Comparison of the Thermal and Photochemical Reactions of (η^1-Cyclopentadienyl)Re(CO)$_5$ and (η^1-9-Fluorenyl)Re(CO)$_5$: Nonthermal Chemical Reactions from the Lowest Excited State

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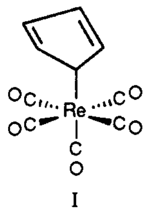
Abstract: Near-UV (366 nm) irradiation of the new complexes (η^1-R)Re(CO)$_5$ (R = C_5H_5, 9-fluorenyl) in alkane solution at 295 K yields predominantly radical products, whereas thermolysis yields only the fully ring-slipped (η^5-R)Re(CO)$_3$ species. Irradiation at 366 nm of (η^1-C_5H_5)Re(CO)$_5$ in deoxygenated alkane solutions at 295 K yields some CO loss to give (η^5-C_5H_5)Re(CO)$_3$, $\Phi = 0.007 \pm 0.002$, and mainly Re–R bond cleavage giving Re(CO)$_5$ and R radicals with $\Phi = 0.06 \pm 0.02$. The ultimate radical products are $Re_2(CO)_{10}$ and $C_{10}H_{10}$ in the absence of radical traps. Only Re–R cleavage is observed for (η^1-9-fluorenyl)Re(CO)$_5$ upon irradiation at 366 nm with $\Phi = 0.04 \pm 0.004$ in deoxygenated alkane to give $Re_2(CO)_{10}$ and 9,9′-bifluorene. Thermolysis of (η^1-R)Re(CO)$_5$ (R = C_5H_5, 9-fluorenyl) leads to quantitative conversion to the fully ring-slipped products, (η^5-C_5H_5)Re(CO)$_3$ or (η^5-fluorenyl)Re(CO)$_3$, respectively. Thermal ring slippage of (η^1-9-fluorenyl)Re(CO)$_5$ to (η^5-fluorenyl)Re(CO)$_3$ is reversible and occurs with a rate of $\sim 1 \times 10^{-3}$ s^{-1} at 400 K. The rate of ring slippage is suppressed by a factor of >100 under 1 atm of CO. In the presence of 0.05 M PPh$_3$, (η^1-9-fluorenyl)Re(CO)$_4$PPh$_3$ is the exclusive thermolysis product and forms with ΔH^* of 28.3 ± 1 kcal mol^{-1} and ΔS^* of 7 ± 3 cal mol^{-1} K^{-1}. (η^5-Fluorenyl)Re(CO)$_3$ reacts at 295 K with CO to quantitatively regenerate (η^1-9-fluorenyl)Re(CO)$_5$ with a rate of 9.7×10^{-5} s^{-1} under 1 atm of CO. The rate of thermal ring slippage of (η^1-C_5H_5)Re(CO)$_5$ to (η^5-C_5H_5)Re(CO)$_3$ is 4.2×10^{-4} s^{-1} at 325 K ($\Delta H^* = 25.2 \pm 1.6$ kcal mol^{-1} and $\Delta S^* = 7 \pm 3$ cal mol^{-1} K^{-1}) and is not affected by 1 atm of CO. The rate of thermal ring slippage is decreased by ~60% at 295 K by 1200 psig CO. (η^5-C_5H_5)Re(CO)$_3$ does not react with up to 1200 psig of CO at 295 K. Optical and photochemical measurements on $CH_3Re(CO)_5$ show lowest excited state behavior consistent with results for the η^1-C_5H_5 and η^1-9-fluorenyl species. The thermal behavior of $CH_3Re(CO)_5$ (qualitatively slower reactions) is in accord with the conclusion that CO loss from η^1-C_5H_5 and η^1-9-fluorenyl species is assisted by the unsaturated hydrocarbon ligand. Irradiation at 254 or 366 nm of (η^1-C_5H_5)Re(CO)$_5$ in alkane glasses at 95 K leads to CO loss as the only detectable photoprocess: the ring-slipped (η^3-C_5H_5)Re(CO)$_4$ and (η^5-C_5H_5)Re(CO)$_3$ are formed. Irradiation at 254 nm of (η^1-9-fluorenyl)Re(CO)$_5$ under the same conditions leads to the formation of (η^3-fluorenyl)Re(CO)$_4$ and a new, isomeric (fluorenyl)Re(CO)$_5$ product, but 366-nm irradiation yields predominantly (>90%) isomerization, not CO loss. The identities of the η^3 intermediates from (η^1-C_5H_5)Re(CO)$_5$ and (η^1-9-fluorenyl)Re(CO)$_5$ have been established spectroscopically and by chemical trapping experiments.

We wish to report a quantitative study of the thermal chemistry and primary photoprocesses of the new complexes (η^1-R)Re(CO)$_5$ (R = C_5H_5, 9-fluorenyl), I and II. The principal aim of our work has been to establish the relative importance of CO loss and Re–R homolysis upon photoexcitation of (η^1-R)Re(CO)$_5$ (eq 1 and 2).



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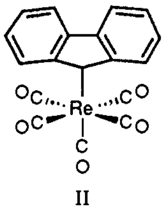

II

$$RRe(CO)_5 \xrightarrow{h\nu} RRe(CO)_4 + CO \quad (1)$$

$$RRe(CO)_5 \xrightarrow{h\nu} Re(CO)_5 + R \quad (2)$$

Few examples of the photochemistry of RRe(CO)$_5$ (R = σ-bonded C donor) have been reported.[1] UV irradiation of (η^1-C_3H_5)Re(CO)$_5$ in alkane solution at 295 K is reported to yield $Re_2(CO)_{10}$ (37%) and (η^3-C_3H_5)Re(CO)$_4$ (55%).[2] Irradiation of (η^5-C_5H_5)(η^1-C_5H_5)Re(CO)$_2$H in a matrix at 12 K gives CO loss that leads to the eventual formation of (η^5-C_5H_5)$_2$ReH as well as (η^5-C_5H_5)(η^2-C_5H_6)Re(CO)$_2$ from hydride insertion; no evidence for Re–R homolysis was reported.[3] XRe(CO)$_5$ (X = Cl, Br, I) have been investigated and appear to only give CO loss as a primary photochemical process.[1c] These examples indicate that *both* CO loss and Re–R cleavage are likely to be important reactions following excitation of RRe(CO)$_5$ complexes.

To explore the factors that effect the reactivity of RRe(CO)$_5$ complexes that have two potential primary photoprocesses, CO loss and Re–R bond cleavage, we have undertaken a study of (η^1-C_5H_5)Re(CO)$_5$ and (η^1-9-fluorenyl)Re(CO)$_5$. These two compounds can form the relatively stable C_5H_5 or fluorenyl radicals[4] upon Re–R homolysis. CO loss could be followed by ring slippage to give (η^3-R)Re(CO)$_4$ or (η^5-R)Re(CO)$_3$, consistent with the results reported for (η^1-C_3H_5)Re(CO)$_5$[2] and (η^5-C_5H_5)(η^1-C_5H_5)Re(CO)$_2$H[3] (eq 3 and 4).

$$(\eta^1\text{-R})Re(CO)_4 \xrightarrow{\Delta} (\eta^3\text{-R})Re(CO)_4 \quad (3)$$

$$(\eta^3\text{-R})Re(CO)_4 \xrightarrow{h\nu \text{ or } \Delta} (\eta^5\text{-R})Re(CO)_3 + CO \quad (4)$$

In addition to establishing the factors that influence CO loss versus Re–R cleavage, the (η^1-R)Re(CO)$_5$ compounds are also of interest because ring slippage is a possible reaction pathway following CO extrusion. Casey has reported[5,6] that (η^5-R)Re(CO)$_3$ (R = C_5H_5, indenyl) can react with PMe$_3$ thermally and ring slip to give (η^1-R)Re(CO)$_3$(PMe$_3$)$_2$. This ring slippage is thermally

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reversible for R = C_5H_5, although in neither case were any η^3-coordinated species observed. However, η^3-C_5H_5 and η^3-indenyl systems have been observed in a variety of cases,[7] and several η^3-C_5H_5[7,8] and η^3-indenyl[7,9] systems have been structurally characterized. Basolo and co-workers[10] have observed an intermediate η^1-fluorenyl species in the substitution reactions of (η^5-fluorenyl)Mn(CO)$_3$ with very basic phosphines. In studies of RMn(CO)$_5$ (R = η^1-C_5Cl_5, η^1-$C_6H_5CH_2$)[11] and (η^1-C_5H_5)(η^5-C_5H_5)Fe(CO)$_2$,[12] we were able to observe η^3-R intermediates following light-induced CO loss. We are interested in (η^1-C_5H_5)Re(CO)$_5$ because it is a prototypical η^1-C_5H_5 complex. (η^1-9-Fluorenyl)Re(CO)$_5$ is of interest because of its remarkable thermal stability. Our new work adds additional information concerning ring-slipped intermediates in reactions of cyclopentadienyl complexes.

Experimental Section

Instruments and Equipment. UV–vis spectra were recorded on a Cary 17 UV–vis–near-IR absorption spectrometer or on a HP 8451A diode array spectrometer. IR spectra were recorded on a Nicolet 60SX or 170SX FTIR. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL300, a Bruker WM250, or a Bruker WM270 Fourier transform spectrometer. Mass spectra were recorded on a Finnigan Mat System 8200.

Emission spectra were recorded with a Perkin-Elmer MPF-44 spectrophotometer equipped with a Hamamatsu HR777 PMT detector and a high-pressure Xe arc lamp excitation source powered by a Perkin-Elmer Model 150 Xe power supply. Spectra were measured at 77 K in a methylcyclohexane glass by placing solutions in 5-mm o.d. quartz tubes in a quartz Dewar cooled with liquid N_2. The excitation wavelength was 300 nm for all samples. The PMT output was collected and stored on a Nicolet 4094 digital oscilloscope and subsequently transferred to an IBM PC for data analysis.

IR spectra were recorded in deoxygenated alkane solutions except where noted. Solutions of the complexes were held in a cell with CaF_2 windows. Low-temperature IR spectra were recorded with the cell mounted in a Specac Model P/N 21000 Dewar assembly, using liquid N_2 as coolant. The temperature of the cell was measured with a Cu-constantan thermocouple in contact with the inner window of the cell. Irradiations were effected with a Bausch and Lomb SP200 high-pressure Hg lamp filtered by a 10-cm H_2O filter with quartz windows and a Bausch and Lomb Model 33-86-79 high-intensity monochromator for 313- and 366-nm irradiations. The 254-nm irradiations were effected by using the unfiltered output from an Ultra-Violet Products Inc. Model PCQX1 low-pressure Hg lamp.

HPLC data were obtained with a HP 1084B HPLC equipped with a HP 1040A diode array detector. Compounds were identified based on their retention times and UV–vis spectra, compared with those for authentic samples. The column used was either a 15-cm Rainin Instruments Dynamax RP-C18 column with a CH_3CN/H_2O gradient (55–80%) or a 15-cm Rainin Instruments Microsorb Si column with isocratic C_6H_{14}/CH_2Cl_2 (99:1) as eluant.

Materials. All solvents were reagent or spectroscopic grade and were distilled and/or dried prior to use. Methylcyclohexane (MCH) and 3-methylpentane (3MP) for photochemical experiments were deoxygenated by purging with Ar prior to use. Hexane and tetrahydrofuran (THF) were distilled from CaH_2 under N_2. Chlorinated solvents were freshly distilled from P_2O_5 under Ar and stored in the dark. MCH-d_{14} (Cambridge Isotope Laboratories), C_6D_{12} (Aldrich), C_6D_6 (Cambridge Isotope Laboratories), CD_2Cl_2 (Aldrich), and $CDCl_3$ (Cambridge Isotope Laboratories) were used as received.

Silica gel for column chromatography was EM Science Keiselgel 60, 230–400 mesh. Re(CO)$_5$Cl (Pressure Chemical), Re(CO)$_5$Br (Pressure Chemical), fluorene ($C_{13}H_{10}$) (Aldrich), and 9,9′-bifluorene (Aldrich) were used as received. 9-Bromofluorene (Aldrich) was recrystallized from dry EtOH. C_5H_6 was freshly prepared by cracking $C_{10}H_{12}$ (Fluka). $C_6H_5CH_2Br$ (Kodak) was distilled under reduced pressure and stored under Ar in the dark; all other alkyl halides were filtered through activated Al_2O_3 before use. PPh$_3$ (Fluka) was recrystallized from C_2H_5OH and dried in vacuo. Na[C_5H_5] and Na[fluorenide] were prepared by reaction of NaH with the corresponding hydrocarbons in THF under Ar. Bicyclopentadiene ($C_{10}H_{10}$)[13] and CH_3Re(CO)$_5$[14] were prepared by following the literature procedures. All reactions and manipulations of organometallic compounds were carried out in a Vacuum Atmospheres drybox under Ar or on a conventional Schlenk line under Ar. Elemental analyses were performed by Galbraith Laboratories Inc.

(η^1-C_5H_5)Re(CO)$_5$ was prepared by adding solid Re(CO)$_5$Br (1.0 g, 2.5 mmol) to a stirred solution of Na[C_5H_5] (0.53 g, 6.0 mmol) in 30 mL of THF under Ar. The reaction was stirred at 295 K and continued until >90% Re(CO)$_5$Br was consumed as monitored by IR spectroscopy (typically ~30 min). The reaction mixture was then diluted with 50 mL of C_6H_{14} and washed with ~10 mL of H_2O. The combined organic solution was washed with saturated aqueous NaCl and dried over $MgSO_4$. The solvent was then evaporated under reduced pressure, and the residue was chromatographed at 280 K on silica gel with 8:1 C_5H_{12}/CH_2Cl_2 as the eluant. (η^5-C_5H_5)Re(CO)$_3$ eluted first and was followed closely by (η^1-C_5H_5)Re(CO)$_5$. (η^1-C_5H_5)Re(CO)$_5$ was obtained as a yellow oil (0.26 g, 26%) that solidified on cooling to 275 K: ^{1}H NMR (C_6D_{12}) 5.94 (s) ppm; ^{13}C NMR (C_6D_{12}) 112.4, 184.0 ppm; exact mass (found) 389.9665 ± 0.0004, (calculated) 389.9667. Slow reaction of (η^1-C_5H_5)Re(CO)$_5$ occurs even at 295 K and yields (η^5-C_5H_5)Re(CO)$_3$, a known compound.[15] (η^5-C_5H_5)Re(CO)$_3$ was obtained as colorless crystals: mp 109–111 °C; ^{1}H NMR (C_6D_{12}) 5.35 (s) ppm; ^{13}C NMR (C_6D_{12}) 84.9, 193 ppm. We find that solid Re(CO)$_5$X (X = Br or Cl) gives identical yields of (η^1-C_5H_5)Re(CO)$_5$, but addition of a solution of Re(CO)$_5$X (X = Br or Cl) (instead of the solid) to the solution of Na[C_5H_5] results in a greatly decreased yield of (η^1-C_5H_5)Re(CO)$_5$, with more (η^5-C_5H_5)Re(CO)$_3$ being formed. Reverse order of addition has no effect on the yields of the two products.

(η^1-9-Fluorenyl)Re(CO)$_5$ was prepared by the addition of solid Re(CO)$_5$Cl (0.72 g, 2.0 mmol) to a stirred solution of Na[fluorenide] (0.37 g, 2.2 mmol) in 30 mL of THF under Ar. The reaction mixture was refluxed until >90% of the Re(CO)$_5$Cl was consumed as monitored by IR spectroscopy (~1–2 h). The reaction mixture was poured into 50 mL of C_6H_{14} and extracted with H_2O and saturated aqueous NaCl. The organic solution was dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was then chromatographed on silica gel (5% CH_2Cl_2/C_6H_{14}). (η^1-9-Fluorenyl)Re(CO)$_5$ was obtained as a pale yellow solid (0.42 g, 43%): mp 155–157 °C; ^{1}H NMR ($CDCl_3$) 7.90 (d, 7.6 Hz, 2 H), 7.53 (d, 7.6 Hz, 2 H), 7.27–7.34 (m, 2 H), 7.16–7.21 (m, 2 H), 4.59 (s, 1 H) ppm; ^{13}C NMR (C_6D_{12}) 22.9, 120.6, 122.8, 124.0, 126.3, 136.6, 160.5, 184.2 ppm. Anal. Calcd for $C_{18}H_9O_5Re$: C, 43.99; H, 1.85. Found: C, 44.27; H, 1.93.

(η^5-Fluorenyl)Re(CO)$_3$ was prepared by refluxing a solution of (η^1-9-fluorenyl)Re(CO)$_5$ (0.50 g, 1.0 mmol) in 40 mL of nonane with an Ar purge for ~90 min. The crude reaction mixture was filtered and the solvent evaporated. The residue was recrystallized from C_6H_{14} to give (η^5-fluorenyl)Re(CO)$_3$ (0.27 g, 61%): mp 174–176 °C; ^{1}H NMR (C_6D_6) 7.47 (d, 8.3 Hz, 2 H), 6.98 (d, 8.5 Hz, 2 H), 6.60–6.75 (m, 4 H), 5.34 (s, 1 H) ppm; ^{13}C NMR (CD_2Cl_2) 58.2, 98.0, 112.0, 123.0, 123.9, 124.8, 128.5, 193.3 ppm. Anal. Calcd for $C_{16}H_9O_3Re$: C, 44.13; H, 2.08. Found: C, 44.49; H, 2.01.

cis-(η^1-9-Fluorenyl)Re(CO)$_4$PPh$_3$ was prepared by heating (η^1-9-fluorenyl)Re(CO)$_5$ (0.14 g, 0.28 mmol) with PPh$_3$ (0.09 g, 0.34 mmol) in 30.0 mL of octane to 100 °C for ~90 min. The solution was cooled and the product collected as pale yellow crystals (0.15 g, 73%): mp 189–191 °C; ^{1}H NMR (CD_2Cl_2) 7.54–7.84 (m, 17 H), 6.97–7.1 (m, 6 H), 4.41 (d, 8.9 Hz, 1 H) ppm; ^{31}P NMR (CD_2Cl_2) 9.1 ppm. Anal. Calcd for $C_{35}H_{24}O_4PRe$: C, 57.92; H, 3.33; P, 4.27. Found: C, 58.19; H, 3.41; P, 4.46.

UV–vis and IR spectroscopic data for relevant compounds are included in Table I.

Irradiations. Quantum yields were measured at 295 and 280 K under Ar in deoxygenated MCH solutions using a Hanovia medium-pressure Hg lamp with the appropriate solution and glass filters to isolate the 366- or 313-nm emission or with the unfiltered output from the Ultra-Violet Products low-pressure Hg lamp for 254 nm. Concentrations of starting materials and products were determined by IR spectroscopy. Ferrioxalate actinometry[16] was used to measure the light intensity for each

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Table I. Spectroscopic Data for Relevant Compounds[a]

compd	*T*, K	IR (ν_{CO}) ($\epsilon \times 10^{-3}$)[b]	UV–vis ($\epsilon \times 10^{-3}$)[c]
$(\eta^1\text{-}C_5H_5)Re(CO)_5$	295	2130 (0.8), 2062 (0.4), 2022 (17.3), 1984.5 (6.4)	220 (25), 270 (7.2)
	200	2031 (*1*), 2063 (*0.6*), 2021 (*17.5*), 1984 (*7*)	
	95	2132 (1.0), 2062 (1.0), 2018 (15), 1980 (6.1)	
$(\eta^3\text{-}C_5H_5)Re(CO)_4$	95	2098 (*1*), 2003 (*7*), 1980 (*3*), 1940 (*5*)	
$(\eta^5\text{-}C_5H_5)Re(CO)_3$	295	2029 (5.5), 1940 (14.6)	224 (~7), 262 (3.0)
	95	2028 (5.5), 1932 (9.4), 1924 (4.9)	
$(\eta^5\text{-}C_5H_5)Re(CO)_2$	95	1945 (*1*), 1877 (*1.4*)	
$(\eta^1\text{-}C_5H_5)Re(CO)_4PPh_3$	295	2084 (*1*), 2009 (*1.2*), 1978 (*3*), 1945 (*1.8*)	
$(\eta^1$-fluorenyl)$Re(CO)_5$	295	2130 (1.1), 2062 (0.8), 2022 (13.0), 2018 (12), 1987 (6.8)	228 (38), 258 (18), 294 (11), 355 (3)
	95	2032 (1.2), 2062 (0.6), 2021 (14), 2017 (10.6), 1983 (4.8)	
$(\eta^3$-fluorenyl)$Re(CO)_4$	295	2092 (1), 1998 (5), 1988 (~1), 1953 (3.5)	
	95	2094, 1997, 1988, 1957	
$(\eta^5$-fluorenyl)$Re(CO)_3$	295	2027 (7.8), 1935 (14.4)	235 (34), 290 (sh), 320 (4.0)
	95	2025, 1934, 1923	
$(\eta^1$-fluorenyl)$Re(CO)_4PPh_3$[d]	295	2085 (1.9), 2009 (2.5), 1992 (1.3), 1980 (4.8), 1948 (2.2), 1941 (2.4)	
$(\eta^1\text{-}C_3H_5)Re(CO)_5$[e]	295	2129 (s), 2050 (m), 2020 (vs, br), 1970 (vs)	
$(\eta^3\text{-}C_5H_5)Re(CO)_4$[e]	295	2091 (s), 1990 (vs), 1980 (vs), 1953 (vs)	
$FcRe(CO)_5$[f]	295	2132 (0.7), 2049 (0.19), 2016 (10.0), 1982 (2.2)	
$Re_2(CO)_{10}$	295	2070 (7.5), 2015 (47.5), 1978 (14.8)	276 (17.5), 310 (19.0)
$Re(CO)_5$[g]	12	1995 (4), 1977 (1)	
$Re_2(CO)_9$[h]	12	2066, 2015, 1999, 1987, 1955, 1943	
$CH_3Re(CO)_5$	295	2128 (0.2), 2043 (0.1), 2013 (25.7), 1982 (6.1)	234 (11), 286 (3.6), 305 (sh)
$CH_3Re(CO)_4PPh_3$	295	2078, 1991, 1971, 1937	
$(\eta^5\text{-}C_5H_5)Re(CO)_2H_2$[i]	295	2022 (m), 1954 (s)	
$(\eta^5\text{-}C_5H_5)_2Re_2(CO)_5$[j]	295	1992 (0.7), 1956 (10), 1923 (9), 1904 (1.2), 1740 (4.5)	
$Re(CO)_5Cl$	295	2045 (17), 1984 (7.1)	
$Re_2(CO)_8Cl_2$	295	2114 (w), 2032 (s), 2000 (m), 1959 (m)	
$Re(CO)_5Br$	295	2045 (14.3), 1985 (4.1)	236 (6), 272 (2), 310 (1), 330 (1.8), 358 (0.6)
$Re_2(CO)_8Br_2$	295	2113 (w), 2031 (s), 2000 (m), 1959 (m)	
$HRe(CO)_5$[k]	295	2014, 2005, 1982	
$Re_2(CO)_9PPh_3$[l]	295	2107 (*0.01*), 2034 (*0.06*), 1998 (*1.0*), 1969 (*0.25*), 1941 (*0.24*)	
$Re_2(CO)_8(PPh_3)_2$[l]	295	1988 (w), 1965 (s)	
cis-$BrRe(CO)_4PPh_3$	295	2104 (m), 2020 (s), 2002 (vs), 1945 (s)	
cis-$ClRe(CO)_4PPh_3$	295	2105 (*0.24*), 2018 (*0.71*), 2002 (*1.0*), 1945 (*0.56*)	

[a] All data recorded in alkane solution except where noted. [b] Band positions in cm^{-1}. Extinction coefficients in M^{-1} cm^{-1}. Italicized entries are relative extinction coefficients. [b] Band positions in nm. Extinction coefficients are in M^{-1} cm^{-1}. [d] 1% CH_2Cl_2 in MCH solution. [e] Reference 2. [f] Fc = ferrocenyl. [g] Huber, H.; Kundig, E. P.; Ozin, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 5585. [h] Firth, S.; Hodges, P. M.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 4608. Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 793. [j] Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65. [k] Braterman, P. S.; Harrill, R. W.; Kaesez, H. D. *J. Am. Chem. Soc.* **1967**, *89*, 2851. [l] Dunkin, I. R.; Härter, P.; Shields, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 7248.

sample at 295 K. For irradiations at 280 K, light intensities were measured relative to the disappearance quantum yield of $(\eta^1\text{-}C_5Cl_5)Mn(CO)_5$ in MCH.[11] Typical light intensities were 10^{-7}–10^{-8} einstein min^{-1} cm^{-2}.

Irradiations to determine qualitative aspects of the photochemistry were effected by using Ar- or CO-purged alkane solutions containing approximately 10^{-3} M of the metal carbonyl. Irradiations were monitored by IR spectroscopy and typically were carried to 5–10% conversion based on consumption of starting material. A Model A High Energy Micro Pulser from Xenon Corp. was used for flash photolyses. The pulser is equipped with two xenon Fp series Micropulse Flashtubes used at a discharge voltage of ~3 kV.

Kinetic Measurements. Typical kinetic determinations were made by heating a deoxygenated alkane solution of $\sim 10^{-3}$ M of the metal carbonyl complex to the desired temperature under a purge of Ar or CO. Temperatures were maintained with a Haake Model FS constant-temperature bath or with a thermostated oil bath and were constant to ±1.0 °C. Aliquots were withdrawn via syringe, and the reaction was monitored by IR spectroscopy at 295 K. Reactions were typically followed for 3 half-lives.

Results

Optical Absorption and Emission Spectroscopy. The complexes studied show at most tail absorptions in the visible region of the optical spectrum and are white or yellow in color. Figure 1 shows the UV–vis spectra at 295 K of two of the complexes studied and relevant hydrocarbons, C_5H_6 and fluorene. $(\eta^1\text{-}C_5H_5)Re(CO)_5$ shows UV maxima at 270 nm (ϵ = 7200 cm^{-1} M^{-1}) and 220 nm (ϵ = 25 000 cm^{-1} M^{-1}). $(\eta^1$-9-Fluorenyl)$Re(CO)_5$ shows a longer wavelength first absorption maximum than the C_5H_5 species, 355 nm (ϵ = 3000 cm^{-1} M^{-1}), with higher energy maxima at 294 nm (ϵ = 11 000 cm^{-1} M^{-1}), 258 nm (ϵ = 18 000 cm^{-1} M^{-1}), and 228 nm (ϵ = 38 000 cm^{-1} M^{-1}) (Figure 1). $CH_3Re(CO)_5$ was prepared and its optical spectrum recorded in order to assess the role of the unsaturated hydrocarbon ligand in the $(\eta^1\text{-}R)Re(CO)_5$ species. The first absorption maximum is at 286 nm (ϵ = 3600 cm^{-1} M^{-1}) with a shoulder at 305 nm. Thus, the first absorption in $CH_3Re(CO)_5$ is very similar to that for $(\eta^1\text{-}R)Re(CO)_5$. From the absorption spectra it is evident that photochemical reactions of the $(\eta^1\text{-}R)Re(CO)_5$ species could be possible following excitation with light in the near-UV region of the spectrum. The photochemical results (vide infra) are consistent with lowest excited states which involve population of σ_z^* or σ_{xy}^* orbitals from overlap

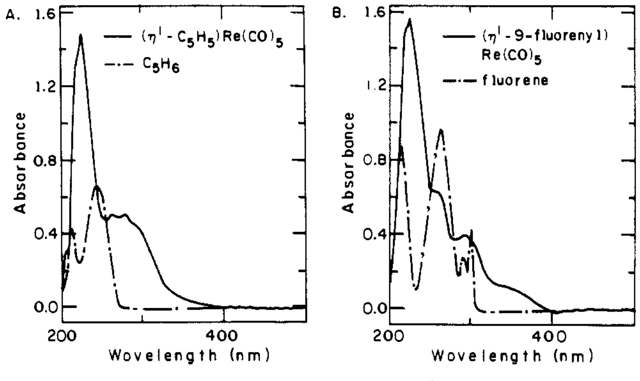

Figure 1. (A) UV–vis absorption spectra for $(\eta^1\text{-}C_5H_5)Re(CO)_5$ (8.4 × 10^{-5} M) (λ_{max} (ϵ): 220 (25 000), 270 (7200)) and C_5H_6 (7.3 × 10^{-4} M) (λ_{max} (ϵ): 210 (2300), 242 (3400)) in MCH at 295 K. (B) UV–vis spectra for $(\eta^1$-9-fluorenyl)$Re(CO)_5$ (4.0 × 10^{-5} M) (λ_{max} (ϵ): 228 (38 000), 258 (18 000), 294 (11 000), 355 (3000)) and fluorene (6.0 × 10^{-5} M) (λ_{max} (ϵ): 216 (14 000), 264 (15 000), 292 (4200), 302 (6300)) in MCH at 295 K.

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(16) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

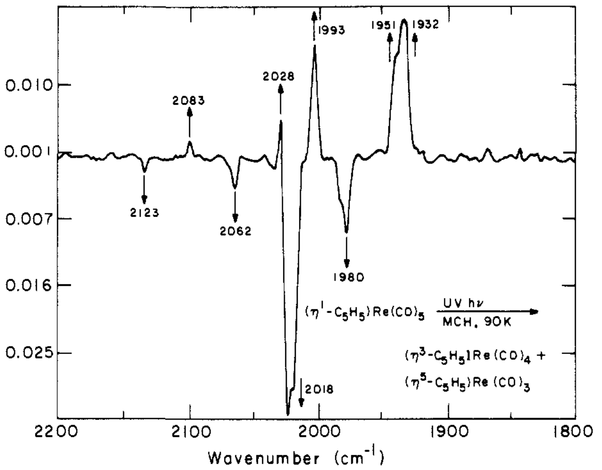

Figure 2. IR difference spectrum resulting from near-UV irradiation of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in a MCH matrix at 90 K. Negative peaks are due to consumption of starting material. Positive peaks at 2083, 1993, 1972 (obscured by starting material), and 1951 cm^{-1} are due to $(\eta^3\text{-}C_5H_5)$-$Re(CO)_4$. Peaks at 2028 and 1932 cm^{-1} are due to formation of $(\eta^5\text{-}C_5H_5)Re(CO)_3$.

of Re $5d_{z^2}$ or $5d_{x^2-y^2}$ orbitals with ligand-centered σ orbitals. UV-vis spectra recorded at 95 K in MCH glass show no new spectral features for $(\eta^1\text{-9-fluorenyl})Re(CO)_5$; specifically, no fine structure or band resolution appears. However, in the UV-vis spectrum of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ at 95 K, a new shoulder at 305 nm becomes visible.

Study of the emission (λ_{ex} = 300 nm) of $(\eta^1\text{-9-fluorenyl})Re(CO)_5$, fluorene, and 9-bromofluorene in an MCH glass at 77 K was undertaken. Fluorene itself has an intense ultraviolet fluorescence and a strong, structured phosphorescence between 420 and 510 nm.[16] In contrast, neither 9-bromofluorene nor $(\eta^1\text{-9-fluorenyl})Re(CO)_5$ exhibits detectable emission at ≥100 times the sensitivity used for the fluorene measurement.

Photochemistry of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ at 95 K. Near-UV irradiation of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in MCH containing ~2% 3MP at 95 K results in the conversion of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ to the ring-slipped products $(\eta^3\text{-}C_5H_5)Re(CO)_4$ and $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (eq 5 and 6). The ratio of η^3 and η^5 complexes formed upon

$$(\eta^1\text{-}C_5H_5)Re(CO)_5 \xrightarrow{h\nu} (\eta^3\text{-}C_5H_5)Re(CO)_4 + CO \quad (5)$$

$$(\eta^3\text{-}C_5H_5)Re(CO)_4 \xrightarrow{h\nu \text{ or } \Delta} (\eta^5\text{-}C_5H_5)Re(CO)_3 + CO \quad (6)$$

irradiation decreases with increasing irradiation time, consistent with formation of the η^5 species via irradiation of the η^3 species. The growth of four bands in the IR at 2098, 2003, 1980 (obscured by starting material), and 1940 cm^{-1} is associated with the formation of $(\eta^3\text{-}C_5H_5)Re(CO)_4$, and the two bands at 2028 (obscured by starting material) and 1932 cm^{-1} are attributed to the production of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (Figure 2). The relative positions and intensities of the bands assigned to $(\eta^3\text{-}C_5H_5)Re(CO)_4$ correspond with the positions expected based on the related $(\eta^1\text{-}C_3H_5)Re(CO)_5$ to $(\eta^3\text{-}C_3H_5)Re(CO)_4$ conversion.[2]

There are no features in the photoproduct spectrum at 95 K that can be assigned to the 16e$^-$ $(\eta^1\text{-}C_5H_5)Re(CO)_4$, which is the presumed prompt photoproduct resulting from CO loss. The bands assigned to $(\eta^5\text{-}C_5H_5)Re(CO)_3$ are identical with those for an authentic sample recorded under the same conditions. The absorbance[17] for free CO expected at 2132 cm^{-1} is obscured by the starting material. Larger extent conversions do show free CO but only when it is apparent that secondary photochemistry is occurring and significant amounts of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $(\eta^5\text{-}C_5H_5)Re(CO)_2$ are formed. In a matrix the chemical yields of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $(\eta^3\text{-}C_5H_5)Re(CO)_4$ are estimated to be ~55% and ~45%, respectively, at ~10% consumption of $(\eta^1\text{-}C_5H_5)Re(CO)_5$. No IR absorbances for $Re(CO)_5$ (Table I) or other $Re(CO)_5$-containing products are observable in a matrix, indicating that no net Re–R bond homolysis occurs under such conditions. Importantly, there is no dependence of the primary photoproduct on excitation wavelength (254–366 nm).

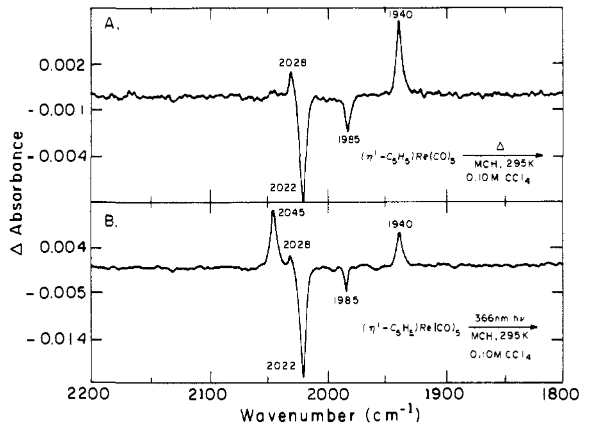

Figure 3. (A) IR difference spectrum showing thermal reaction for 8 min at 295 K of 1.15 × 10^{-3} M $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in MCH containing 0.1 M CCl_4. (b) IR difference spectrum resulting from 8-min irradiation at 366 nm of 1.15 × 10^{-3} M $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in 0.1 M CCl_4 in MCH at 295 K. Negative peaks are due to consumption of starting material. The positive peak at 2045 cm^{-1} is due to formation of $Re(CO)_5Cl$ (the 1984-cm^{-1} peak of $Re(CO)_5Cl$ is obscured by starting material). Positive peaks at 2028 and 1940 cm^{-1} are due to formation of $(\eta^5\text{-}C_5H_5)Re(CO)_3$.

Upon warming a matrix containing $(\eta^3\text{-}C_5H_5)Re(CO)_4$ to 295 K there is formation of additional $(\eta^5\text{-}C_5H_5)Re(CO)_3$, and no regeneration of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ is observed. Such warm-up experiments show that conversion of $(\eta^3\text{-}C_5H_5)Re(CO)_4$ to $(\eta^5\text{-}C_5H_5)Re(CO)_3$ can be a thermal process (eq 7). If the warm-up experiment is effected in a solution that contains ~3 mM CO, there is significant regeneration, ~10–15%, of $(\eta^1\text{-}C_5H_5)Re(CO)_5$. That regeneration of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ is observed is consistent with the conclusion that back reaction of $(\eta^3\text{-}C_5H_5)Re(CO)_4$ with CO to form $(\eta^1\text{-}C_5H_5)Re(CO)_5$ (eq 8 and 9) can be competitive with thermal CO loss and ring slippage

$$(\eta^3\text{-}C_5H_5)Re(CO)_4 \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)Re(CO)_3 + CO \quad (7)$$

$$(\eta^3\text{-}C_5H_5)Re(CO)_4 \overset{\Delta}{\rightleftharpoons} (\eta^1\text{-}C_5H_5)Re(CO)_4 \quad (8)$$

$$(\eta^1\text{-}C_5H_5)Re(CO)_4 + CO \xrightarrow{\Delta} (\eta^1\text{-}C_5H_5)Re(CO)_5 \quad (9)$$

to $(\eta^5\text{-}C_5H_5)Re(CO)_3$ under these conditions. It should be noted, however, that the η^3 species could react directly with the CO in a concerted process (cf. Discussion). $(\eta^3\text{-}C_5H_5)Re(CO)_4$ is very thermally reactive upon warming and completely reacts to form $(\eta^5\text{-}C_5H_5)Re(CO)_3$ in <10 min at 150 K in the absence of added CO. $(\eta^3\text{-}C_5H_5)Re(CO)_4$ is, however, thermally inert at 95 K, and $(\eta^5\text{-}C_5H_5)Re(CO)_3$ must form via photoexcitation of $(\eta^3\text{-}C_5H_5)Re(CO)_4$ (eq 6).

Warming a matrix containing photogenerated $(\eta^3\text{-}C_5H_5)Re(CO)_4$ in the presence of 0.05 M PPh_3 to 295 K results in the formation of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $(\eta^1\text{-}C_5H_5)Re(CO)_4PPh_3$ (vide infra) in estimated yields of 60% and 40%, respectively. This result and the warm-up result with CO indicate that 2e$^-$ donor ligands can trap the intermediate $(\eta^3\text{-}C_5H_5)Re(CO)_4$ in competition with ring slippage to form $(\eta^5\text{-}C_5H_5)Re(CO)_3$.

Room-Temperature Photochemistry of $(\eta^1\text{-}C_5H_5)Re(CO)_5$. Irradiation of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in deoxygenated alkane solution at 295 K produces $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $Re_2(CO)_{10}$ as the only metal carbonyl products. HPLC analysis of a photoproduct mixture produced by 366-nm irradiation of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in MCH solution shows formation of bicyclopentadiene ($C_{10}H_{10}$) as the major organic product, which typically accounts for ~75–80% of the starting material consumed. Photolysis at 366 nm in deoxygenated alkane solvents containing 0.25 M CCl_4 leads to the formation of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $Re(CO)_5Cl$. On the time scale of the irradiation there is significant thermal reaction

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[17] Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* **1985**, *24*, 2792.

Table II. Rate Constants for the Thermal Ring Slippage of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ to $(\eta^5\text{-}C_5H_5)Re(CO)_3$

[Re],[a] mM	[PPh$_3$],[b] mM	*T*, K	$k \times 10^3$,[c] s^{-1}
9.1	0	338	4.1
2.9	0	338	4.4
0.93	0	338	4.2
2.7	0	326	1.2
2.7	0	314	0.34
2.8	0	302	0.043
3.3	0	302	0.041
2.7	0.10[d]	302	0.041
2.9	0.01[d]	302	0.038

[a] Initial concentration of $(\eta^1\text{-}C_5H_5)Re(CO)_5$. [b] Initial concentration of PPh$_3$. [c] ±10%. [d] Some $(\eta^1\text{-}C_5H_5)Re(CO)_4PPh_3$ is formed.

to form primarily $(\eta^5\text{-}C_5H_5)Re(CO)_3$. Figure 3 shows the IR difference spectra resulting from 8-min thermal reaction and a parallel experiment except the sample was irradiated at 366 nm to effect reaction of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ in 0.1 M CCl$_4$ in MCH at 295 K. The difference between these two spectra represents the net photochemical reaction and corresponds to formation of 80–85% $Re(CO)_5Cl$ and 8–10% $(\eta^5\text{-}C_5H_5)Re(CO)_3$.

If irradiation of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ is effected in alkane solutions containing 0.25 M $C_6H_5CH_2Br$, $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $Re(CO)_5Br$ are formed. $C_6H_5CH_2Br$, however, reacts more rapidly thermally with $(\eta^1\text{-}C_5H_5)Re(CO)_5$ than does CCl$_4$ and makes quantification difficult (vide infra). Irradiation of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in alkane solutions containing 0.25 M $C_6H_5CH_2Br$ and 0.05 M PPh$_3$ results in photochemical formation of $Re(CO)_5Br$ (~65%), *cis*-$BrRe(CO)_4PPh_3$ (~10%), and *cis*-$(\eta^1\text{-}C_5H_5)Re(CO)_4PPh_3$ (~15%). The *cis*-$BrRe(CO)_4PPh_3$ results from known chemistry of $Re(CO)_5$ in the presence of PPh$_3$ and halogen atom donors.[18] The *cis*-$(\eta^1\text{-}C_5H_5)Re(CO)_4PPh_3$ is identified by comparison of the IR bands with other $RRe(CO)_4L$ complexes[19] and from thermal results (vide infra).

Irradiation of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ at 366, 313, or 254 nm in alkane solution results in the formation of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $Re_2(CO)_{10}$. The mass balance in these irradiations is typically only ~50–60%, and significantly less $Re_2(CO)_{10}$ is observed than expected based on the expected yield of radical products from the CCl$_4$ trapping result at 366 nm. This is consistent with the conclusion that either the very reactive $Re(CO)_5$ radical decomposes via reaction with impurities in the solvent instead of coupling to form $Re_2(CO)_{10}$, or the $Re_2(CO)_{10}$ formed undergoes secondary photolysis leading to decomposition. $Re_2(CO)_{10}$ is known to have a high quantum yield for Re–Re bond homolysis.[20]

Quantum yields at 280 K for the disappearance of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ and the appearance of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ in alkane solvents were measured at 366, 313, and 254 nm. For 366-nm excitation the disappearance Φ was 0.07 ± 0.02, and the Φ for $(\eta^5\text{-}C_5H_5)Re(CO)_3$ appearance was 0.007 ± 0.002. At 313 nm the Φ for consumption of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ is 0.25 ± 0.06 and the Φ for appearance of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ is 0.05 ± 0.01, while at 254 nm the values were 0.45 ± 0.1 and 0.1 ± 0.02, respectively. Quantum yields at 280 K for the disappearance of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ and the appearance of $Re(CO)_5Br$ and $(\eta^5\text{-}C_5H_5)Re(CO)_3$ in MCH containing 0.05 M $C_6H_5CH_2Br$ were measured at 366 nm. The disappearance quantum yield was 0.1 ± 0.03, and the appearance quantum yields were 0.06 ± 0.01 and 0.005 ± 0.001, respectively. The large uncertainty in the Φ's is due to the facile thermal conversion of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ to $(\eta^5\text{-}C_5H_5)Re(CO)_3$, which occurs even at 280 K.

Thermal Chemistry of $(\eta^1\text{-}C_5H_5)Re(CO)_5$. Alkane solutions of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ react thermally at 295 K in the dark to quantitatively form $(\eta^5\text{-}C_5H_5)Re(CO)_3$ with a half-life of ~12 h (eq 10). We find no detectable yield of $Re_2(CO)_{10}$ or $C_{10}H_{10}$,

$$(\eta^1\text{-}C_5H_5)Re(CO)_5 \xrightarrow[\text{alkane}]{\Delta} (\eta^5\text{-}C_5H_5)Re(CO)_3 + 2CO \quad (10)$$

the radical products formed photochemically, under these conditions. $(\eta^1\text{-}C_5H_5)Re(CO)_5$ also thermally decomposes in the solid state at 295 K, yielding $(\eta^5\text{-}C_5H_5)Re(CO)_3$. However, alkane solutions of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ can be stored at 230 K for several weeks. The rate of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ to $(\eta^5\text{-}C_5H_5)Re(CO)_3$ conversion was measured as a function of temperature and $(\eta^1\text{-}C_5H_5)Re(CO)_5$ concentration (Table II and Figure 4). The Arrhenius plot is shown in Figure 5. The reaction is first order in $(\eta^1\text{-}C_5H_5)Re(CO)_5$ and has an E_a of 25.9 ± 1.6 kcal mol^{-1} and log *A* of 14.4 ± 1.1 (*A* has units of s^{-1}); these correspond to $\Delta H^\ddagger$ of 25.2 ± 1.6 kcal mol^{-1} and $\Delta S^\ddagger$ of 7 ± 3 cal mol^{-1} K^{-1} at 338 K. The rate of reaction at 295 K is unaffected by the addition of 1 atm of CO, but the rate does decrease by ~60% at 295 K under 1200 psig CO. If $(\eta^5\text{-}C_5H_5)Re(CO)_3$ is stirred at 295 K for 15 h under 1200 psig CO no reaction occurs and specifically no $(\eta^1\text{-}C_5H_5)Re(CO)_5$ is formed.

Thermolysis of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in MCH containing 0.1 M CCl$_4$ at 298 K results in the formation of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (~92%) and $Re(CO)_5Cl$ (~8%); the rate of consumption of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ is the same as measured in the absence of CCl$_4$. However, thermolysis of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ in the presence of 0.1 M $C_6H_5CH_2Br$ at 302 K is complex and results in an increase in the rate of consumption of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ by a factor of ~3 over that found in the absence of $C_6H_5CH_2Br$. In addition, $Re(CO)_5Br$ is formed in ~30% yield with $(\eta^5\text{-}C_5H_5)Re(CO)_3$ formed in only ~35% yield. These results are consistent with direct reaction of $C_6H_5CH_2Br$ with $(\eta^1\text{-}C_5H_5)Re(CO)_5$ via nondissociative processes. The key result from the reaction with halocarbons capable of trapping $Re(CO)_5$ radicals is that ring slippage remains the dominant chemical process, but the direct

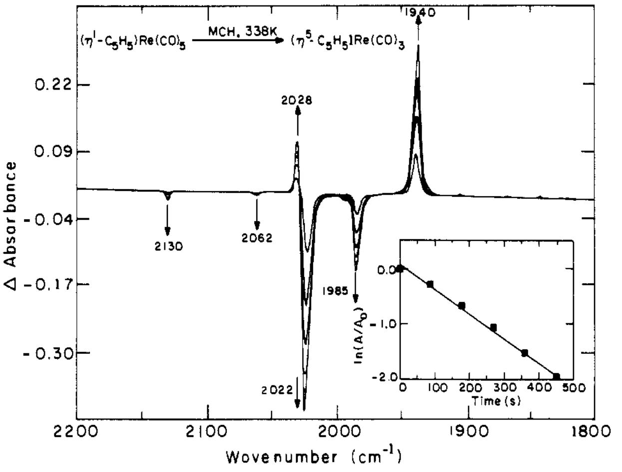

Figure 4. IR difference spectra resulting from the thermolysis of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ at 338 K. Negative peaks are due to consumption of $(\eta^1\text{-}C_5H_5)Re(CO)_5$, and positive peaks are due to formation of $(\eta^5\text{-}C_5H_5)Re(CO)_3$. The inset shows the first-order rate plot for consumption of $(\eta^1\text{-}C_5H_5)Re(CO)_5$.

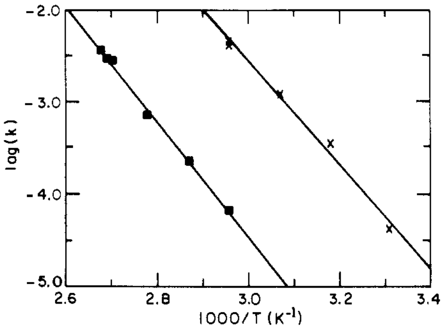

Figure 5. Arrhenius plot for reaction of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ to $(\eta^5\text{-}C_5H_5)Re(CO)_3$ in MCH solution (×); E_a = 25.9 ± 1.6 kcal mol^{-1}, log *A* = 14.4 ± 1.1. Arrhenius plot for reaction of $(\eta^1\text{-}9\text{-fluorenyl})Re(CO)_5$ with PPh$_3$ under pseudo-first-order conditions to give $(\eta^1\text{-}9\text{-fluorenyl})Re(CO)_4PPh_3$ (■); E_a = 29 ± 1 kcal mol^{-1}, log *A* = 14 ± 1.

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(18) Kochi, J. K. *Organometallic Mechanism and Catalysis*; Academic Press: New York, 1978.

(19) McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3066.

(20) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

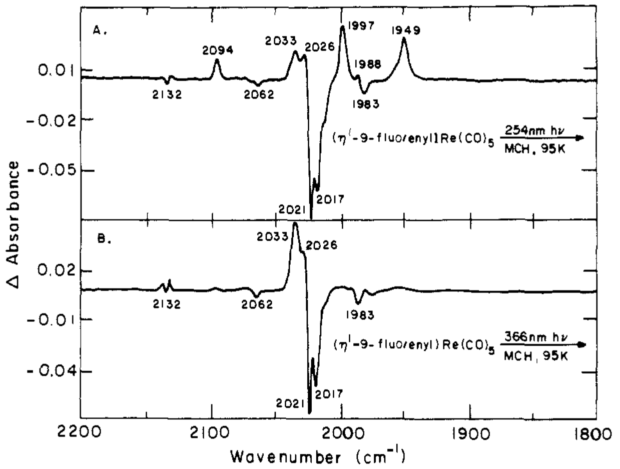


Figure 6. IR difference spectra resulting from irradiation of (η^1-9-fluorenyl)Re(CO)$_5$ in a MCH matrix at 95 K. (A) IR spectral changes upon 254-nm irradiation. (B) IR spectral changes accompanying 366-nm irradiation. Negative peaks are due to consumption of starting material, and positive peaks at 2094, 1997, 1988, and 1957 cm^{-1} are due to formation of (η^3-fluorenyl)Re(CO)$_4$. Positive peaks at 2130, 2033, and 2026 cm^{-1} and a band at 1983 cm^{-1} (obscured by starting material) are due to a new, isomeric (fluorenyl)Re(CO)$_5$ complex.

reactions with $C_6H_5CH_2Br$ and CCl_4 preclude quantitative assessment.

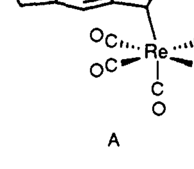
(η^1-C_5H_5)Re(CO)$_5$ reacts with 0.1 M PPh$_3$ in MCH at 302 K to form a compound having bands in the IR spectrum at 2084, 2009, 1978, and 1945 cm^{-1} (Table I). No (η^5-C_5H_5)Re(CO)$_3$ is formed under these conditions. The positions and intensities of the product bands are consistent with those expected for *cis*-(η^1-C_5H_5)Re(CO)$_4$PPh$_3$.[19] At lower PPh$_3$ concentrations, e.g., 0.01 M, (η^5-C_5H_5)Re(CO)$_3$ is formed as well as *cis*-(η^1-C_5H_5)-Re(CO)$_4$PPh$_3$. The rate of consumption of (η^1-C_5H_5)Re(CO)$_5$ in the presence of PPh$_3$ (0.01–0.1 M) at 302 K is found to be the same as for the consumption of (η^1-C_5H_5)Re(CO)$_5$ in the absence of PPh$_3$ and is independent of PPh$_3$ concentration (0.1–0.01 M).

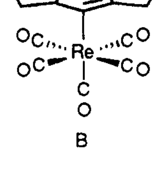
Low-Temperature Photochemistry of (η^1-9-Fluorenyl)Re(CO)$_5$. Irradiation of (η^1-9-fluorenyl)Re(CO)$_5$ at 254, 313, or 366 nm in a MCH matrix at 95 K leads to a decrease in intensity of IR bands for (η^1-9-fluorenyl)Re(CO)$_5$ and growth of two sets of new bands (Figure 6). None of the product bands are attributable to Re(CO)$_5$. The ratio of the two sets of new bands depends strongly on the irradiation wavelength. IR bands at 2094, 1997, 1988 (obscured by starting material), and 1957 cm^{-1} are in the expected positions and intensities for (η^3-fluorenyl)Re(CO)$_4$ based on the related (η^3-C_3H_5)Re(CO)$_4$[2] and (η^3-C_5H_5)Re(CO)$_4$ (vide supra) (eq 11). The other set of bands at 2130, 2033, 2026, and 1983 (obscured by starting material) cm^{-1} is believed to be an isomer of the starting (η^1-9-fluorenyl)Re(CO)$_5$ complex (eq 12).

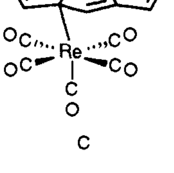
$$(\eta^1\text{-9-fluorenyl})\text{Re(CO)}_5 \xrightarrow[-\text{CO}]{h\nu} (\eta^3\text{-fluorenyl})\text{Re(CO)}_4 \quad (11)$$

$$(\eta^1\text{-9-fluorenyl})\text{Re(CO)}_5 \xrightarrow{h\nu} (\text{C}_{13}\text{H}_9)\text{Re(CO)}_5 \quad (12)$$

We speculate that the complex may have one of the structures A, B, or C. The pattern of bands in the IR spectrum is consistent


A


B


C

with a (η^1-R)Re(CO)$_5$ moiety. The new complex might arise from a photochemical 1,3 metal migration (structure A), photochemical isomerization of the coordinated fluorene (structure B), or cleavage of the Re–fluorene σ bond followed by coupling of the Re(CO)$_5$ and $C_{13}H_9$ radicals at a different C atom (structure A or C). The absorbance[17] for free CO at 2132 cm^{-1} is obscured by starting material absorbances. The two photoproducts from (η^1-9-fluorenyl)Re(CO)$_5$ are thermally inert in a matrix at 95 K. Importantly, there is a strong wavelength dependence on the relative amount of the two products from low-temperature irradiation of (η^1-9-fluorenyl)Re(CO)$_5$ (Figure 6). Following 254-nm irradiation of (η^1-9-fluorenyl)Re(CO)$_5$ there is 10 times as much (η^3-fluorenyl)Re(CO)$_4$ as is observed following 366-nm irradiation at 10% consumption of starting material. The isomeric (η^1-R)-Re(CO)$_5$ is the predominant (>90%) photoproduct following 366-nm excitation of (η^1-9-fluorenyl)Re(CO)$_5$.

Exhaustive 254-nm irradiation (>50% consumption) of (η^1-9-fluorenyl)Re(CO)$_5$ in an MCH matrix at 95 K results in the eventual formation of (η^5-fluorenyl)Re(CO)$_3$ (~10%) as well as extensive other secondary photoproducts. Warm-up to 295 K of the photoproduct mixture following >50% consumption of starting material results in regeneration of (η^1-9-fluorenyl)Re(CO)$_5$ and additional formation of (η^5-fluorenyl)Re(CO)$_3$. At 295 K, the (η^5-fluorenyl)Re(CO)$_3$ accounts for ~15–20% of the (η^1-9-fluorenyl)Re(CO)$_5$ that was consumed at 95 K. That additional (η^5-fluorenyl)Re(CO)$_3$ is detected indicates that it is thermally stable under the conditions of the warm-up experiment (vide infra). The (η^1-9-fluorenyl)Re(CO)$_5$ formed on warming accounts for ~50–55% of that consumed in the photolysis at 95 K. Thus, even at high extent conversion the majority (~70–75%) of the (η^1-9-fluorenyl)Re(CO)$_5$ consumed at 95 K can be accounted for by (η^5-fluorenyl)Re(CO)$_3$ or regenerated (η^1-9-fluorenyl)Re(CO)$_5$.

Warming a matrix containing (η^3-fluorenyl)Re(CO)$_4$ and the isomeric (fluorenyl)Re(CO)$_5$ to 295 K results in the quantitative (>95%) regeneration of (η^1-9-fluorenyl)Re(CO)$_5$. No (η^5-fluorenyl)Re(CO)$_3$ is observed in the IR spectrum of the photoproduct mixture after warm-up. These results are consistent with the conclusion that (η^3-fluorenyl)Re(CO)$_4$ can thermally back react with photogenerated CO to form (η^1-9-fluorenyl)Re(CO)$_5$ (eq 13 and 14) and that thermal ring slippage to give (η^5-fluorenyl)Re(CO)$_3$ is not competitive under these conditions.

$$(\eta^3\text{-fluorenyl})\text{Re(CO)}_4 \rightleftarrows (\eta^1\text{-9-fluorenyl})\text{Re(CO)}_4 \quad (13)$$

$$(\eta^1\text{-9-fluorenyl})\text{Re(CO)}_4 \xrightarrow{\text{CO}} (\eta^1\text{-9-fluorenyl})\text{Re(CO)}_5 \quad (14)$$

Warm-up of the photoproduct mixture also indicates that the isomeric (fluorenyl)Re(CO)$_5$ formed will thermally isomerize to regenerate (η^1-9-fluorenyl)Re(CO)$_5$ (eq 15). If the warm-up is

$$(\text{C}_{13}\text{H}_9)\text{Re(CO)}_5 \xrightarrow{\Delta} (\eta^1\text{-9-fluorenyl})\text{Re(CO)}_5 \quad (15)$$

effected in the presence of 0.05 M PPh$_3$, the (η^3-fluorenyl)Re(CO)$_4$ is trapped quantitatively as (η^1-9-fluorenyl)Re(CO)$_4$PPh$_3$. The (η^1-9-fluorenyl)Re(CO)$_4$PPh$_3$ was identified based on comparison with an authentic sample (vide infra).

Room-Temperature Photochemistry of (η^1-9-Fluorenyl)Re(CO)$_5$. Irradiation at 366 nm of (η^1-9-fluorenyl)Re(CO)$_5$ in deoxygenated alkane solution at 295 K results in the formation of Re$_2$(CO)$_{10}$ as the only metal carbonyl product in ~60% yield. HPLC analysis of a photoproduct mixture produced by 366-nm irradiation of (η^1-9-fluorenyl)Re(CO)$_5$ in MCH solutions shows 9,9′-bifluorene to be the major product derived from the fluorenyl fragment. The 9,9′-bifluorene accounts for ~80% of the fluorenyl radical formed.

If irradiation of (η^1-9-fluorenyl)Re(CO)$_5$ is effected at 366 nm in deoxygenated alkane solutions containing 0.25 M $C_6H_5CH_2Br$, Re(CO)$_5$Br is formed and accounts for typically 90% of the (η^1-9-fluorenyl)Re(CO)$_5$ consumed; no other metal carbonyl species are detected by IR spectroscopy (Figure 7). HPLC analysis shows the formation of 9,9′-bifluorene in the expected yield (~80%); no evidence for the formation of 9-bromofluorene was detected by HPLC. Importantly, no thermal reaction occurs between (η^1-9-fluorenyl)Re(CO)$_5$ and $C_6H_5CH_2Br$ at 295 K. Irradiation at 366 nm of (η^1-9-fluorenyl)Re(CO)$_5$ in MCH solutions containing 0.25 M $C_6H_5CH_2Br$ and 0.05 M PPh$_3$ results in the formation of only Re(CO)$_5$Br and *cis*-BrRe(CO)$_4$PPh$_3$, both

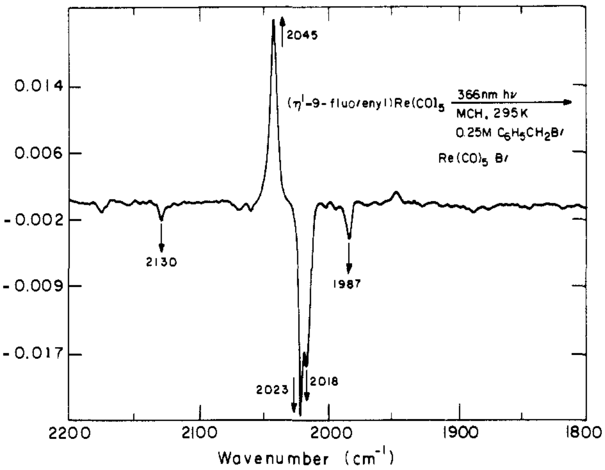


Figure 7. IR difference spectrum accompanying 366-nm irradiation of (η^1-9-fluorenyl)$Re(CO)_5$ in MCH solution containing 0.25 M $C_6H_5CH_2Br$ at 295 K. Negative peaks are due to consumption of starting material, and positive peaks are due to formation of $Re(CO)_5Br$.

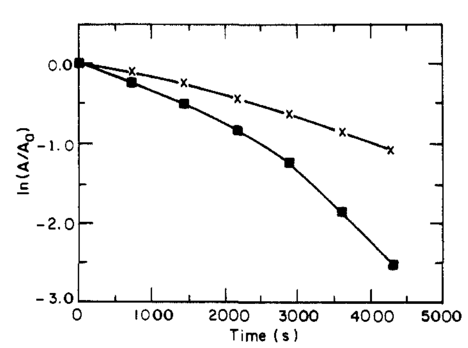


Figure 8. Rate plot for the reaction of (η^1-9-fluorenyl)$Re(CO)_5$ to (η^5-fluorenyl)$Re(CO)_3$ at 372 K. Initial concentration of (η^1-9-fluorenyl)$Re(CO)_5$ is 2.0 mM (■) and 6.4 mM (×).

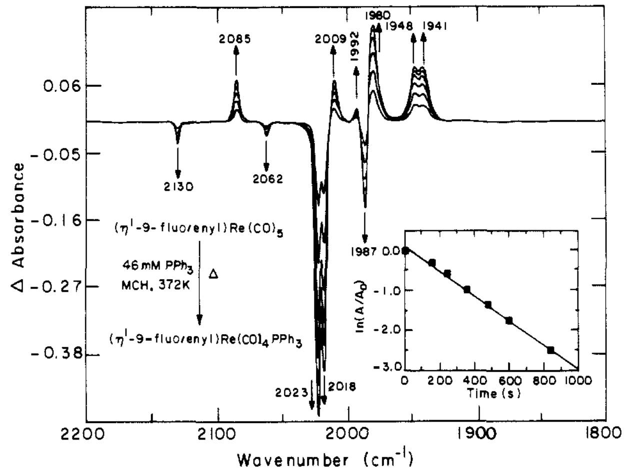


Figure 9. IR difference spectra for the reaction of (η^1-9-fluorenyl)$Re(CO)_5$ with 46 mM PPh_3 at 372 K. Negative peaks are due to consumption of (η^1-9-fluorenyl)$Re(CO)_5$, and positive peaks are due to formation of (η^1-9-fluorenyl)$Re(CO)_4PPh_3$. The inset shows the first-order rate plot for the consumption of (η^1-9-fluorenyl)$Re(CO)_5$.

Table III. Rate Constants for the Thermal Reaction of (η^1-9-Fluorenyl)$Re(CO)_5$ with PPh_3 To Give (η^1-9-Fluorenyl)$Re(CO)_4PPh_3$

[Re],[a] mM	[PPh_3],[b] mM	T, K	$k \times 10^3$,[c] s^{-1}
1.7	94	372	3.0
1.7	44	372	3.0
1.3	19	373	3.6
1.1	44	373	3.7
5.4	44	371	2.9
2.1	44	360	0.71
2.1	44	349	0.21
2.1	44	338	0.064
2.1	44	338	0.067

[a] Initial concentration of (η^1-9-fluorenyl)$Re(CO)_5$. [b] Initial concentration of PPh_3. [c] ±10%.

derived from $Re(CO)_5$. No features are observed in the IR spectrum that are attributable to a CO loss product such as (η^3-fluorenyl)$Re(CO)_4$ or (η^1-9-fluorenyl)$Re(CO)_4PPh_3$.

Flash photolysis or brief (<1 min) irradiation of (η^1-9-fluorenyl)$Re(CO)_5$ at 254 or 313 nm in MCH solutions at 295 K results in formation of $Re_2(CO)_{10}$ and (η^3-fluorenyl)$Re(CO)_4$. Irradiation at 366 nm for times <1 min shows no IR spectral features for (η^3-fluorenyl)$Re(CO)_4$. The (η^3-fluorenyl)$Re(CO)_4$ formed by irradiation at 254 nm reacts rapidly thermally to regenerate (η^1-9-fluorenyl)$Re(CO)_5$ at 295 K, and the (η^3-fluorenyl)$Re(CO)_4$ is completely consumed in <2 min under the conditions of the photolysis ([CO] < ~0.1 mM). Longer irradiation times (e.g., 10 min) result in the detection of only $Re_2(CO)_{10}$. Irradiation of (η^1-9-fluorenyl)$Re(CO)_5$ in MCH containing 0.1 M PPh_3 at 313 or 254 nm (where PPh_3 absorbs significantly) results in the formation of *cis*-(η^1-9-fluorenyl)$Re(CO)_4PPh_3$ as well as $Re_2(CO)_{10}$ and $Re_2(CO)_9PPh_3$. The simple substitution product logically results from CO loss, and $Re_2(CO)_9PPh_3$ is expected from the known[18] behavior of $Re(CO)_5$ in the presence of PPh_3.

Quantum yields at 295 K for the disappearance of (η^1-9-fluorenyl)$Re(CO)_5$ and the appearance of $Re(CO)_5Br$ were measured for irradiations effected in deoxygenated MCH containing 0.25 M $C_6H_5CH_2Br$ at 366 nm. The dissappearance Φ of (η^1-9-fluorenyl)$Re(CO)_5$ is 0.045 ± 0.005, and the appearance Φ of $Re(CO)_5Br$ is 0.04 ± 0.004 for 366-nm excitation. For irradiation of (η^1-9-fluorenyl)$Re(CO)_5$ in MCH at 254 nm the disappearance quantum yield is 0.23 ± 0.07.

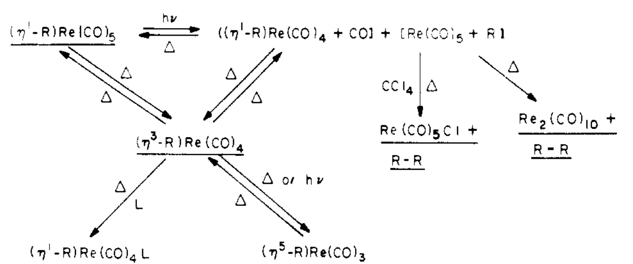
Thermal Chemistry of (η^1-9-Fluorenyl)$Re(CO)_5$. In deoxygenated MCH solutions with an Ar purge at 400 K, (η^1-9-fluorenyl)$Re(CO)_5$ converts in high yield (>95%) to (η^5-fluorenyl)$Re(CO)_3$. Plots of ln (A/A_0) versus time are curved, with the rate becoming greater as the reaction proceeds (Figure 8). Addition of 0.1 M $C_6H_5CH_2Br$ or 10^{-3} M (η^5-fluorenyl)$Re(CO)_3$ does not effect the rates or the product formed. The initial rate is found to be dependent on the starting concentration of (η^1-9-fluorenyl)$Re(CO)_5$, with slower initial rates at higher starting concentrations of (η^1-9-fluorenyl)$Re(CO)_5$. This is consistent with the conclusion that (η^1-9-fluorenyl)$Re(CO)_5$ has a significant equilibrium constant for dissociation of CO (eq 16),

$$(\eta^1\text{-9-fluorenyl})Re(CO)_5 \rightleftarrows (\eta^1\text{-9-fluorenyl})Re(CO)_4 + CO \quad (16)$$

and the dissociated CO suppresses the ring-slippage reaction. As the reaction proceeds the concentration of (η^1-9-fluorenyl)$Re(CO)_5$ decreases and hence the concentration of CO increases and the reaction rate decreases. We find that under 1 atm of CO the rate of conversion of (η^1-9-fluorenyl)$Re(CO)_5$ to (η^5-fluorenyl)$Re(CO)_3$ decreases by a factor of >100, and prolonged (~6 h) thermolysis under CO yields slow reaction and small yields (~5–10%) of fluorene, presumably via a radical process.

If (η^1-9-fluorenyl)$Re(CO)_5$ is heated in MCH containing PPh_3 (0.1–0.01 M), no (η^5-fluorenyl)$Re(CO)_3$ is detected, but a new product with IR absorbances at 2085, 2009, 1992, 1980, 1948, and 1941 cm^{-1} is formed. The relative positions and intensities of these bands are consistent with those expected for *cis*-(η^1-9-fluorenyl)$Re(CO)_4PPh_3$.[19] That there are more than four carbonyl bands observed for pure *cis*-(η^1-9-fluorenyl)$Re(CO)_4PPh_3$, while only four bands are observed for *cis*-(η^1-C_5H_5)$Re(CO)_4PPh_3$ and other $RRe(CO)_4L$ complexes,[19] suggests that there may be hindered rotation due to the bulky substituents around the Re atom. The substitution reaction is first order in (η^1-9-fluorenyl)$Re(CO)_5$ (Figure 9), and the rate is found to be independent of PPh_3 concentration between 0.1 and 0.01 M. The temperature dependence of the PPh_3 substitution of (η^1-9-fluorenyl)$Re(CO)_5$ between 372 and 338 K was measured, giving an E_a of 29 ± 1

Scheme I. Thermal and Photochemical Reactions of (η^1-R)Re(CO)$_5$[a]



[a] Underlined species have been observed.

kcal mol^{-1} and log A of 14 ± 1 (A has units of s^{-1}); these correspond to ΔH^* of 28.3 ± 1 kcal mol^{-1} and ΔS^* of 7 ± 3 cal mol^{-1} K^{-1} (Table III and Figure 5). At 295 K (η^5-fluorenyl)Re(CO)$_3$ reacts quantitatively with CO to re-form (η^1-9-fluorenyl)Re(CO)$_5$; with 1 atm of CO the reaction is first order in (η^5-9-fluorenyl)-Re(CO)$_3$ and occurs with a rate of 9.7 × 10^{-5} s^{-1} at 295 K (eq 17, 18, 13, and 14).

$$(\eta^5\text{-fluorenyl})\text{Re(CO)}_3 \rightleftarrows (\eta^3\text{-fluorenyl})\text{Re(CO)}_3 \quad (17)$$

$$(\eta^3\text{-fluorenyl})\text{Re(CO)}_3 \xrightarrow{\text{CO}} (\eta^3\text{-fluorenyl})\text{Re(CO)}_4 \quad (18)$$

Photochemistry of CH$_3$Re(CO)$_5$. Flash photolysis of CH$_3$-Re(CO)$_5$ in CO deoxygenated MCH at 295 K leads to the formation of Re$_2$(CO)$_{10}$ as the only detectable metal carbonyl product. The Re$_2$(CO)$_{10}$ formed typically accounts for ~35–40% of the starting material consumed. Photolysis at 313 nm of CH$_3$Re(CO)$_5$ in MCH containing 0.2 M CCl$_4$ results in the formation of Re(CO)$_5$Cl in a yield of ~35%. However, if CH$_3$Re(CO)$_5$ is irradiated at 313 nm in MCH containing 0.05 M PPh$_3$, *cis*-CH$_3$Re(CO)$_4$PPh$_3$ is formed. These results are consistent with both CO loss[1d] and Re–R bond homolysis being primary photoprocesses for CH$_3$Re(CO)$_5$.

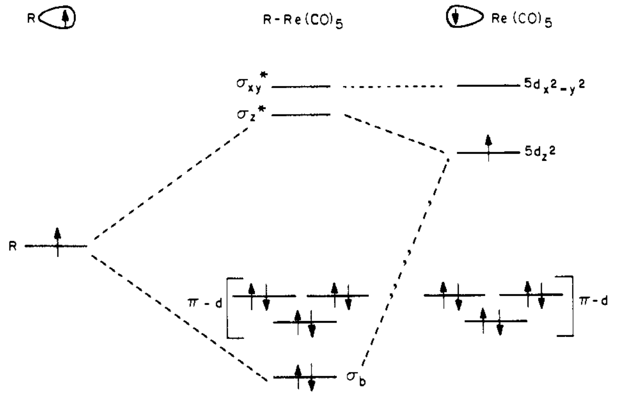
Thermal Chemistry of CH$_3$Re(CO)$_5$. CH$_3$Re(CO)$_5$ reacts with 44 mM PPh$_3$ at 372 K with a half-life of >6 h. Monitoring the reaction by IR spectroscopy shows the growth of bands associated with CH$_3$Re(CO)$_4$PPh$_3$; however, the product bands are small and do not increase as more CH$_3$Re(CO)$_5$ is consumed. As the reaction proceeds, the solution becomes turbid, and analysis of the product mixture after complete consumption of CH$_3$Re(CO)$_5$ shows a complex mixture of products. Our results are consistent with the reported thermal chemistry of CH$_3$Re(CO)$_5$ and CH$_3$Re(CO)$_4$PPh$_3$.[19] Our main finding is that CH$_3$Re(CO)$_5$ reacts qualitatively more slowly than either (η^1-C$_5$H$_5$)Re(CO)$_5$ or (η^1-9-fluorenyl)Re(CO)$_5$.

Discussion

Scheme I summarizes the thermal and photochemical processes observed for the two (η^1-R)Re(CO)$_5$ systems studied. For neither compound have we spectroscopically detected any of the presumed primary 16e$^-$ or 17e$^-$ species. However, in both cases the η^3 species have been well characterized at 95 K. The (η^3-9-fluorenyl)Re-(CO)$_4$ is relatively thermally and photochemically inert in comparison to (η^3-C$_5$H$_5$)Re(CO)$_4$ with respect to further CO loss. The latter species is both thermally and photochemically labile with respect to CO loss and reacts rapidly thermally, even at temperatures <150 K, to form (η^5-C$_5$H$_5$)Re(CO)$_3$. (η^3-Fluorenyl)-Re(CO)$_4$ has been observed as a transient in solution at 295 K and reacts rapidly with CO to yield (η^1-9-fluorenyl)Re(CO)$_5$.

For both (η^1-R)Re(CO)$_5$ complexes (R = C$_5$H$_5$, 9-fluorenyl) thermolysis in alkane solution results in only CO loss chemistry, with (η^5-R)Re(CO)$_3$ being formed in high yield. This is in contrast to the 295 K photochemistry, where R–Re bond homolysis is the major reaction path. Indeed, following 366-nm irradiation of (η^1-9-fluorenyl)Re(CO)$_5$, only products derived from R–Re homolysis are formed. There is, however, a strong excitation wavelength dependence on the photoproducts formed. Additionally, the disappearance quantum yields increase at shorter irradiation wavelengths. Low-energy irradiation (366 nm) of (η^1-9-fluorenyl)Re(CO)$_5$ yields only radical-derived products, while higher energy irradiation, 254 nm, results in both CO loss and R–Re bond cleavage. The low-temperature photochemistry of (η^1-9-fluorenyl)Re(CO)$_5$ shows the same wavelength dependence for product formation. Irradiation at 254 nm results in principally CO loss giving (η^3-fluorenyl)Re(CO)$_4$ while lower energy irradiation (366 nm) irradiation gives <10% CO loss derived products.

Scheme II. Electronic Structure of RRe(CO)$_5$



For (η^1-C$_5$H$_5$)Re(CO)$_5$ the 95 K photochemistry does not give any indication of wavelength dependence, as only (η^3-C$_5$H$_5$)Re-(CO)$_4$ and (η^5-C$_5$H$_5$)Re(CO)$_3$ are formed following 254–366-nm excitation. However, the results from the 295 K excitation indicate that while Re–R bond homolysis is favored at all wavelengths, CO loss is a more important process following high-energy (254 nm) irradiation. Following 366-nm irradiation, (η^5-C$_5$H$_5$)Re(CO)$_3$ formation accounts for ~10% of the (η^1-C$_5$H$_5$)Re(CO)$_5$ consumed, while following 254-nm excitation, CO loss accounts for ~25% of the (η^1-C$_5$H$_5$)Re(CO)$_5$ consumed.

Comment on the electronic structure of (η^1-R)Re(CO)$_5$ and the relationship with photochemical reactivity is appropriate. An important finding is that the product resulting from thermolysis of (η^1-R)Re(CO)$_5$ is not the same product that results from population of the lowest electronic excited state. This allows the conclusion that the lowest excited state does not relax to an upper level of the ground state capable of CO loss, the predominant ground-state process. Moreover, the predominant ground-state process, CO loss, is the process of an upper excited state. However, the excited-state process is likely a purely dissociative process, whereas the ground-state process is likely a hydrocarbon ligand assisted removal of CO (vide infra). It should be noted that the upper excited state is likely competitively relaxing to the lower excited state, accounting for some of the Re–R bond cleavage upon short-wavelength irradiation.

All of the excited states of (η^1-R)Re(CO)$_5$ involving population of σ^* levels arising from overlap of the Re 5d$_{x^2-y^2}$, 5d$_{z^2}$, and ligand σ orbitals should be labile with respect to dissociative processes.[1c] Scheme II shows an orbital diagram relevant to (η^1-R)Re(CO)$_5$. The wavelength-dependent photochemistry allows the conclusion that at least two different excited states yield chemistry. Since long-wavelength excitation favors Re–R bond cleavage products compared to CO loss derived products, we conclude that long-wavelength excitation results in predominantly the population of the σ^* level derived from the 5d$_{z^2}$ orbital, σ^*_z. Population of the σ^*_z orbital results in selective labilization of the ligands on the z axis, yielding Re–R homolysis or Re–CO$_{\text{axial}}$ cleavage. Population of the σ^* orbital derived from the 5d$_{x^2-y^2}$, the σ^*_{xy}, at higher energy, labilizes the cis CO's, leading to ring slippage and ligand substitution. The wavelength dependence of product formation following excitation of (η^1-R)Re(CO)$_5$ indicates that an excited state involving population of σ^*_z must be the lowest lying excited state, as was found to be the case in the related (η^1-R)Mn(CO)$_5$ (R = C$_5$Cl$_5$, C$_6$H$_5$CH$_2$).[11]

The orbital origin of the transitions that terminate in the σ^* orbitals is possibly the filled πd set. As for other C_{4v} low-spin d^6 systems, the first absorption is then associated with the e(d$_{xz}$,d$_{yz}$) → a$_1$(d$_{z^2}$) transition.[1c,21] However, both (η^1-9-fluorenyl)Re(CO)$_5$

and $(\eta^1\text{-}C_5H_5)Re(CO)_5$ can be viewed either as derivatives of $RRe(CO)_5$ or as derivatives of cyclopentadiene or fluorene. Examination of the electronic absorption spectra (Figure 1) indicates that neither cyclopentadiene nor fluorene has significant absorptions at $\lambda > 300$ nm. Significantly, 9-bromofluorene, possibly a better model for the electronic structure of the fluorenyl moiety in $(\eta^1\text{-9-fluorenyl})Re(CO)_5$, also has no absorption features at wavelengths >300 nm. The optical spectra support the conclusion that the first absorption and the chemistry resulting from 366-nm excitation for both $(\eta^1\text{-R})Re(CO)_5$ complexes are largely associated with excitation of Re-centered electrons. At higher energies, i.e., 254 nm, the electronic absorptions involve πd to σ^* excitations as well as πd to $\pi^*(CO)$ and intraligand excitations.

High-energy irradiation may involve a $\sigma_b \rightarrow \sigma^*_z$ transition that is similar to that observed in $Mn_2(CO)_{10}$.[22a] The $\sigma_b \rightarrow \sigma^*_z$ excited state in $(\eta^1\text{-R})Re(CO)_5$ is likely to be close in energy to the $\pi d \rightarrow \sigma^*_z$ excited state. The general increase in the quantum yields at short wavelengths for $(\eta^1\text{-R})Re(CO)_5$ could be due to population of a $\sigma_b \rightarrow \sigma^*_z$ state. Higher quantum yields for radical formation are consistent with a second, upper, excited state that produces radicals. $Mn_2(CO)_{10}$ shows both CO loss and Mn–Mn cleavage, with CO loss being more efficient at shorter wavelengths.[22] Our principal conclusion regarding the electronic structure and reactivity of $(\eta^1\text{-R})Re(CO)_5$ is that the photochemical reactions are mainly due to the lability associated with population of the σ^*_z or σ^*_{xy} orbitals; however, the orbital origin of the reactive excited states is uncertain. The optical and photochemical properties of $CH_3Re(CO)_5$, for which Scheme II applies more directly, are in accord with our conclusion regarding the $\eta^1\text{-}C_5H_5$ and η^1-9-fluorenyl species.

Consider now the thermal chemistry of $(\eta^1\text{-R})Re(CO)_5$. The temperature dependence of the reaction of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ yielding $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and that of $(\eta^1\text{-9-fluorenyl})Re(CO)_5$ with PPh_3 yielding $(\eta^1\text{-9-fluorenyl})Re(CO)_4PPh_3$ give essentially identical ΔS^* of 7 ± 3 cal mol^{-1} K^{-1}, indicating that for both complexes the transition state involves significant Re–CO bond breaking. At 338 K, $(\eta^1\text{-}C_5H_5)Re(CO)_5$ reacts with a half-life of ~2 min, while for $(\eta^1\text{-9-fluorenyl})Re(CO)_5$, reacting under pseudo-first-order conditions with PPh_3, the half-life is ~5 h. At 372 K, where $(\eta^1\text{-9-fluorenyl})Re(CO)_5$ reacts with PPh_3 with a half-life of ~5 min, $CH_3Re(CO)_5$ has a half-life of >6 h under the same conditions. Our basic observation is that the $\eta^1\text{-}C_5H_5$ species reacts many orders of magnitude more rapidly than the CH_3 species. What is surprising, considering the marked difference in the thermal stability of the two $(\eta^1\text{-R})Re(CO)_5$ (R = C_5H_5, 9-fluorenyl) complexes is that the ΔH^* values for CO loss are almost equal, at 25 ± 2 and 28 ± 1 kcal mol^{-1}. Both values of ΔH^* are significantly smaller than the average Re–CO bond energy of 43.2 ± 0.4 kcal mol^{-1} for $CH_3Re(CO)_5$,[23] though it is likely that the bond dissociation energy for loss of the first CO is less than the average. We conclude that there is some intramolecular R assistance in the CO loss chemistry of $(\eta^1\text{-R})Re(CO)_5$, based on the reactivity of R = C_5H_5 and R = 9-fluorenyl compared to $CH_3Re(CO)_5$. The similarity in the values of ΔH^* for the two species studied indicates that the uncoordinated olefins in the coordinated R ligand assist CO loss to approximately the same degree, but it appears that R assistance of CO replacement is more important for R = C_5H_5 than in the R = 9-fluorenyl case. It is, however, worth noting that for substitution of CO in $XRe(CO)_5$ (X = I, Br, Cl) by PPh_3, a system where there can be no intramolecular assistance of CO dissociation, ΔH^* varied from ~28 to 30.5 kcal mol^{-1} and ΔS^* varied from ~2 to 18 cal mol^{-1} K^{-1}.[24] The values of ΔH^* and ΔS^* are very similar to ours for $(\eta^1\text{-R})Re(CO)_5$, but the $XRe(CO)_5$ species have a very different electronic structure and the similarity may be fortuitous.

Scheme I shows two routes to $(\eta^1\text{-R})Re(CO)_4PPh_3$, one via the $16e^-$ $(\eta^1\text{-R})Re(CO)_4$ by light-induced CO loss, and the other via a direct thermal route. The hydrocarbon ligand assisted CO loss that we infer in the thermal route is not invoked for the excited state that yields CO loss. The principle of microscopic reversibility demands that there is a thermal route back to $(\eta^1\text{-R})Re(CO)_5$ that is the reverse of the forward thermal route. This suggests that formation of $(\eta^1\text{-R})Re(CO)_4L$ (L = PPh_3, CO) could be formed by direct reaction of L with $(\eta^3\text{-}C_5H_5)Re(CO)_4$. However, the principle of microscopic reversibility also allows the thermal reversion of $(\eta^3\text{-R})Re(CO)_4$ to the $16e^-$ $(\eta^1\text{-R})Re(CO)_4$, which can then be attacked by L to yield $(\eta^1\text{-R})Re(CO)_4L$. We favor the $\eta^3 \rightleftarrows \eta^1$ interconversion as a route to $(\eta^1\text{-R})Re(CO)_4L$, but unfortunately we do not have direct evidence of the ability of L to intercept the $16e^-$ $(\eta^1\text{-R})Re(CO)_4$.

The final point to be made concerns the thermal lability of η^3 species formed via photoexcitation of $(\eta^1\text{-R})Re(CO)_5$. $(\eta^3\text{-}C_5H_5)Re(CO)_4$ reacts rapidly at low temperatures <150 K and, in the absence of $2e^-$ donor ligands, forms $(\eta^5\text{-}C_5H_5)Re(CO)_3$. However, generation of $(\eta^3\text{-}C_5H_5)Re(CO)_4$ in the presence of CO or PPh_3 results in the formation of significant yields of the trapped product, $(\eta^1\text{-}C_5H_5)Re(CO)_4L$ (L = CO, PPh_3). $(\eta^3\text{-Fluorenyl})Re(CO)_4$ appears to be more inert than $(\eta^3\text{-}C_5H_5)Re(CO)_4$ with respect to further CO loss to give an η^5 species. $(\eta^3\text{-Fluorenyl})Re(CO)_4$ has been observed in solution at 295 K as a transient intermediate. $(\eta^3\text{-Fluorenyl})Re(CO)_4$ reacts rapidly with CO and PPh_3 to form the $(\eta^1\text{-9-fluorenyl})Re(CO)_4L$ adducts, and even $(\eta^5\text{-fluorenyl})Re(CO)_3$ reacts with 1 atm of CO at 295 K to quantitatively form $(\eta^1\text{-9-fluorenyl})Re(CO)_5$. Our results suggest that there is the need to consider the $\eta^3 \rightarrow \eta^1$ conversion in situations where $\eta^5\text{-} \rightarrow \eta^3$-cyclopentadienyl processes[7,25] are invoked in reactions of η^5-cyclopentadienyl complexes.

Conclusion

The photochemistry and the thermal chemistry of $(\eta^1\text{-}C_5H_5)Re(CO)_5$ and $(\eta^1\text{-9-fluorenyl})Re(CO)_5$ give differing selectivities for reaction, with CO loss being the dominant thermal process and Re–R cleavage being the dominant photochemical reaction upon long-wavelength excitation. The photochemistry of $(\eta^1\text{-R})Re(CO)_5$ exhibits a strong wavelength dependence, however, with CO loss showing significant importance upon high-energy irradiation. $(\eta^1\text{-}C_5H_5)Re(CO)_5$ is much more thermally reactive than the R = CH_3 and 9-fluorenyl species, reacting many orders of magnitude faster than the R = CH_3 species under the same conditions. This fact suggests that the cyclopentadienyl group assists the loss of CO from $(\eta^1\text{-}C_5H_5)Re(CO)_5$.

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