3(PPh_3)$ that would be expected for exchange via a simple loss of Ph_3SiH followed by oxidative addition of Et_3SiD. Rather, the ^2H and ^1H NMR data show formation of both Ph_3SiD and Ph_3SiH along with some Et_3SiH. The total amount of Ph_3SiH and Et_3SiH equals (±15%) the initial amount of *cis-mer*-$HM(SiPh_3)(CO)_3(PPh_3)$. The M-containing products include both *cis-mer*-$DM(SiEt_3)(CO)_3(PPh_3)$ and *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ as determined by ^2H and ^1H NMR, respectively. No *cis-mer*-$DM(SiPh_3)(CO)_3(PPh_3)$ could be detected in the ^2H NMR, possibly because there is an excess of Et_3SiD. In any event, the distribution of photoproducts in the presence of Et_3SiD demands a component of a mechanism other than one beginning with the light-induced loss of Ph_3SiH. The process represented by eq 9 and 10 could lead to the D/H scrambling, but other mechanisms for the scrambling are not easily ruled out with the available data. For example, concerted four-center exchange processes, binuclear, and free radical processes could also account for the observed results. However, we do not observe the irreproducibility in quantum yields often found for radical reactions and we have not detected products that could arise from binuclear reactions such as M–M bonded complexes. While it is difficult to rule out the four-center mechanisms, we favor the process represented by eq 9 and 10 because CO loss from 1 is a primary photoprocess. The conservation of protons in the hydride region of the ^{1}H NMR during the light-induced R_3SiH exchange reactions rules out other reductive elimination processes (such as H_2 or disilane formation) from a species such as the dihydride in eq 9 and 10.

Reactivity of the Intermediate from Reductive Elimination of Et_3SiH from 1 Compared to Intermediate Formed from CO Loss from $M(CO)_4PPh_3$. Light-induced loss of CO from $M(CO)_4PPh_3$ occurs to yield the 16-electron species $M(CO)_3PPh_3$ that can be scavenged by a two-electron donor such as $P(OCH_2)_3CEt$ or by an oxidative addition substrate such as R_3SiH. Likewise, reductive elimination of Et_3SiH from 1 yields, presumably, the same $M(CO)_3PPh_3$. As a test of whether the $M(CO)_3PPh_3$ from light-induced CO loss from $M(CO)_4PPh_3$ has the same reactivity as from light-induced reductive elimination of R_3SiH from 1, we have irradiated samples of **1b** or $Ru(CO)_4PPh_3$ in hydrocarbon solutions of $P(OCH_2)_3CEt$ and Ph_3SiH and examined the initial ratio of $Ru(CO)_3(PPh_3)(P(OCH_2)_3CEt)$ and *cis-mer*-$HRu(SiPh_3)(CO)_3(PPh_3)$ as a function of the ratio of $P(OCH_2)_3CEt$ and Ph_3SiH. The results are consistent with the conclusion that the reactivity is the same for the $Ru(CO)_3PPh_3$ generated from irradiation of $Ru(CO)_4PPh_3$ or **1b** because the product ratio (Table III) is the same. The irradiation of **1b** in the presence of $P(OCH_2)_3CEt$ does yield CO substitution, but this does not affect the ratio of *cis-mer*-$HRu(SiPh_3)(CO)_3(PPh_3)$ to $Ru(CO)_3(PPh_3)(P(OCH_2)_3CEt)$. When the reactivity of $Ru(CO)_3PPh_3$ is investigated by irradiation of $Ru(CO)_4PPh_3$ or **1b** in the presence of Ph_3SiH and PPh_3, the ratio of *cis-mer*-$HRu(SiPh_3)(CO)_3(PPh_3)$ to $Ru(CO)_3(PPh_3)_2$ is different from $Ru(CO)_4PPh_3$ and **1b** at a given ratio of Ph_3SiH to PPh_3. The photoproduct distribution from **1b** is consistently richer in $Ru(CO)_3(PPh_3)_2$, consistent with CO loss from **1b** providing an alternative route, possibly via eq 5–8, to the $Ru(CO)_3(PPh_3)_2$.

Conclusions

Detailed studies of *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ (M = Ru, Fe) show that near-UV irradiation can result in reductive elimination of Et_3SiH as a primary photoprocess. Additionally, qualitative 298 K experiments show that Ph_3SiH, $(MeO)_3SiH$, $(EtO)_3SiH$, and $MeCl_2SiH$ can be reductively eliminated from the appropriate *cis-mer* metal complex, establishing elimination of R_3SiH as a viable process for a wide range of R. From 298 K studies of *cis-mer*-$HRu(SiEt_3)(CO)_3(PPh_3)$, it appears that light-induced reductive elimination of R_3SiH yields the same coordinatively unsaturated $Ru(CO)_3PPh_3$ species formed by light-induced CO loss from $Ru(CO)_4PPh_3$.

Loss of CO from *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ is also a primary photoreaction. Both Et_3SiH and CO can be detected upon near-UV irradiation of *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ in rigid alkane matrices at ~100 K. At 298 K, both the CO and the Et_3SiH have apparent consequence in light-induced exchange processes such as *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ + Ph_3SiH → *cis-mer*-$HM(SiPh_3)(CO)_3(PPh_3)$ + Et_3SiH. The CO loss can also lead to dicarbonyl photoproducts in the presence of small P-donor ligands, but such photosubstitution products have not been isolated. The intriguing possibility is that irradiation of *cis-mer*-$HM(SiR_3)(CO)_3(PPh_3)$ in the presence of an alkene might yield $HM(SiR_3)(CO)_2(alkene)(PPh_3)$, possibly a precursor to the catalytic products observed when $M(CO)_4PPh_3$ is irradiated in the presence of an excess of a 1/1 mole ratio of R_3SiH/alkene.[3] At least, loss of CO as a primary result from photoexcitation of *cis-mer*-$HM(SiEt_3)(CO)_3(PPh_3)$ provides a rationale for the observed photocatalysis of R_3SiH/alkene mixtures.

Observation of light-induced reductive elimination of R_3SiH from a metal complex raises the question of the nature of the excited state responsible for such chemistry. Given the similarity in the chemistry of H–H and R_3Si–H with respect to oxidative addition, it is reasonable to expect that excited states of $MH(SiR_3)$ species will be similar to those for MH_2 species.[2] One difference of note, however, is that the nature of SiR_3 can be "tuned" by varying R. Work is underway to establish whether light-induced reductive elimination of R_3SiH is as general as H_2 elimination.

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Registry No. **1a**, 90414-09-8; **1b**, 90414-10-1; **2** (M = Fe), 90527-93-8; **2** (M = Ru), 90458-38-1; **3** (M = Fe), 90458-36-9; $Fe(CO)_4PPh_3$, 14649-69-5; $Fe(CO)_3PPh_3$, 70460-14-9; $Fe(CO)_3(PPh_3)(2\text{-}MeTHF)$, 90414-11-2; $Fe(CO)_2(PPh_3)(2\text{-}MeTHF)_2$, 90414-12-3; $Fe(CO)_3(PPh_3)_2$, 14741-34-5; $Fe(CO)_3(PPh_3)(P(OCH_2)_3CEt)$, 90414-13-4; $Fe(CO)_3(PPh_3)(1\text{-}C_5H_{10})$, 81522-98-7; *cis-mer*-$HFe(SiPh_3)(CO)_3(PPh_3)$, 90458-37-0; *cis-mer*-$HFe[Si(OMe)_3](CO)_3(PPh_3)$, 90414-14-5; *cis-mer*-$HFe[Si(OEt)_3](CO)_3(PPh_3)$, 90414-15-6; $Ru(CO)_4PPh_3$, 21192-23-4; $Ru(CO)_3PPh_3$, 90414-16-7; $Ru(CO)_3(PPh_3)(2\text{-}MeTHF)$, 90414-17-8; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $Ru(CO)_3(PPh_3)(P(OCH_2)_3CEt)$, 90414-18-9; $Ru(CO)_3(PPh_3)(1\text{-}C_5H_{10})$, 81523-01-5; *cis-mer*-$HRu(SiPh_3)(CO)_3(PPh_3)$, 90414-19-0; *cis-mer*-$HRu(SiMeCl_2)(CO)_3(PPh_3)$, 82807-26-9; *cis-mer*-$HRu[Si(OMe)_3](CO)_3(PPh_3)$, 90414-20-3; *cis-mer*-$HRu[Si(OEt)_3](CO)_3(PPh_3)$, 90414-21-4; $HRu(SiEt_3)(CO)_2(PPh_3)(P(OCH_2)_3CEt)$, 90414-22-5.