The exception to the above procedure was compound **14**, for which 0.94 mg (0.00634 mmol) of **14** and 0.98 mg (0.00661 mmol) of **8a** were dissolved together in 0.250 mL of 0.250 M benzophenone in benzene and the solution degassed by five freeze–pump–thaw cycles. Irradiation was performed as described above and analysis done by gas chromatography on column F (conditions above) using **8a** as an internal actinometer and the benzophenone as an internal standard.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., the Camille and Henry Dreyfus Foundation, and the National Science Foundation (Grant No. CHE-8024664), for support of this work and the use of the Southern California Regional NMR Facility (NSF Grant 7916324A1). We also thank Dr. William R. Croasmun for assistance in obtaining high-field NMR data.

Registry No. 3, 82482-48-2; **6**, 89597-60-4; **8a**, 82482-45-9; **8b**, 82482-46-0; *endo*-**8c**, 82482-47-1; **11**, 82494-77-7; **12** (E = EtOCO), 82482-51-7; **13**, 89597-58-0; **14**, 89597-61-5; **15**, 3641-77-8; **15**-T, 89597-57-9; **15-C**, 89673-94-9; **21**, 82494-76-6; **27a**, 89597-54-6; **27b**, 89597-55-7; **28c**, 89597-56-8; **29**, 89597-59-1; 5-diazo-1,3-cyclopentadiene, 1192-27-4; *p*-toluenesulfonyl chloride, 98-59-9; tosyl azide, 941-55-9; 1,3-cyclopentadiene, 542-92-7; cyclobutene, 822-35-5; diethyl azodicarboxylate, 1972-28-7; *N*-phenyltriazolinedione, 4233-33-4; *exo*-**8c**, 89673-95-0.

A Novel, Dinuclear Mechanism for Catalytic Olefin Dimerization. Photochemical Reactivity of (μ-Hydrido)(μ-alkenyl)dirhenium Octacarbonyl Compounds[1]

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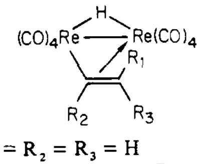
Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. Received August 26, 1983

Abstract: UV photolysis of (μ-hydrido)(μ-ethenyl)dirhenium octacarbonyl, (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_8$ (I), in the presence of ethylene affords (μ-hydrido)(μ-butenyl)dirhenium octacarbonyl complexes. A mechanism is proposed in which the initial step is photodissociation of CO from I, as photolysis of I in the presence of ^{13}CO or PPh$_3$ results in CO substitution. Subsequent steps in the formation of the μ-hydrido μ-butenyl species are coordination of ethylene, insertion of ethylene into the Re–H or Re–ethenyl σ bond, recoordination of CO, C–C or C–H reductive elimination to yield Re$_2$(CO)$_8$(1-butene), and oxidative addition of a vinylic C–H bond of coordinated butene. Slow catalytic production of 1-butene and *trans*-3-hexene occurs in the photochemical reaction of I with ethylene; butene formation is the result of thermal reaction of the (μ-hydrido)(μ-butenyl)dirhenium octacarbonyl species with ethylene, while hexene results from photochemical reaction. Removal of photodissociated CO from the system via an ethylene purge during photolysis results in subsequent catalytic production of butene and hexene under thermal (25 °C) conditions. Photolysis of (μ-hydrido)(μ-propenyl)dirhenium octacarbonyl, (μ-H)(μ-CH=CHCH$_3$)-Re$_2$(CO)$_8$, in the presence of propylene yields 2-hexene. A general mechanism for dimerization of olefins is proposed in which a dinuclear metal catalyst effects the insertion of one olefin into a vinylic C–H bond of another. Additionally, cis–trans photoisomerization of the bridging alkenyl ligand of (μ-H)(μ-CH=CHR)Re$_2$(CO)$_8$ complexes is discussed.

We recently reported the synthesis of (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl compounds (I–III) via UV photolysis of Re$_2$(CO)$_{10}$ in the presence of simple olefins.[2,3] Analogues to these compounds exist in osmium cluster chemistry; reactions of olefins (and acetylenes) with H$_2$Os$_3$(CO)$_{10}$ and H$_4$Os$_4$(CO)$_{12}$ yield μ-hydrido μ-alkenyl tri-[4] and tetraosmium[5] products, respectively. Additionally, dirhodium μ-hydrido μ-alkenyl complexes have been prepared by the reaction of ((μ-H)Rh[P(O-*i*-C$_3$H$_7$)$_3$]$_2$)$_2$ with dialkyl- and diarylalkynes.[6]



I, R$_1$ = R$_2$ = R$_3$ = H
IIa, R$_1$ = R$_2$ = H; R$_3$ = CH$_3$
IIb, R$_2$ = R$_3$ = H; R$_1$ = CH$_3$
IIIa, R$_1$ = R$_2$ = H; R$_3$ = C$_2$H$_5$
IIIb, R$_2$ = R$_3$ = H; R$_1$ = C$_2$H$_5$
IIIc, R$_1$ = R$_3$ = H; R$_2$ = C$_2$H$_5$
IV, R$_1$ = R$_2$ = H; R$_3$ = OCH$_3$
V, R$_1$ = R$_2$ = H; R$_3$ = CH$_2$CH$_2$OCH$_3$

We have found the dirhenium compounds to be remarkably reactive, both thermally and photochemically. Treatment of I–III with a variety of substrates (CO, pyridine, phosphorus nucleophiles, olefins, terminal acetylenes, H$_2$, etc.) under mild thermal conditions results in elimination of olefin and production of a substituted dirhenium octacarbonyl complex.[2] A very interesting and novel photochemical reaction pathway was first manifested by the formation of μ-hydrido μ-butenyl species III upon UV photolysis (λ >297 nm) of I in the presence of ethylene.[2] We thus initiated a thorough investigation of the photochemical reactivity of the dirhenium hydrido alkenyl compounds with olefins and other substrates. We now report the results of these studies, most notably the identification of a mechanism for olefin dimerization which requires a dinuclear metal catalyst.

Experimental Section

General. Dirhenium decacarbonyl was purchased from Pressure Chemical Co. and used without further purification. Hexane and toluene

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(1) This research was sponsored by the National Science Foundation through research Grant NSF CHE 81-19525.

(2) (a) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4955. (b) Nubel, P. O.; Brown, T. L. *Ibid.* **1984**, *106*, 644.

(3) Cyclic mono- and polyenes react similarly: Franzreb, K.-H.; Kreiter, C. G. *J. Organomet. Chem.* **1983**, *246*, 189.

(4) (a) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Organomet. Chem.* **1974**, *80*, C53. (b) Keister, J. B.; Shapley, J. R. *Ibid.* **1975**, *85*, C29.

(5) (a) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Rehani, S. K. *J. Organomet. Chem.* **1976**, *113*, C42. (b) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Mann, A. L.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 547.

(6) (a) Burch, R. R.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 4257. (b) Burch, R. R.; Shusterman, A. J.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *Ibid.* **1983**, *105*, 3546.

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were treated with concentrated H_2SO_4, rinsed with aqueous $NaHCO_3$, dried over $MgSO_4$, and fractionally distilled from CaH_2 under argon. Cyclohexane (Spectranalyzed grade, Fischer Scientific) was employed without further purification for UV-visible spectra. Pyridine was predried over KOH, distilled under argon, and stored over 3-Å molecular sieves (Linde). Triphenylphosphine was recrystallized twice from ethanol. CP grade CO was obtained from Linde and used directly. ^{13}CO, 99% ^{13}C enriched, was obtained from Monsanto Research Corp., Mound Facility (Miamisburg, OH).

CP grade ethylene, propylene, 1-butene, *trans*-2-butene, *cis*-2-butene (99%), isobutane, and methyl vinyl ether were obtained from Linde and used directly. C_2D_4, 99 atom % D, was purchased from KOR Isotope. Styrene (99%) was obtained from Aldrich and degassed prior to use.

Reagent grade solvents (hexane, CH_2Cl_2) were used without purification for chromatography and recrystallization. Silica gel (70–230 mesh, EM Reagents) was employed for column chromatography. Preparative TLC plates (20 × 20 cm, 2.0 mm silica with UV_{254} fluorescent indicator) were obtained from Brinkmann Instruments, Inc.

Infrared spectra were obtained by using a Beckman IR-4240 spectrophotometer. Electronic spectra were recorded on a Cary-219 spectrophotometer using matched 1.0-cm quartz cells. Electron impact mass spectra were recorded at 70 eV with a Varian MAT CH-5 instrument. All m/e values are reported relative to $Re_2 = 372$. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. ^1H NMR data were obtained by using a Nicolet NT-360 instrument at 360.06 MHz. Spectra were recorded at ambient temperature except where indicated.

All photochemical reactions employed a General Electric 275-W Sunlamp[7] and Pyrex reaction vessels. The Pyrex-filtered radiation consists primarily of 366-nm wavelength;[8] significant emission is also observed at 313, 334, 406, and 436 nm. Essentially no emission below λ 297 nm occurs.

Preparation of Compounds. (μ-H)(μ-*trans*-CH=$CHCH_3$)$Re_2(CO)_8$ (IIa) was prepared by the photochemical reaction of $Re_2(CO)_{10}$ with propylene.[2] $Re_2(CO)_{10}$ (0.300 g, 0.460 mmol) was dissolved in 10 mL of toluene under argon in a 50-mL Pyrex Schlenk flask. The solution was saturated with propylene (1 atm) and then photolyzed for 15–20 h at 25 °C. (A Sunlamp was placed 5 cm from the reaction vessel; the solution was maintained at room temperature by forced-air cooling.) IR analysis after photolysis indicated near complete (~90%) conversion of $Re_2(CO)_{10}$ to (μ-H)(μ-CH=$CHCH_3$)$Re_2(CO)_8$. Reaction of the remaining $Re_2(CO)_{10}$ was effected by vacuum degassing the reaction solution to remove evolved CO, resaturating with 1 atm of propylene, and photolyzing 2–3 h more. IIa, a pale yellow oil, was isolated by column chromatography (4:1 hexane/CH_2Cl_2) and subsequent sublimation (0.1 mm, 50 °C) of the chromatographed product. Yield: 0.20–0.24 g (70–80%). Anal. Calcd for $C_{11}H_6O_8Re_2$: C, 20.69; H, 0.95. Found: C, 21.05; H, 0.98. IR (hexane): ν_{CO} 2114 (vw), 2083 (w), 2017 (s), 1994 (m), 1979 (ms), 1975 (sh), 1967 (m) cm^{-1}. Mass spectrum: m/e 638 (M^+). ^1H NMR ($CDCl_3$): δ −14.42 (s, 1 H, μ-H), 6.51 (d, 1 H, H_2), 5.30 (dq, 1 H, H_1), 2.20 (d, 3 H, CH_3); $J_{H_1-H_2} = 15.9$ Hz, $J_{H_1-CH_3} = 5.4$ Hz.

(μ-H)(μ-*trans*-CH=CHC_2H_5)$Re_2(CO)_8$ (IIIa) was prepared in similar yield by an analogous procedure using 1-butene instead of propylene. IIIa is also a pale yellow oil at 25 °C. Anal. Calcd for $C_{12}H_8O_8Re_2$: C, 22.09; H, 1.24. Found: C, 22.27; H, 1.25. IR (hexane): ν_{CO} 2114 (vw), 2083 (w), 2017 (s), 1995 (m), 1979 (ms), 1976 (sh), 1967 (m) cm^{-1}. Mass spectrum: m/e 652 (M^+). ^1H NMR ($CDCl_3$): δ −14.45 (s, 1 H, μ-H), 6.55 (d, 1 H, H_2), 5.36 (dt, 1 H, H_1), 2.29 (qd, 2 H, CH_2), 1.14 (t, 3 H, CH_3); $J_{H_1-H_2} = 16.1$ Hz, $J_{H_1-CH_2} = 5.2$ Hz, $J_{CH_2-CH_3} = 7.3$ Hz.

(μ-H)(μ-CH=CH_2)$Re_2(CO)_8$ (I) was prepared in similar yield by thermal reaction of IIa with ethylene.[2] IIa (0.23 g, 0.36 mmol) was dissolved in 10 mL of toluene under 1 atm of C_2H_4 and stirred for 10 h at 40 °C. The solution was then vacuum degassed (at 25 °C), resaturated with 1 atm of C_2H_4, and stirred at 40 °C for an additional 10 h. The degas/ethylene-treatment procedure was repeated, after which conversion of IIa to I was complete (by IR, ^1H NMR). I, a pale yellow crystalline solid, was purified by column chromatography (4:1 hexane/CH_2Cl_2) and subsequent sublimation (0.1 mm, 70 °C). Anal. Calcd for $C_{10}H_4O_8Re_2$: C, 19.23; H, 0.65. Found: C, 19.46; H, 0.77. IR (hexane): ν_{CO} 2117 (vw), 2085 (w), 2021 (s), 1998 (m), 1988 (m), 1978 (mw), 1970 (m) cm^{-1}. Mass spectrum: m/e 624 (M^+). ^1H NMR ($CDCl_3$): δ −14.72 (s, 1 H, μ-H), 7.18 (dd, 1 H, H_2), 4.46 (dd, 1 H, H_1), 6.26 (dd, 1 H, H_3); $J_{H_1-H_2} = 17.2$ Hz, $J_{H_2-H_3} = 10.9$ Hz, $J_{H_1-H_3} = 2.9$ Hz.

(μ-D)(μ-CD=CD_2)$Re_2(CO)_8$ (I-d_4) was prepared by an analogous procedure using C_2D_4.[2] Elemental analysis and IR (ν_{CO}) data are identical with those of I. Mass spectrometric analysis indicates the actual isotopic distribution to be 97% $D_4C_{10}O_8Re_2$ and 3% $D_3HC_{10}O_8Re_2$, consistent with the C_2D_4 isotopic enrichment (99 atom % D).

(μ-H)(μ-*trans*-CH=CHPh)$Re_2(CO)_8$ was prepared by thermal reaction of I with styrene.[2] Dissolution of I in neat styrene resulted in essentially quantitative conversion (by IR, ^1H NMR) to (μ-H)(μ-*trans*-CH=CHPh)$Re_2(CO)_8$ within 5–6 h at 25 °C. The product was isolated as a pale yellow oil by preparative TLC (10:1 hexane/CH_2Cl_2) and subsequent evaporation of solvent under vacuum. IR (pentane): ν_{CO} 2113 (vw), 2083 (w), 2017 (s), 1996 (m), 1988 (m), 1974 (w, sh), 1969 (m) cm^{-1}. Mass spectrum: m/e 700 (M^+). ^1H NMR (CD_2Cl_2): δ −14.16 (s, 1 H, μ-H), 7.53 (d, 1 H, H_1 or H_2), 7.41–7.43 (m, 4 H, Ph_α + Ph_β), 7.28–7.34 (m, 1 H, Ph_γ), 6.22 (d, 1 H, H_2 or H_1); $J_{H_1-H_2} = 16.6$ Hz.

$[Re(CO)_3OH]_4$ was prepared by the method of Gard and Brown.[8]

Gas Chromatographic Analyses. Gas chromatographic analyses for C_4 and C_5 hydrocarbons were performed by using a Varian Aerograph Series 2700 gas chromatograph equipped with a 12 ft × $^1/_4$ in. glass column packed with Durapak 17% *n*-octane/Porasil C (Waters). A flame ionization detector was employed, and the column flow rate (N_2) was set at 15 mL/min. With a column temperature of 51 °C and injection port temperature of 25 °C the following retention times (min) were measured for C_4 hydrocarbons: isobutane, 7.2; *n*-butane, 8.0; 1-butene, 10.0; *trans*-2-butene, 12.0; *cis*-2-butene, 13.0 (ethylene, 3.4). Quantitative butene analyses were performed by head-gas sampling of stirred reaction solutions; isobutane was employed as an internal standard. With the column at 55 °C and injection port at 200 °C, the following C_5 retention times (min) were observed: 1-pentene, 22.0; *trans*-2-pentene, 27.4; *cis*-2-pentene, 28.8. Authentic samples were obtained from ICN Pharmaceuticals, Inc., K and K Labs Division. C_5 (and C_6) analyses were performed by using solution samples.

In order to confirm the identity of C_6 hydrocarbon products, three gas chromatographic systems were employed. The first was the above-described apparatus with the column at 81 °C and injection port at 200 °C, for which the following retention times (min) were measured: *n*-hexane, 14.0; 1-hexene, 15.2; *trans*-2-hexene, 16.6; *cis*- and *trans*-3-hexene, 16.6; *cis*-2-hexene, 17.4 (unable to separate *trans*-2- and 3-hexene). The second was a Varian Series 3700 gas chromatograph equipped with a 25-m SE-30 capillary column and flame ionization detector. With a flow rate (He) of 30 mL/min, column temperature of 31 °C, and injection port temperature of 260 °C, the following retention times were observed: n-hexane, 5.42; *trans*-4-methyl-2-pentene, 4.65; 2-ethyl-1-butene, 5.38; 1-hexene, 5.08; *trans*-2-hexene, 5.56; *cis*-2-hexene, 5.88; *cis*- and *trans*-3-hexene (unable to separate), 5.48. Separation of *cis*- and *trans*-3-hexene was achieved by using a Hewlett-Packard 5730A gas chromatograph equipped with a thermal conductivity detector and a 24 ft × $^1/_8$ in. column packed with 20% β,β'-oxydipropionitrile supported on 100/120 Chromosorb W-HP. With a column temperature of 25 °C (injection port temperature, 210 °C) and flow rate (He) of 20 mL/min, the retention times of *cis*- and *trans*-3-hexene were 7.8 and 7.3 min, respectively. Authentic samples were obtained from Aldrich and from ICN Pharmaceuticals, Inc.

Photochemical Reactions. All photochemical reactions, except those involving olefin purging (vide infra), were performed by using a cylindrical Pyrex Schlenk vessel approximately 1.5 cm in diameter and 10 cm in height (inner volume ~20 cm^3). A septum inlet was mounted at the top. The vessel was surrounded by a Pyrex-walled jacket, ~0.5 cm thick, through which temperature-controlled distilled water was circulated in order to maintain a constant reaction temperature during photolysis. Photolyses were performed with the Sunlamp positioned 0.5 cm from the reaction vessel (distance from outer jacket wall). Reaction solutions were magnetically stirred during irradiation. The initial concentration of the (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl compound employed was typically 0.5–1.5 × 10^{-2} M (0.01–0.04 mmol in 1–4 mL of solvent). The reaction vessel was thoroughly cleaned (acid washed) after each experiment.

A. Photolyses of I–III in the Absence of Added Ligands. The (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl compound (0.010–0.015 mmol) was loaded into the photochemical reaction vessel and dissolved in 1–2 mL of solvent (toluene or hexane) under argon. The solution was equilibrated at the desired temperature (5, 25, or 45 °C) and then photolyzed. Toluene-d_8 solvent was employed for experiments involving IIa or IIIa; immediately following cessation of photolysis the reaction solution was transferred via a gas-tight syringe to an NMR tube immersed in a −78 °C CO_2/2-propanol bath. The ^1H NMR spectrum was subsequently obtained by rapidly transferring the sample to a chilled (~−50 °C) NMR probe and recording the spectrum at −20 °C.

B. Photolyses in the Presence of ^{13}CO, PPh_3. I or IIa (0.015 mmol) was loaded into the reaction vessel and dissolved in 3 mL of ^{13}CO-saturated solvent (hexane or toluene) under 1 atm of ^{13}CO. The solution was

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(7) General Electric Lighting Business Group, "RS Sunlamp Report", Nela Park, Cleveland, OH.

(8) Gard, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 6340.

photolyzed immediately thereafter and maintained at 25 °C by the above-described temperature control system. After photolysis, solvent was removed under vacuum, and mass spectral analysis of the residue was performed.

I (0.0205 g, 0.033 mmol) and PPh_3 (0.0086 g, 0.033 mmol) were loaded into the reaction vessel and dissolved in 4 mL of hexane under argon. The solution was photolyzed immediately thereafter at 25 °C for 45 min. Solvent was removed under vacuum after photolysis, leaving a yellow solid as residue.

C. Photolyses of I in the Presence of Olefins. In experiments involving ethylene, I (0.015 g, 0.024 mmol) was loaded into the reaction vessel and dissolved in 2.0 mL of ethylene-saturated toluene under 1 atm of ethylene. The solution was then equilibrated at the desired temperature (25 °C or 50 °C) and photolyzed. Toluene-d_8 solvent was employed for NMR experiments; immediately following cessation of photolysis the reaction solution was transferred to a chilled (−78 °C) NMR tube, and the ^1H NMR spectrum was recorded at −20° as described above. In experiments involving analysis for butene and hexene products, 0.80 mL of isobutane was injected into the reaction vessel (through the septum inlet) via a syringe prior to photolysis. Head-gas aliquots (~0.05 mL) were withdrawn via a gas-tight syringe during the photochemical reaction and analyzed by GC. Quantitation of butene products was accomplished by comparison of butene/isobutane GC response ratios with those of standard solutions. Quantitation of hexene products was performed by GC analysis of a 2.0-μL reaction solution aliquot and comparison of the GC response to those of standard solutions. Additionally, two other solution aliquots (~0.2 mL each) were withdrawn via a gas-tight syringe. One of these was transferred to a Schlenk vessel under argon and then vacuum distilled (at 25 °C) to dryness; 2.0 μL of the distillate, collected in a cold trap, was GC analyzed for hexene as above. The second aliquot was syringed into a 5-mL vessel containing 10 μL of pyridine; the resulting solution was allowed to stand at room temperature for 2 h and was then GC analyzed as above.

In experiments involving methyl vinyl ether, I (0.015 g, 0.024 mmol) was dissolved in 3 mL of toluene under argon. The solution was equilibrated at 25 °C and then 5 mL of methyl vinyl ether was injected into the reaction vessel via a syringe. Photolysis was begun immediately thereafter and continued for a 5-h period. Solvent was removed under vacuum after photolysis. The residue was dissolved in CD_2Cl_2, and the ^1H NMR was subsequently recorded at ambient temperature. In experiments involving low-temperature (−20 °C) ^1H NMR analysis, a hexane solution (2 mL) of I (0.010 g, 0.016 mmol) and methyl vinyl ether (5 mL injected) was photolyzed for 90 min at 25 °C; with the Sunlamp still on, solvent was then removed rapidly (within 2 min) under vacuum. The residue was dissolved in CD_2Cl_2 in the dark, and the resulting solution was immediately chilled to −78 °C and the ^1H NMR obtained at −20 °C as previously described.

In experiments involving propylene, I (0.015 g, 0.024 mmol) was dissolved in 2.5 mL of propylene-saturated toluene (or toluene-d_8) under 1 atm of propylene. Photolysis (at 25 °C) was begun immediately thereafter; solution aliquots for GC analysis were withdrawn via a gas-tight syringe. Pyridine treatment was performed by adding 10 μL of pyridine to a 0.2-mL reaction solution aliquot and allowing the resulting solution to stand at room temperature (in a sealed 5-mL vial) for 2 h before GC analysis.

D. Photolyses of $(\mu\text{-D})(\mu\text{-CD=CD}_2)Re_2(CO)_8$ (I-d_4) in the Presence of Olefins. In experiments involving propylene, I-d_4 (0.010 g, 0.016 mmol) was dissolved in 3 mL of propylene-saturated hexane under 1 atm of propylene; photolysis at 25 °C was begun immediately thereafter. Solvent was rapidly removed under vacuum after cessation of photolysis, requiring less than 3 min. The residue was dissolved in CD_2Cl_2, and the ^1H NMR was recorded at ambient temperature immediately thereafter. Electron-impact mass spectra of reaction product mixtures were obtained after vacuum removal of solvent; ion resonances (M^+, $[M - n(CO)]^+$) of II do not overlap with the molecular ion multiplet of I-d_{0-4}.

In experiments involving ethylene, I-d_4 (0.020 g, 0.032 mmol) was dissolved in 4 mL of ethylene-saturated hexane under 1 atm of C_2H_4. The solution was immediately photolyzed for a 15-min period at 25 °C; ^1H NMR and mass spectra were obtained as above.

E. Photolyses of II in the Presence of Olefins. In experiments involving ethylene, IIa (0.014 g, 0.022 mmol) was dissolved in 2.5 mL of toluene. The solution was photolyzed at 25 °C under an argon or propylene (1 atm) atmosphere for 60 min. With the Sunlamp still on, the solution was vacuum degassed at 25 °C and then saturated with ethylene (1 atm). Photolysis was continued; solution aliquots for GC analysis were withdrawn after 15- and 60-min continued irradiation. GC analyses for pentene products were performed as described in section C regarding hexene analyses.

In experiments involving propylene, IIa (0.015 g, 0.024 mmol) was dissolved in 3.0 mL of propylene-saturated toluene under 1 atm of propylene. The solution was equilibrated at the desired temperature (25 °C or 45 °C) and then photolyzed. Solution aliquots for GC analysis were withdrawn during the photochemical reactions; GC analyses for hexene products were performed as previously described (section C).

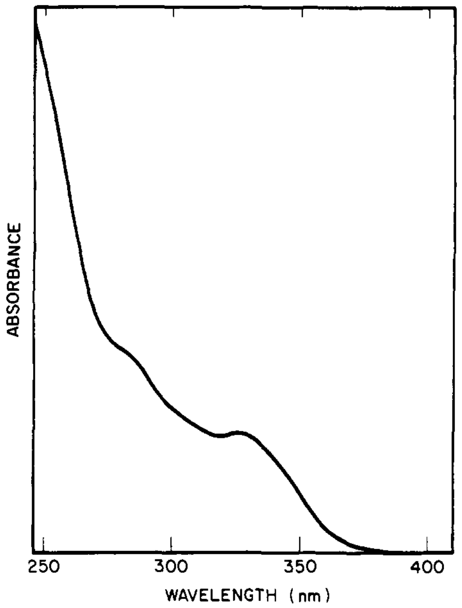

Figure 1. UV–visible spectrum of $(\mu\text{-H})(\mu\text{-CH=CH}_2)Re_2(CO)_8$ (I) in cyclohexane solution.

F. Photolyses of Olefin-Flushed Systems: Subsequent Thermal Reactivity. Reactions involving olefin purging employed a 50-mL Pyrex round-bottom Schlenk flask equipped with a septum inlet. Olefin purging was accomplished by bubbling an olefin stream through the toluene reaction solution via a syringe needle inserted through the septum. A second needle was employed to allow escape of purge gases. The reaction vessel was placed 3 cm from the Sunlamp during photolysis; forced-air cooling was employed to maintain the vessel at room temperature (~25 °C). Some evaporation of solvent occurred during the purging procedure, amounting to 2–3 mL after 45 min.

In experiments involving ethylene, I (0.020 g, 0.032 mmol) was dissolved in 7 mL of toluene under 1 atm of C_2H_4. After photolysis for 45 min while ethylene was bubbled through the solution, the reaction vessel was closed off under 1 atm of C_2H_4. The vessel was then immersed in a temperature-regulated water bath of the desired temperature (25 °C or 40 °C). GC analyses for butene and hexene products were performed as previously described. A similar procedure was employed for reactions involving IIa (0.016 g, 0.025 mmol) and propylene in toluene solution (8 mL).

Results

UV–Visible Spectra. The UV–visible spectrum (250–400 nm) of I in cyclohexane (Figure 1) shows a shoulder at 328 nm ($3.2 \times 10^3\ M^{-1}\ cm^{-1}$) and a weak shoulder at ~285 nm. The spectrum of IIIa is nearly identical, with corresponding absorptions at 328 nm ($3.0 \times 10^3\ M^{-1}\ cm^{-1}$) and about 284 nm.

Photolyses of I–III in the Absence of Added Ligands. Photolysis of a toluene or hexane solution of I at 25 °C results in little or no reaction other than slow decomposition to $[Re(CO)_3OH]_4$, presumably due to the presence of trace water in solution.[8,9]

Photolysis of a toluene solution of IIa at 25 °C results in rapid isomerization to IIb.[10] Within 30 min, a stationary-state mixture of the two isomers is achieved in which the ratio of IIa to IIb is 1.4:1. Due to the tendency of IIb to isomerize thermally to IIa,[11] this measurement was performed by immediately chilling the solution after photolysis and recording the ^1H NMR at low tem-

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(9) (a) Herberhold, M.; Süss, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 700. (b) Herberhold, M.; Süss, G.; Ellermann, J.; Gabelein, H. *Chem. Ber.* **1978**, *111*, 2931.

(10) ^1H NMR of IIb (CD_2Cl_2, −10 °C): δ −14.26 (s, 1 H, μ-H), 6.82 (d, 1 H, H_2), 7.37 (dq, 1 H, H_3), 2.25 (d, 3 H, CH_3), $J_{H_2\text{-}H_3} = 11.9$ Hz, $J_{H_3\text{-}CH_3} = 6.5$ Hz (see ref 2b).

(11) IIb and IIIb isomerize to IIa and IIIa, respectively, in CH_2Cl_2 solution in the dark in the absence of excess olefin with a half-life of about 10 min at 25 °C (see ref 2b).

perature (−20 °C). Photolysis at 5 °C yields a stationary-state IIa/IIb mixture of the same composition (1.4:1); however, photolysis at 45 °C results in a IIa:IIb = 5.5:1 steady-state mixture.

Photolysis of a toluene solution of IIIa at 25 °C affords a 1.7:1 IIIa/IIIb[12] stationary-state composition within 30 min.

Photolyses in the Presence of ^{13}CO, PPh$_3$. Photolysis of I or IIa at 25 °C in the presence of ^{13}CO (1 atm, hexane or toluene solution) results in rapid production of (μ-H)(μ-alkenyl)Re$_2$(^{13}CO)$_n$(CO)$_{8-n}$ species. Mass spectral analysis after 15–30-min photolysis of I reveals that only a trace of starting material (n = 0) remains in comparison to the amounts of n = 1–4 species; small amounts of n = 5–8 ^{13}CO-incorporated species are also detected. No incorporation occurs over a few hours time at 25 °C without irradiation. Slow formation of Re$_2$(CO)$_{10}$ occurs thermally[2] or photochemically in the presence of CO. Complete conversion to Re$_2$(CO)$_{10}$ requires more than a day at 25 °C, as monitored by IR.

Photolysis of I in the presence of 1 equiv of PPh$_3$ for a 45-min period at 25 °C affords (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_7$(PPh$_3$) in approximately 40% yield (by ^{1}H NMR) with 25% I remaining unreacted. Little or no (≤5%) disubstituted product is detected; a small amount (5–10% yield) of HRe(CO)$_4$(PPh$_3$)[13] is produced. The monosubstituted product, (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_7$(PPh$_3$), was isolated as a pale yellow solid from the reaction mixture residue by preparative TLC (5:1 hexane/CH$_2$Cl$_2$). However, separation from HRe(CO)$_4$(PPh$_3$) was not achieved. A mass spectrum of the collected product exhibits a parent ion at m/e 858 and daughter ions corresponding to loss of 1–4 carbonyls (m/e 830, 802, 774, 746). The IR spectrum exhibits absorptions in the carbonyl region at 2107 (vw), 2088 (w), 2083 (sh), 2055 (vw), 2038 (m), 2019 (m), 1990 (s), 1979 (s), 1968 (m), 1957 (ms), 1948 (sh), and 1928 (w) cm^{-1} (pentane solution). The shoulder at 2083 cm^{-1} is assigned to the HRe(CO)$_4$(PPh$_3$) impurity.[13] ^{1}H NMR analysis (CD$_2$Cl$_2$, 33 °C) indicates only one major isomer of (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_7$(PPh$_3$): δ −13.55 (d, 1 H, μ-H), 4.55 (dd, 1 H, H$_1$), 6.18 (dd, 1 H, H$_3$), 6.26 (dt, 1 H, H$_2$), 7.48 (m, PPh$_3$); $J_{H_1-H_2}$ = 16.7 Hz, $J_{H_2-H_3}$ = 11.0 Hz, $J_{H_1-H_3}$ = 4.0 Hz, $J_{^{31}P-H_2}$ = 11 Hz, $J_{^{31}P-(\mu-H)}$ = 8.5 Hz.[14,15] Small amounts of two other isomers are also detected: minor isomer 1, δ −13.87 (d, 1 H, μ-H), 4.25 (dd, 1 H, H$_1$), 5.93 (dd, 1 H, H$_3$), $J_{H_1-H_2}$ = 15.3 Hz, $J_{H_1-H_3}$ = 2 Hz, $J_{H_2-H_3}$ = 10.1 Hz, $J_{^{31}P-(\mu-H)}$ = 16.6 Hz; minor isomer 2, δ −13.95 (d, 1 H, μ-H), 3.64 (m, 1 H, H$_1$ or H$_2$), 5.78 (dd, 1 H, H$_3$), 6.71 (m, 1 H, H$_2$ or H$_1$); $J_{H_2-H_3}$ = 10.7 Hz, $J_{H_1-H_3}$ = 3.5 Hz, $J_{^{31}P-(\mu-H)}$ = 11.5 Hz.

The ^{1}H NMR spectrum of the major isomer of (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_7$(PPh$_3$) was monitored as a function of temperature. Upon cooling, the hydride resonance (doublet at δ −13.55) broadens and separates into two doublets. At −70 °C (stopped exchange) the two resonances appear at δ −13.75 ($J_{^{31}P-(\mu-H)}$ = 7.1 Hz) and −13.82 ($J_{^{31}P-(\mu-H)}$ = 8.4 Hz) of relative intensity 4:5. From the observed coalescence temperature (−30 °C), the free energy of activation ($\Delta G^{\ddagger}{}_C$) for the dynamic process is calculated to be 12.2 kcal/mol.[16] The vinyl proton resonances show similar behavior, i.e., broadening followed by separation into two resonances upon lowering temperature. For example, H$_1$ (dd, δ 4.55 at 33 °C) splits into two resonances, δ 4.61 (dd, $J_{H_1-H_2}$ = 17.3 Hz, $J_{H_1-H_3}$ = 2.4 Hz) and δ 4.35 (dd, $J_{H_1-H_2}$ = 16.9 Hz, $J_{H_1-H_3}$ = 3.0 Hz), at −60 °C, of relative intensity 4:5. From the coalescence temperature (−15 °C) and $\Delta\nu$ = 94 Hz (stopped exchange −60 °C), $\Delta G^{\ddagger}{}_C$ is calculated to be 12.3 kcal/mol, essentially the same value obtained from the hydride resonance data. H$_2$ and H$_3$ also split into two resonances, but assignments are precluded by resonance overlap problems in the stopped exchange (−60 °C) spectrum.

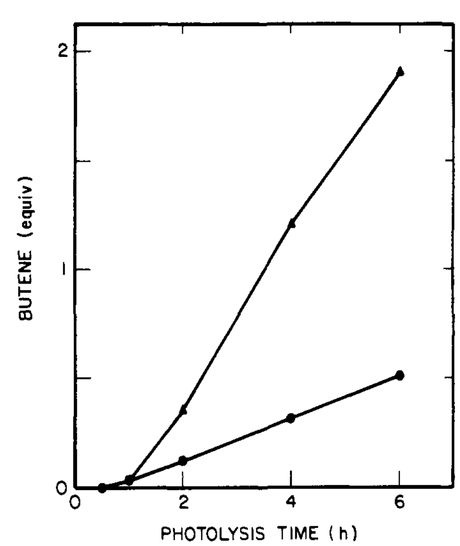

Figure 2. Butene production vs. photolysis time for the photochemical reactions of I with ethylene at 25 °C (●) and 50 °C (▲).

Photolyses of I in the Presence of Olefins. (A) Ethylene. Photolysis of a toluene solution of I at 25 °C in the presence of 1 atm of ethylene results in production of the μ-hydrido μ-butenyl complexes, IIIa–c. No reaction is observed in the absence of irradiation.[2] After short photolysis periods (≤15 min, corresponding to <15% reaction of I), isomer IIIc[17] predominates; an approximate 9:2:1 ratio of IIIc:IIIa:IIIb is observed by ^{1}H NMR analysis. Due to the tendency of IIIc[18] and IIIb[11] to isomerize thermally to IIIa, this measurement was performed by immediately chilling the solution after photolysis and recording the NMR at low temperature (−20 °C). Isomer IIIc still predominates after longer photolysis times (1–5 h) although the amount relative to IIIa,b is smaller, probably due to thermal isomerization. Complete conversion of I to III is not observed; within a 1–2-h photolysis time a 2:1 III/I ratio (~65% yield of III) is reached which remains constant for at least an additional day of photolysis. No other organometallic products are detected except for [Re(CO)$_3$OH]$_4$.[19] Slow production of this complex is observed, presumably due to the presence of trace water in solution.[8,9]

Production of free butene and hexene occurs during the photolysis; the butene is greater than 95% 1-butene, while the hexene is primarily (80–90%) *trans*-3-hexene.[20] Formation of these olefins does not occur at 25 °C without irradiation. After 1.0-h photolysis at 25 °C, 50–60% conversion of I to III is observed along with 0.03 equiv[21] of 1-butene. The rate of butene production (Figure 2) increases to approximately 0.1 equiv/h within 1–2 h; 0.12, 0.32, 0.51, and 2 equiv of 1-butene are observed after 2-, 4-, 6-, and 24-h photolysis, respectively. Hexene production is somewhat slower; 0.20 and 0.7 equiv are detected after 6- and 24-h photolysis, respectively. The isomeric distribution is 80–90% *trans*-3-hexene, ≤10% *cis*-3-hexene, 3–6% 1-hexene, <5% 2-hexene, and essentially no (<2%) branched hexenes. GC analyses of the reaction solutions before and after vacuum distillation (at 25 °C were identical. Also, GC analyses of the solutions before and after treatment with excess pyridine, which reacts with (μ-

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(12) ^{1}H NMR of IIIb (CD$_2$Cl$_2$, −10 °C): δ −14.32 (s, 1 H, μ-H), 6.82 (d, 1 H, H$_2$), 7.22 (dt, 1 H, H$_3$), 2.22 (quintet, 2 H, CH$_2$), 1.17 (t, 3 H, CH$_3$); $J_{H_2-H_3}$ = 11.8 Hz, $J_{H_3-CH_2}$ = $J_{CH_2-CH_3}$ = 7.2 Hz (see ref 2b).

(13) ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ −5.06 (d, $J_{H-^{31}P}$ = 22.4 Hz) [lit. ^{1}H NMR (benzene): δ −4.33 (d, $J_{H-^{31}P}$ = 22.0 Hz)]. See: Flitcroft, N.; Leach, J. M.; Hopton, F. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 137.

(14) Assignments and measurement of coupling constants aided by decoupling experiments.

(15) The δ 6.18 (H$_3$) and 6.26 (H$_2$) resonances are distorted due to strong coupling effects (AB pattern, $\Delta\nu_{H_2-H_3}$ = 2.6 $J_{H_2-H_3}$).

(16) Activation energy was calculated by using the relations $k_c = \pi(\Delta\nu)/2^{1/2}$ and $k_c = (k_bT_c/h)\exp(-\Delta G_c^{\ddagger}/RT_c)$, where k_c is the first-order rate constant, k_b is the Boltzmann constant, h is Planck's constant, T_c is the coalescence temperature, and $\Delta\nu$ is the stopped exchange separation of the two resonances.

(17) ^{1}H NMR of IIIc ((μ-H)(μ-C(Et)=CH$_2$)Re$_2$(CO)$_8$) (CDCl$_3$, 25 °C): δ −14.42 (s, 1 H, μ-H), 5.76 (d, 1 H, H$_1$ or H$_3$), 4.06 (d, 1 H, H$_3$ or H$_1$), 2.88 (br q, 2 H, allyl CH$_2$), 1.31 (t, 3 H, CH$_3$); $J_{H_1-H_3}$ = 2.2 Hz, $J_{CH_2-CH_3}$ = 7.4 Hz (see ref 2).

(18) IIIc isomerizes to IIIa in the dark at room temperature with a half-life of about 10 h (toluene solution, no excess olefin).

(19) IR of [Re(CO)$_3$OH]$_4$: ν_{CO} 2038 (s), 1935 (vs) cm^{-1} (toluene).

(20) No C$_3$ or C$_5$ products are detected.

(21) One equivalent is defined as the initial molar amount of I.

hydrido)(μ-alkenyl)dirhenium octacarbonyl compounds to afford $Re_2(CO)_8(py)_2$ and olefin quantitatively,[2] were essentially identical. Thus, only free hexene is produced in the photochemical reaction; little or none is present in the form of (μ-hydrido)(μ-hexenyl)dirhenium complexes. Additionally, little or no production of octenes occurs (<0.01 equiv after 6-h photolysis). After 24-h photolysis, ~40% of initial I has decomposed to $[Re(CO)_3OH]_4$, with the remainder present as I and III (vide supra).

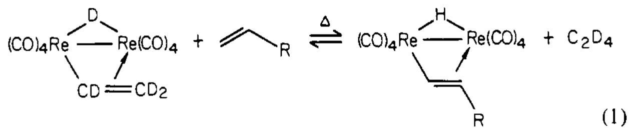
By use of an identical procedure, photolysis of I in the presence of 1 atm of ethylene (toluene solution) at 50 °C results in more rapid generation of butene and hexene. After 1-h photolysis, 0.03 equiv[21] of free 1-butene is observed. However, the rate of butene production (Figure 2) increases to 0.3–0.4 equiv/h within 1–2 h; 0.35, 1.2, and 1.9 equiv of butene are detected after 2-, 4-, and 6-h photolysis at 50 °C, respectively. The butene is predominantly (>90%) 1-butene, although the relative amount of 2-butene increases slowly during photolysis; 2-butene (primarily trans) accounts for 4% of evolved butene after 4-h photolysis, 8% after 6-h photolysis. The hexene generated, 0.35 equiv after 6- photolysis, is mostly *trans*-3-hexene, with 10–15% 1-hexene and 5–10% 2-hexene. Decomposition of I to $[Re(CO)_3OH]_4$ occurs at the same rate as in photolyses at 25 °C.

(B) Methyl Vinyl Ether. Photolysis of I at 25 °C in the presence of methyl vinyl ether affords IV and V. ^1H NMR for IV (CD_2Cl_2): δ −14.19 (s, 1 H, μ-H), 6.91 (d, 1 H, H_1 or H_2), 5.10 (d, 1 H, H_2 or H_1), 3.69 (s, 3 H, OCH_3); $J_{H_1-H_2} = 13.6$ Hz. ^1H NMR for V (CD_2Cl_2): δ −14.40 (s, 1 H, μ-H), 6.71 (d, 1 H, H_2), 5.29 (dt, 1 H, H_1), 3.65 (t, 2 H, $-CH_2O-$), 3.45 (s, 3 H, OCH_3), 2.51 (q, 2 H, allyl CH_2); $J_{H_1-H_2} = 16.1$ Hz, $J_{H_1-CH_2} = 6$ Hz, $J_{CH_2-CH_2} = 6$–6.5 Hz. After a 5-h irradiation period, the ratio of IV/V/I (unreacted) was observed to be 8:3:10 by ^1H NMR analysis (25 °C). Hydride resonances of very weak intensity relative to these are also observed at δ −13.28 (s), −13.74 (s), −14.03 (s), and −14.12 (s). When the reaction solution is immediately chilled after photolysis and the NMR recorded at −20 °C, a hydride resonance at δ −14.35 is also detected. The intensity of this signal is about half that of V (δ −14.46 at −20 °C); upon warming to 25 °C the δ −14.35 signal diminishes (disappearance within $^1/_2$ h) with concomitant increase in the intensity of V (δ −14.46). By analogy with the chemical shifts and isomerization behavior of IIa,b and IIIa,b, the δ −14.35 resonance is assigned to a cis isomer of V, i.e., (μ-H)(μ-*cis*-$CH{=}CHCH_2CH_2OCH_3)Re_2(CO)_8$, which thermally isomerizes to V.

(C) Propylene. The only organometallic product detected (by ^1H NMR, IR) after 25 °C photolysis of I in the presence of 1 atm of propylene (hexane or toluene solvent) is II; a spectrum recorded at ambient temperature after 90-min photolysis reveals an approximate 1:1 ratio of I:II.[22] Production of II (isomer a) occurs at a similar rate in the absence of irradiation.[2] GC analysis indicates that production of free pentene, primarily 1-pentene, occurs during the photochemical, but not thermal, reaction. Less than 0.05 equiv of pentene is detected after $^1/_2$-h photolysis.[21] Addition of pyridine to the reaction solution after cessation of photolysis results in a modest (less than twofold) increase in the amount of free 1-pentene in solution. This indicates that some 1-pentene (<0.05 equiv) is complexed after $^1/_2$-h photolysis, probably in the form of (μ-hydrido)(μ-pentenyl)dirhenium octacarbonyl species. The relatively small quantities of these products in the reaction solutions apparently preclude NMR detection. The isomeric distribution of evolved pentene, measured after thermal pyridine treatment after 5-, 10-, and 20-min photolysis, is ~70% 1-pentene, ~25% *trans*-2-pentene, <5% *cis*-2-pentene, and <5% branched pentenes.

Photolyses of (μ-D)(μ-$CD{=}CD_2$)$Re_2(CO)_8$ (I-d_4) in the Presence of Olefins. (A) Propylene. Photolysis of a hexane solution of (μ-D)(μ-$CD{=}CD_2$)$Re_2(CO)_8$ (I-d_4) at 25 °C in the presence of 1 atm of propylene results, in addition to formation of II, in H/D exchange at the hydride and vinyl positions of I. Mass spectrometric (EI) and ^1H NMR results indicate the major initial product of exchange is (μ-H)(μ-$CD{=}CD_2$)$Re_2(CO)_8$; vinyl H/D exchange occurs subsequently. After a 45-min irradiation period, at which point I → II conversion is ~50% complete (by IR), the isotopic distribution of remaining I is approximately 14% $D_4C_2Re_2(CO)_8$ (I-d_4), 36% $D_3HC_2Re_2(CO)_8$ (I-d_3), 36% $D_2H_2C_2Re_2(CO)_8$ (I-d_2), 11% $DH_3C_2Re_2(CO)_8$ (I-d_1), and 3% $H_4C_2Re_2(CO)_8$ (I), as determined by mass spectrometric analysis. In the ^1H NMR data, an intensity ratio of 10:3:5:4 is observed for the μ-H:H_1:H_2:H_3 signals of I at δ −14.68 (br s), 6.29 (m), 7.18 (br s), and 4.50 (m), respectively (CD_2Cl_2). No H/D exchange of I occurs under similar conditions in the absence of irradiation; only conversion of I-d_4 to IIa is detected. Little or no H/D exchange is observed after similar photolysis of I-d_4 in hexane solution under an argon atmosphere in the absence of propylene.

(B) Ethylene. As with propylene, 25 °C photolysis of a hexane solution of I-d_4 in the presence of 1 atm of C_2H_4 results in H/D exchange at the hydride and vinyl positions of I. After 15-min photolysis d_4–d_0 species are detected by MS; the intensity of the hydride signal (δ −14.68) is approximately twice that of each vinyl proton signal (δ 6.29, 7.18, 4.50). A larger proportion of d_0 (fully protonated) product is observed, relative to the photochemical reaction with propylene, due to the known thermal reaction:[2]



(1)

Mass spectrometric (EI) analysis after 15-min photolysis, corresponding to 10–15% I → III conversion, indicates the following isotopic distribution of μ-hydrido μ-butenyl product (III) $D_nH_{8-n}C_4Re_2(CO)_8$: 14% $n = 0$, 4% $n = 1$, 13% $n = 2$, 35% $n = 3$, 31% $n = 4$, <2% $n = 5$, <1%[23] $n = 6$–8. In the ^1H NMR data, recorded at ambient temperature after photolysis, an intensity ratio of 10:2:2:21:33 is observed for the μ-H:H_1:H_3:CH_2:CH_3 signals of IIIc at δ −14.38 (s), 5.79 (d), 4.09 (d), 2.90 (br s), and 1.30 (m), respectively (CD_2Cl_2). As previously described, isomer IIIc accounts for ~75% of product (III) at this stage of the photochemical reaction. The NMR and MS results indicate a much greater amount of deuterium present at the vinyl positions of IIIc than at the hydride, methylene (allyl), and methyl positions. This is also true for isomer IIIa, although NMR results for IIIa are less accurate due to the relatively low yield of this isomer; an intensity ratio of 2:0.8:1:6.3:7.6 is observed for the μ-H:H_2:H_1:CH_2:CH_3 resonances of IIIa.

Photolyses of II in the Presence of Olefins. (A) Ethylene. Addition of 1 atm of ethylene to a photostationary-state mixture of IIa,b (1.4:1 a:b at 25 °C, toluene solution, vide supra) followed by continued photolysis at 25 °C results in slow production of free pentene, primarily *trans*-2-pentene. Less than 0.1 equiv[24] of pentene is evolved after 1-h irradiation. The only organometallic product detected (by ^1H NMR, IR) is I, which is generated at a similar rate in the absence of irradiation.[2] Pentene formation, however, does not occur thermally at 25 °C. The isomeric distribution, as measured after 15- and 60-min photolysis, is 85% *trans*-2-pentene, 10–12% *cis*-2-pentene, and 3–5% 1-pentene. Only free pentene is produced, with little or none present in the form of μ-hydrido μ-pentenyl complexes, inasmuch as GC analyses before and after vacuum distillation and before and after pyridine treatment were essentially identical.

(B) Propylene. Photolysis of a toluene solution of IIa at 25 °C in the presence of 1 atm of propylene results in slow production of hexene, predominantly 2-hexene. As in the absence of excess propylene, a 1.4:1 photostationary-state mixture of IIa:b is reached within a 30-min irradiation time. After 1.0-, 7.5-, and 20-h photolysis, GC analysis indicates 0.015, 0.10, and 0.19 equiv[24] of hexene present in the reaction solution. Production of hexene ceases when photolysis is discontinued. No C_2, C_4, or C_5 products

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[22] A mixture of IIa and IIb is observed immediately after photolysis; however, IIb thermally isomerizes rapidly to IIa (see ref 11).

[23] None detected.

[24] One equivalent defined as initial amount of II.

are detected (by GC). The isomer distribution of hexenes, which remains essentially constant from 1 to 20 h of photolysis, is 50% *trans*-2-hexene, 35% *cis*-2-hexene, 5% 1-hexene, 5% *trans*-4-methyl-2-pentene, and ≤5% 3-hexene plus other branched hexenes. GC analyses indicate that only free hexene is produced; little or none is present in the form of (μ-hydrido)(μ-hexenyl)dirhenium complexes. After 20-h irradiation, about half of the initial II has decomposed to $[Re(CO)_3OH]_4$.

When the photolysis is performed at 45 °C, the hexene distribution changes, although the rate of production remains about the same. After 0.5-, 1.0-, and 6.5-h photolysis, GC analysis indicates 0.007, 0.014, and 0.06 equiv of hexene evolved. The isomeric distribution, as measured after 1 and 6.5 h, is 75% *trans*-2-hexene, 10–15% *cis*-2-hexene 2–3% 1-hexene, 7–9% *trans*-4-methyl-2-pentene, and <5% 3-hexene plus other branched hexenes. Again, no C_2, C_4, or C_5 products are observed. C_9 species (nonenes) are also not detected (<0.001 equiv after 6.5-h photolysis). As in the absence of excess propylene, a 5.5:1 stationary-state mixture of IIa:b is reached within 30 min.

Photolyses of Olefin-Flushed Systems: Subsequent Thermal Reactivity. (A) I, Ethylene. After room-temperature photolysis of a toluene solution of I for 45 min while ethylene was bubbled through the solution, bands at 2115, 2083, 2018, 1993, 1978, and 1959 cm^{-1} due to I and (μ-hydrido)(μ-butenyl)dirhenium octacarbonyl species dominate the IR spectrum. However, there are also new weak bands at 2105, 2044, and 1920 cm^{-1}. These bands disappear if the solution is treated with CO (1 atm, 5–10 min at 25 °C), while the bands for the hydrido alkenyl octacarbonyl species increase. The new IR bands are thus assigned to (μ-H)(μ-alkenyl)$Re_2(CO)_7(\eta^2\text{-}C_2H_4)$ species, alkenyl = C_2H_3 and/or C_4H_7. Presumably the labile ethylene ligand is easily substituted by CO. The IR spectrum, particularly in the appearance of the 2105-cm^{-1} band, is similar to that observed for (μ-H)(μ-$CH{=}CH_2$)$Re_2(CO)_7(PPh_3)$, which shows a band at 2107 cm^{-1} (vide supra). The yield of the (μ-H)(μ-alkenyl)$Re_2(CO)_7(CH_2{=}CH_2)$ species, determined by IR, is ~15%. We have not been able to achieve higher yields, even by longer periods of photolysis under an ethylene flush.

After the 45-min photolysis/ethylene-flush procedure, room-temperature treatment with CO (1 atm, 5–10 min) followed by excess pyridine (10–50 equiv, 2 h) generates 0.3–0.4 equiv of 1-butene. This results from elimination of butene from the μ-hydrido μ-butenyl octacarbonyl species. However, if the photolyzed solution is allowed to stand under a static ethylene atmosphere (1 atm) at 25 °C in the dark following cessation of irradiation, then a total of 1.0 equiv of butene is evolved within 40 h. The butene is 95% 1-butene; production ceases after 30–40 h. (When a solution of I is photolyzed for 45 min under a *static* ethylene atmosphere and then allowed to stand for 30–40 h, only ~0.3 equiv of butene is obtained.)[25] An IR spectrum of the final reaction solution shows that the 2105-, 2044-, and 1920-cm^{-1} bands have disappeared while those of $[Re(CO)_3OH]_4$ and the hydrido alkenyl dirhenium octacarbonyl species have increased somewhat in intensity relative to a spectrum recorded immediately following the photolysis under a C_2H_4 flush. Allowing the photolyzed solution to stand at 40 °C under 1 atm of ethylene results in evolution of 1.1–1.2 equiv of butene;[26] production ceases within 20 h. A greater amount of 2-butene is observed at this temperature; after 20 h, butene is 70–75% 1-butene and 25–30% 2-butene (~2:1 trans:cis).

Thermal production of hexene also occurs after cessation of photolysis carried out under a C_2H_4 flush. Immediately following the 45-min photolysis, GC analysis shows 0.02 equiv of hexene (mostly trans-3 isomer) in solution. After a 40-h subsequent thermal reaction at 25 °C under 1 atm (static) of ethylene, 0.74 equiv of hexene is observed in solution. Thermal production of hexene is thus 0.7 equiv; no additional hexene is evolved after 40 h. The isomeric distribution is 80–90% *trans*-3-hexene, ≤10% *cis*-3-hexene, 2–3% 1-hexene, and <5% 2-hexene. GC analyses before and after vacuum distillation (25 °C) were identical, as were analyses before and after treatment with CO (1 atm) followed by excess pyridine. Thus, only free hexene is produced. Thermal hexene production is not detected following photolysis of a solution of I under a static ethylene atmosphere.

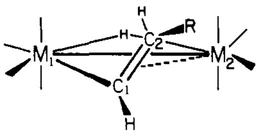


Figure 3. Representation of the geometrical arrangement of the μ-hydrido μ-alkenyl groups.

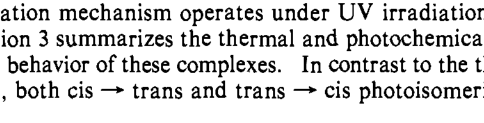
(B) II, Propylene. Room-temperature photolysis of a toluene solution of IIa for 45 min while propylene was bubbled through the solution results in the appearance of weak bands in the IR spectrum at 2105 and 2038 cm^{-1}. These bands disappear if the solution is treated with CO, while the bands for IIa increase. The new IR bands are assigned to (μ-H)(μ-$CH{=}CHCH_3$)$Re_2(CO)_7(\eta^2\text{-}CH_2{=}CHCH_3)$, the yield of which is ~10%.

Thermal production of hexene, predominantly *trans*-2-hexene, occurs when the photolyzed solution is allowed to stand under a static propylene atmosphere (1 atm) at 25 °C in the dark following cessation of irradiation. Thermal hexene production, which ceases after about 17 h, amounts to ~0.01 equiv, calculated by subtracting the amount of hexene present immediately after photolysis from the total detected after thermal reaction. The isomeric distribution is 80–90% *trans*-2-hexene, ~5% *cis*-2-hexene, 5–10% *trans*-4-methyl-2-pentene, and <5% 1-hexene plus other hexenes. Only free hexene is produced. An IR spectrum of the 17-h reaction solution shows that the 2105- and 2038-cm^{-1} bands have disappeared while those of $[Re(CO)_3OH]_4$ and IIa have increased somewhat in intensity relative to a spectrum recorded immediately following the photolysis under C_3H_6 flush. No thermal production of hexene (<0.001 equiv after 17 h) is observed following photolysis of IIa under a static propylene atmosphere.

Discussion

At the outset it is well to have in mind the geometrical arrangement of the μ-alkenyl moiety in relation to the Re–Re bond and the other ligands bound to the metals. An illustration of the orientation of the olefin relative to the metal atoms and the remainder of the structure is shown in Figure 3. In the case where M = Os and R = C_2H_5, in (μ-but-1-enyl)(μ-hydrido)decacarbonyl-*triangulo*-triosmium, the C_1–M_1 and C_1–M_2 distances are 2.15 and 2.28 Å, respectively, while the C_2–M_2 distance is 2.46 Å.[27] The olefin may be considered to be σ bonded to M_1 and π coordinated to M_2. The organic group R points *away* from the remainder of the structure; the C_1–C_2–R angle is 121°.

Cis–Trans Photoisomerization of the Bridging Alkenyl Ligand. We have recently discussed the thermal isomerization of IIb and IIIb to IIa and IIIa, respectively.[2b] The "a" isomers, with the alkyl group of the alkenyl ligand trans to the Re–C σ bond, are thermodynamically most stable. The mechanism of the isomerization, as well as other thermal reactions of these compounds, is proposed to begin with intramolecular C–H reductive elimination (eq 2).



(2)

The resulting intermediate possesses a vacant site at one Re and η^2-coordinated olefin at the other. Oxidative addition of the trans vinylic C–H at the adjacent vacant site affords the "a" (trans) isomer. The results we currently report indicate that a distinct isomerization mechanism operates under UV irradiation.

Equation 3 summarizes the thermal and photochemical isomerization behavior of these complexes. In contrast to the thermal pathway, both cis → trans and trans → cis photoisomerization

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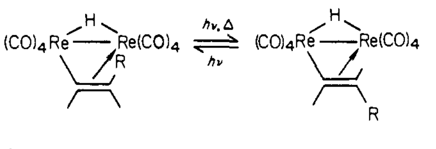
[25] Due to thermal reaction of photogenerated III with C_2H_4.[2]

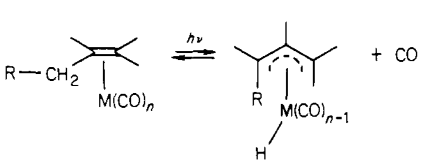
[26] Trial 1, 1.1 equiv; trial 2, 1.2 equiv.

[27] Guy, J. J.; Reichert, B. E.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1976**, B32, 3319.

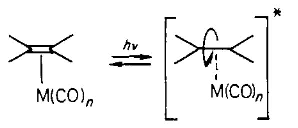

(3)

is observed. This is evidenced by the fact that the IIa/IIb photostationary-state composition is essentially identical at 25 °C and 5 °C. The photostationary state is not shifted toward the trans isomer by the thermal reaction until temperatures above 25 °C are employed. Also, the presence of excess olefin does not affect the stationary-state composition. It is noteworthy that "c" isomers (e.g., IIIc) are not produced by photoisomerization of IIa,b or IIIa,b.

This photochemical behavior resembles the cis–trans photoisomerization of coordinated internal olefins in mononuclear metal carbonyl complexes.[28] Several mechanisms have been proposed regarding these systems, one of which involves photoexcitation of an olefin-localized excited state ($\pi \rightarrow \pi^*$ transition) resulting in cis–trans isomerization via rotation about the olefinic C–C bond.[29] This mechanism is unlikely in the present case in that such transitions are generally of considerably higher energy than the irradiation employed here ($\lambda > 297$ nm). Another mechanism, which has been postulated for both thermal and photochemical isomerizations, is the formation of a π-allyl hydride intermediate following CO dissociation (eq 4) and subsequent rearrangement


(4)

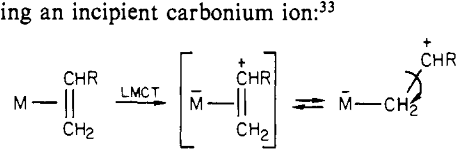
of the π-allyl species to an isomerized-olefin complex. Although photochemical CO loss from I–III does occur (vide infra), a π-allyl mechanism is probably not operative in the present case, in view of our observation that the μ-hydrido μ-styrenyl complex, (μ-H)(μ-CH=CHPh)$Re_2(CO)_8$, which does not possess allylic hydrogens, also undergoes similar cis–trans photoisomerization.[30] A third mechanistic possibility involves excitation to an excited state in which metal-olefin bonding is altered and free rotation about the olefinic C–C bond is possible, e.g., an M → olefin (π^*) charge-transfer (CT) transition (eq 5). Such a mechanism has


(5)

been proposed for cis–trans photoisomerization of stilbene in $M(CO)_5$(stilbene), M = W or Mo,[31] and of dimethyl maleate in $Fe(CO)_4$(dimethyl maleate).[32] Isomerization is believed possible because of reduced olefin C–C bond order caused by population of the olefin π^* orbital.

We regard this third mechanism as the most likely pathway for cis–trans photoisomerization of the (μ-hydrido)(μ-alkenyl)dirhenium complexes.

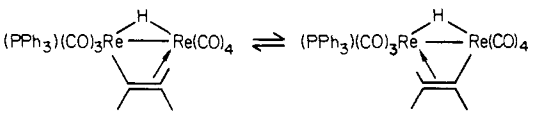
A related alternative involves olefin-to-metal charge transfer, generating an incipient carbonium ion:[33]



Interpretation of the UV–visible spectra of the dirhenium hydrido alkenyl compounds is not straightforward. The shoulder at 328 nm of I and IIIa may be due to an M → olefin CT, a ligand-field transition, or a weak M–M σ–σ^* transition.

Photochemical CO Substitution. The μ-hydrido μ-alkenyl octacarbonyl compounds undergo CO substitution upon irradiation, as evidenced by rapid ^{13}CO incorporation and substitution by PPh_3 under photolysis. CO substitution does not occur under thermal conditions at 25 °C; elimination of olefin with concomitant formation of 1,2-$Re_2(CO)_8L_2$ occurs under thermal conditions in the presence of L = PPh_3, pyridine, or CO.[2] As discussed above, the 328-nm band in the UV–visible spectra of I and IIIa may be a ligand field (LF) transition, irradiation of which results in CO dissociation.[34]

The photochemical reaction of I with PPh_3 yields only one major isomer of the substitution product, (μ-H)(μ-CH=CH_2)$Re_2(CO)_7(PPh_3)$, as detected by ^1H NMR at 25 °C. It is likely that the phosphine occupies a position trans to a carbonyl as in the analogous μ-pyridyl complex, (μ-H)(μ-NC_5H_4)$Re_2(CO)_7(PPh_3)$.[35] The variable-temperature ^1H NMR results are consistent with a fluxional process, rapid at room temperature ($\Delta G^\ddagger = 12.2$ kcal/mol), in which the σ and π bonds of the μ-alkenyl group are interchanged between the bridged rhenium atoms (eq 6). Two


(6)

isomers are thus in a rapid dynamic equilibrium at 25 °C. This type of fluxional behavior has been observed for the octacarbonyl dirhenium complexes ($\Delta G^\ddagger = 10.0$ and 12.7 kcal/mol for IIIa and IIIc, respectively),[2b] as well as analogous triosmium compounds, (μ_2-H)(μ_2-CH=CH_2)$Os_3(CO)_{10}$ ($\Delta G^\ddagger = 10.3$ kcal/mol)[36a] and (μ_2-H)(μ_2-CPh=CHPh)$Os_3(CO)_{10}$ ($\Delta G^\ddagger = 11.3$ kcal/mol).[36b]

Photochemical Olefin Dimerization. I. Reaction of I with Ethylene. (A) Formation of III. The photochemical reaction of I with ethylene to yield IIIa–c is, in effect, an ethylene dimerization process. Interestingly, the major initial product is isomer IIIc, whereas in the thermal and photochemical reactions of I with 1-butene only isomers IIIa (thermal) and IIIa,b (photochemical) are observed as products. Thus, formation of the μ-hydrido μ-butenyl species results from an intramolecular ethylene dimerization process.

Several experimental results indicate that III results from reaction of 1 equiv of ethylene with I. First, photolysis of I in the presence of methyl vinyl ether yields V, a dimerization product resulting from photochemical reaction with 1 equiv of methyl vinyl ether. (Formation of IV is due to thermal reaction with methyl vinyl ether.[2]) The photochemical reaction of I with propylene affords predominantly 1-pentene, the product of ethylene/propylene codimerization. Finally, short-term photolysis of I-d_4 in the presence of C_2H_4 yields primarily the n = 3, 4 species (III-d_3, -d_4) of $D_nH_{8-n}C_4Re_2(CO)_8$, III. III-d_4 clearly results from reaction of I-d_4 with 1 equiv of C_2H_4; the n = 3 (and the smaller amounts of n = 1, 2) species are formed due to photochemical H/D ex-

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(28) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; pp 180–191. (b) Vogler, A. "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; pp 292–295.

(29) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *70*, 283.

(30) ^1H NMR of (μ-H)(μ-*trans*-CH=CHPh)$Re_2(CO)_8$ (CD_2Cl_2, 25 °C): see Experimental Section. ^1H NMR of (μ-H)(μ-*cis*-CH=CHPh)$Re_2(CO)_8$: δ −13.88 (s, 1 H, μ-H), 8.76 (d, 1 H, H_2 or H_3), 7.00 (d, 1 H, H_3 or H_2), 7.61 (d, 2 H, Ph_α), 7.34 (t, 2 H, Ph_β), 7.23 (t, 1 H, Ph_γ), $J_{H_2-H_3} = 12.3$ Hz, $J_{\alpha\beta}(Ph) \approx J_{\beta\gamma}(Ph) \approx 7.5$ Hz. The cis isomer isomerizes to trans at 25 °C in the dark in the absence of excess styrene with a half-life ≈ 2.5 h (CH_2Cl_2).

(31) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3285.

(32) (a) Grevels, F. W. Dissertation, University of Bochum, 1970. (b) Bock, C. R.; Koerner von Gustorf, E. A. *Adv. Photochem.* **1977**, *10*, 221. (c) Grevels, F. W.; Koerner von Gustorf, E. *Justus Liebigs Ann. Chem.* **1975**, 547.

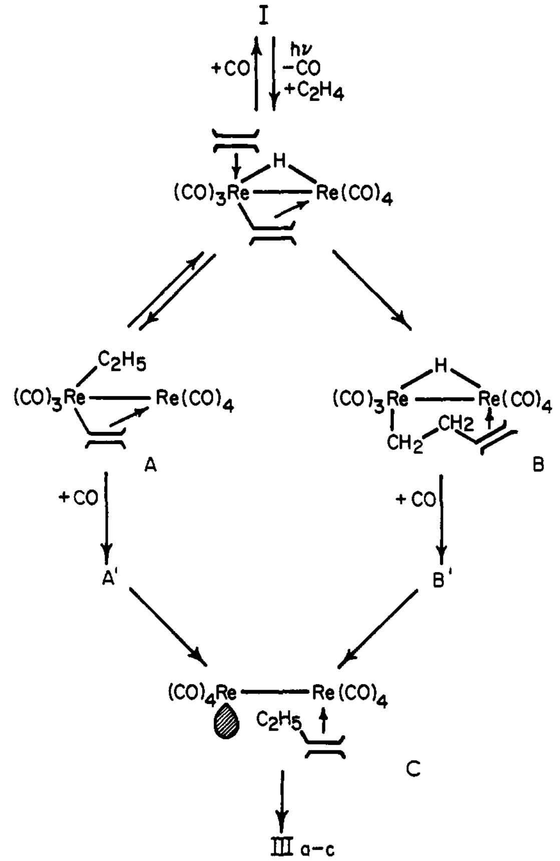
(33) (a) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1981**, *20*, 4036. (b) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

(34) Reference 28a, pp 12–15.

(35) Nubel, P. O.; Wilson, S. R.; Brown, T. L. *Organometallics* **1983**, *2*, 515.

(36) (a) Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *94*, C43. (b) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528.

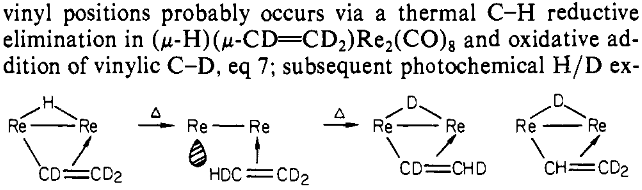
Scheme I



change reactions of I-d_4 and/or III-d_4 with ethylene, discussed below.

The proposed mechanism for the transformation of I to III is presented in Scheme I. The reaction is initiated by photodissociation of CO and coordination of ethylene, proposed by analogy to the observed photosubstitution of I by ^{13}CO or PPh$_3$. The resulting intermediate, (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_7$(CH$_2$=CH$_2$), can rapidly react with CO to regenerate I by thermal loss of ethylene. Small quantities of (μ-H)(μ-alkenyl)Re$_2$(CO)$_7$(CH$_2$=CH$_2$) species, alkenyl = ethenyl and/or butenyl, are detected by IR analysis (2105, 2044, 1920 cm^{-1}) following irradiation while ethylene stream was bubbled through the solution.

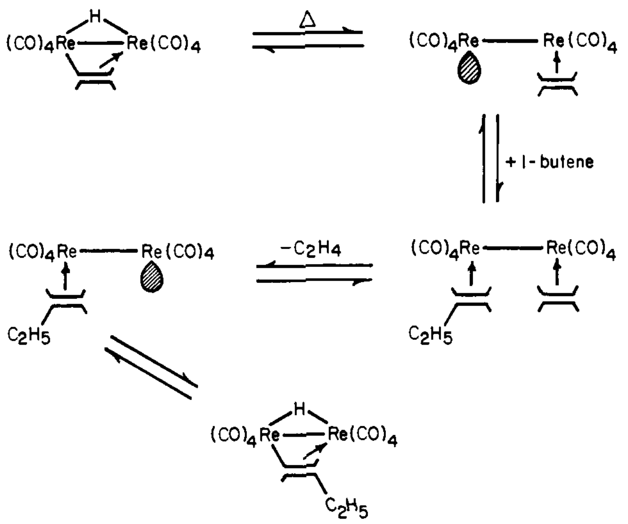
The second step of the mechanism in Scheme I may occur via insertion of coordinated ethylene into the Re–H bond to generate an ethyl μ-ethenyl species, A, or insertion into the σ Re–C (ethenyl) bond to yield intermediate B. Our observation that H/D exchange occurs initially at the hydride position when I-d_4 is photolyzed in the presence of ethylene or propylene is strong evidence for reversible insertion into Re–H (or Re–D). The exchange occurs on a time scale similar to that for conversion of I to III and likely results from insertion/deinsertion of olefin into the Re–D bond of I-d_4 as in Scheme I. Exchange does not occur without irradiation (at 25 °C) inasmuch as initial CO dissociation is necessary to allow coordination of olefin. H/D exchange at vinyl positions probably occurs via a thermal C–H reductive elimination in (μ-H)(μ-CD=CD$_2$)Re$_2$(CO)$_8$ and oxidative addition of vinylic C–D, eq 7; subsequent photochemical H/D ex-



(7)

change at the hydride position occurs as described above. (Thermal C–H reductive elimination/oxidative addition of the (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl compounds has been discussed previously.^{2b}) We cannot, however, exclude the possibility of insertion of coordinated ethylene into the σ Re–C (alkenyl) bond to give intermediate B; Johnson, Lewis, et al. have observed insertion of acetylenes into the Os–C (alkenyl) bond of H$_3$Os$_4$(CO)$_{11}$(μ_2-CH=CH$_2$).^{5b} Insertion of ethylene into the Re–C σ bond could occur at either Re site since the μ-ethenyl ligand of (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_7$(CH$_2$=CH$_2$) probably undergoes a rapid σ/π interchange fluxional process at 25 °C as previously described for (μ-H)(μ-CH=CH$_2$)Re$_2$(CO)$_7$(PPh$_3$).

Scheme II

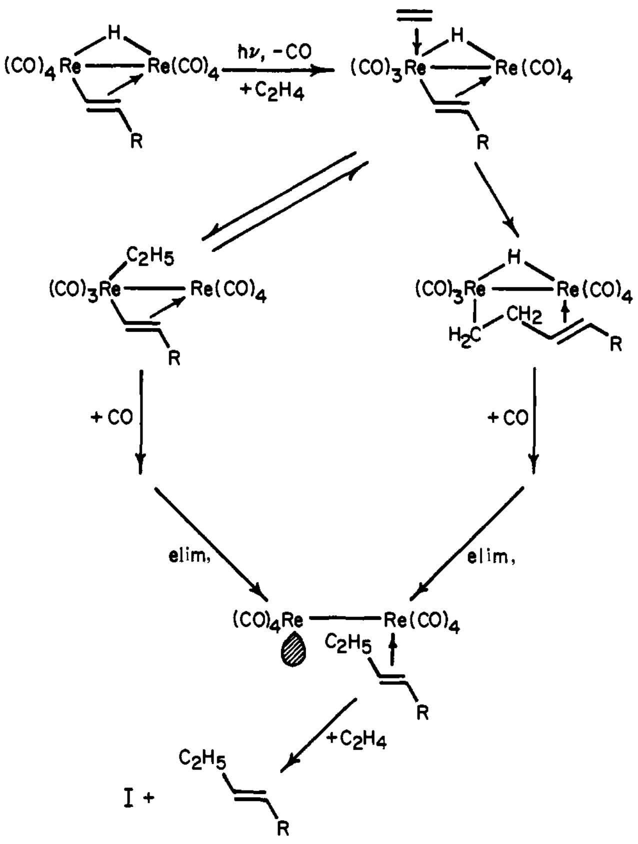


The final steps in the transformation of I to III are recoordination of CO (to A or B) and C–C or C–H reductive elimination (A′ or B′, respectively) to afford an intermediate (C) with 1-butene coordinated to one Re center and a vacant site at the other; vinylic C–H oxidative addition of coordinated 1-butene at the vacant site then follows. Recoordination of CO, which was photochemically dissociated from I, must occur at some point in order to obtain III. However, this may not take place as indicated in Scheme I. Instead, coordination of an olefin (ethylene) ligand at the vacant site of A or B could occur, followed by a later substitution by CO (perhaps after the reductive elimination and oxidative addition steps).

Intermediate C, Re$_2$(CO)$_8$(CH$_3$CH$_2$CH=CH$_2$), which results from C–C reductive elimination in A′ or C–H elimination in B′, is similar to a species proposed as an intermediate in the thermal reaction of I with 1-butene to yield IIIa (Scheme II).^{2b} In the thermal reaction, however, IIIa is the only isomer of III produced, even at short reaction times (10 min at 25 °C). The difference in the product isomeric distribution between this thermal reaction and the photochemical reaction of I with ethylene may be due to the orientation of coordinated butene in the Re$_2$(CO)$_8$(CH$_3$CH$_2$CH=CH$_2$) intermediate. In the thermal reaction (Scheme II), the butene ligand of the Re$_2$(CO)$_8$(CH$_3$CH$_2$CH=CH$_2$)(CH$_2$=CH$_2$) species is likely oriented with the ethyl group pointing away from the adjacent Re center due to steric factors. After dissociation of ethylene, preferential oxidative addition of the trans vinylic C–H will thus occur if oxidative addition is rapid relative to rotation about the Re–butene bond. In the photochemical reaction (Scheme I), the orientation of the butene ligand of Re$_2$(CO)$_8$(CH$_3$CH$_2$CH=CH$_2$), C, immediately after the reductive elimination steps is different; the ethyl group is pointed more toward the adjacent metal center. The vinylic C–H geminal to the ethyl group is closer to the open coordination site at the adjacent Re than are the cis and trans C–H bonds. Thus, if oxidative addition is comparable to or faster than rotation of coordinated butene, geminal C–H oxidative addition will occur to give IIIc as the major isomer.

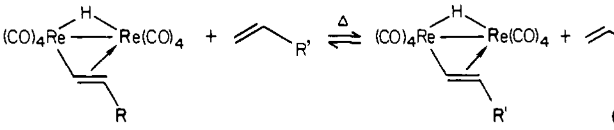
Our proposed mechanism argues that the C–C double bond of the μ-ethenyl ligand in I is maintained throughout the sequence, emerging as the C=C bond of the μ-butenyl ligand of III. This is consistent with the observation that short-term photolysis of I-d_4 in the presence of C$_2$H$_4$ results in a much greater amount of deuterium present at the vinyl positions of IIIa,c than at the

Scheme III



hydride and ethyl group positions. (Hydrogen appears in the hydride position due to photochemical H/D exchange, as described above.) Additionally, the C=C bond of I is clearly maintained in V, (μ-H)(μ-CH=CHCH$_2$CH$_2$OCH$_3$)Re$_2$(CO)$_8$, a product of the photochemical reaction of I with 1 equiv of methyl vinyl ether.

(B) Production of Butene. We have previously discussed the thermal reactivity of the (μ-hydrido)(μ-alkenyl)dirhenium complexes with olefins (eq 1, 8).[2] Our results indicate that formation

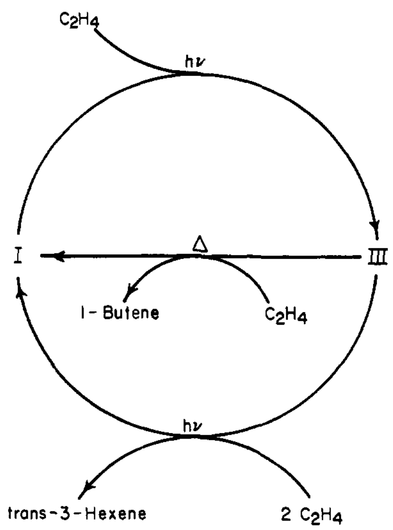


(8)

of free 1-butene in the photochemical reaction of I with ethylene results from thermal reaction of III with excess ethylene to yield I plus 1-butene. This thermal step, which completes the cycle, is slower than the photochemical step (I → III) at 25 °C; after 1-h photolysis, 50–60% conversion of I to III is achieved although only a trace of 1-butene (0.03 equiv, based upon initial I) is observed. After a 1–2-h induction period, the rate of butene production increases to 0.1 equiv/h as a steady-state concentration of III is reached (~65% yield). This rate remains constant for several hours afterward. When the temperature of photolysis is increased to 50 °C, the butene production rate reaches a higher level (0.3–0.4 equiv/h) after the induction period, consistent with a rate-limiting thermal step. We note, however, that increasing amounts of 2-butene are produced at the higher temperature (50 °C), while the product is >95% 1-butene after 1-day irradiation at 25 °C.

Catalytic production of 1-butene occurs under continual irradiation (photoassisted catalysis), although the rate is extremely slow at 25 °C (2–3 turnovers/day). Despite rigorous drying of solvent, catalytic activity is diminished through time by slow formation of [Re(CO)$_3$OH]$_4$. This compound is presumably generated through reaction with trace water in the system; it appears to be inactive toward olefin dimerization under thermal or photochemical conditions. (The mechanism of the formation of this complex from Re$_2$(CO)$_{10}$ and H$_2$O under photolysis has been investigated.[8]) Similarly, Davis and Ojo[37] were unable to eliminate formation of [Re(CO)$_3$OH]$_4$ in the photochemical reaction of Re$_2$(CO)$_{10}$ with cycloheptatriene.

Scheme IV



(C) Production of Hexene. Production of hexene during photolysis of I in the presence of ethylene is presumably a catalytic (photoassisted) process, although slower than the rate of butene production (<1 turnover/day hexene). Interestingly, most of the evolved hexene (80–90%) is the trans-3 isomer. The mechanism we propose to account for specific formation of *trans*-3-hexene is presented in Scheme III, with R = C$_2$H$_5$. The mechanism is essentially the same as proposed in Scheme I for the reaction of I with ethylene; in this case, photochemical CO substitution of IIIa by ethylene occurs, follwed by insertion of coordinated ethylene into Re–H or Re–C (alkenyl), recoordination of CO,[38] and C–C or C–H reductive elimination to yield an Re$_2$(CO)$_8$-(*trans*-C$_2$H$_5$CH=CHC$_2$H$_5$) species. Thermal reaction of this intermediate yields free *trans*-3-hexene and I.[39]

Evidence for the proposed mechanism is seen in the photochemical reaction of II with ethylene: irradiation of a IIa,b mixture under an ethylene atmosphere at 25 °C yields pentene which is primarily (85%) the trans-2 isomer. Reaction of IIa as in Scheme III, R = CH$_3$, accounts for specific formation of *trans*-2-pentene. Inasmuch as only small quantities of the corresponding cis olefins (3-hexene in reaction of I, 2-pentene in reaction of II) are produced, it is likely that the cis ("b") isomers of II and III are less reactive than the respective trans ("a") isomers. A *cis*-μ-alkenyl ligand may cause greater steric hindrance to ethylene coordination and/or insertion (Scheme III) than a *trans*-μ-alkenyl ligand. For similar reasons, isomer IIIc is very likely less reactive than IIIa.[40] Formation of *trans*-3-hexene in the reaction of I is therefore due to subsequent photochemical reaction of IIIa with ethylene, with IIIb and IIIc being substantially less reactive due to steric constraints.

Another possibility for hexene formation is subsequent photochemical reaction of I with 1-butene. Evidence against such a process is provided by the photochemical reaction of I with propylene, in which the major pentene product (after 5–20-min irradiation) is 1-pentene. The mechanism of this reaction is

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(37) Davis, R.; Ojo, I. A. O. *J. Organomet. Chem.* **1976**, *110*, C39.

(38) As discussed regarding Scheme I, coordination of ethylene (instead of CO) may occur, with later substitution by CO.

(39) This is likely to be a fast step, as internal trans olefins do not form (μ-hydrido)(μ-alkenyl)dirhenium complexes (e.g., no thermal reaction of *trans*-2-butene with I).[2]

(40) The product predicted by Scheme III for photochemical reaction of IIIc with ethylene is 2-ethyl-1-butene, which is not detected (by GC) as product in the photochemical reaction of I with C$_2$H$_4$.

(41) This represents butene produced by thermal dimerization of ethylene and does not include butene liberated from photo-generated (μ-hydrido)(μ-butenyl)dirhenium species by thermal reaction with ethylene.

essentially the same as Scheme III, R = H. In this case, however, coordinated *propylene* inserts into Re–H or Re–C (ethenyl). One particular insertion orientation (of the two possible for propylene) is apparently favored, as only small quantities of branched pentenes are formed. (The slow rate of this reaction, as compared to formation of III and 1-butene in the photochemical reaction of I with ethylene, may be due to a slower insertion step.) It is thus concluded that little or none of the *trans*-3-hexene produced in the reaction of I with ethylene results from photochemical reaction of I with 1-butene, although the small amount of 1-hexene generated may be produced in this manner.

(D) Overall Scheme. Scheme IV summarizes the photochemical reaction of I with ethylene. Significantly, little or no octene is produced; ethylene oligomerization ceases at the C_6 stage due to the relative inertness of the product, *trans*-3-hexene, compared to ethylene or 1-butene. Previous studies[2] have indicated that internal trans olefins do not form (μ-hydrido)(μ-alkenyl)dirhenium complexes. Additionally, insertion of internal olefins into Re–H or Re–C is very likely much slower than for ethylene or terminal olefins due to steric factors. Thus, subsequent photochemical reaction of *trans*-3-hexene with ethylene to give a C_8 olefin does not occur.

Aside from cis–trans isomerization of the μ-alkenyl ligand (of II, III), the only photochemical process in the proposed olefin dimerization mechanism is photodissociation of CO from the μ-hydrido μ-alkenyl octacarbonyl compounds. Continual photolysis is necessitated by subsequent recoordination of CO. Thus, in principle, removal of dissociated CO from the system should allow olefin dimerization to continue under thermal conditions. We have found this to be the case when CO is removed by bubbling a stream of ethylene through the solution during photolysis of I; subsequent thermal (25 °C) reaction under a static C_2H_4 atmosphere generates 0.6–0.7 equiv (based upon initial I) of butene[41] and 0.7 equiv of hexene within 40 h. The isomeric distributions, 95% 1-butene and 80–90% *trans*-3-hexene, are essentially identical with those obtained in the photochemical reaction. Unfortunately, production of these olefins ceases within 40 h. Even these small quantities, however, represent several catalytic turnovers inasmuch as the maximum amount of active dirhenium catalyst can only be 0.15 equiv. (The photolysis/ethylene-flush procedure generates ~0.15 equiv of $(\mu\text{-H})(\mu\text{-alkenyl})Re_2(CO)_7(CH_2{=}CH_2)$ species, with I and III comprising the remaining 0.85 equiv.) Loss of catalytic activity appears to be associated with decomposition of the $(\mu\text{-H})(\mu\text{-alkenyl})Re_2(CO)_7(CH_2{=}CH_2)$ species. We do not currently understand the mechanism of the decomposition process. CO is apparently evolved; it reacts with remaining $(\mu\text{-H})(\mu\text{-alkenyl})Re_2(CO)_7(CH_2{=}CH_2)$ to give the octacarbonyl species I and III. A small quantity of $[Re(CO)_3OH]_4$ is also generated. This problem notwithstanding, the demonstration of catalytic production of 1-butene and *trans*-3-hexene under thermal conditions is an important result and lends credence to our proposal that the only function of irradiation is to effect CO loss from I or III.

II. Reaction of II with Propylene: Production of Hexene. The photochemical reaction of IIa,b with propylene to yield hexene is presumably a catalytic process, although much slower than the photo-assisted catalysis of ethylene dimerization by I. Decomposition of dirhenium complex to $[Re(CO)_3OH]_4$ is again observed. Nonetheless, the regiospecificity of propylene dimerization is remarkable: 80–90% of product is 2-hexene. Specific formation of 2-hexene is accounted for by the olefin dimerization mechanism we have put forth: photochemical CO substitution of the μ-hydrido μ-alkenyl complex by olefin, insertion of coordinated olefin into Re–H or Re–C (alkenyl), and C–C or C–H reductive elimination to yield dimerized olefin. The specific catalytic process involving IIa,b and propylene is entirely analogous to that displayed in Schemes I or III. As in the photochemical reaction of I with propylene, one particular insertion orientation of propylene is favored, inasmuch as only small quantities of branched hexenes are produced.

Although the major product of photolysis at 25 °C is *trans*-2-hexene, a large amount of the cis isomer is also generated. Photolysis at 45 °C, however, affords a much greater quantity of trans relative to cis. There is a remarkable similarity between the trans/cis 2-hexene product ratios (1.4:1 at 25 °C, ~6:1 at 45 °C) and the IIa/IIb stationary-state ratios of the irradiated solution (1.4:1 IIa/IIb at 25 °C, 5.5:1 at 45 °C). Photochemical reaction of IIa with propylene yields *trans*-2-hexene, while IIb gives *cis*-2-hexene. It therefore appears that IIa and IIb are about equally reactive toward propylene with respect to photochemical hexene formation. We do not currently understand, however, why IIa is much more reactive than IIb toward ethylene. (Photolysis of 1.4:1 IIa/IIb under ethylene at 25 °C yields predominantly *trans*-2-pentene; vide supra.)

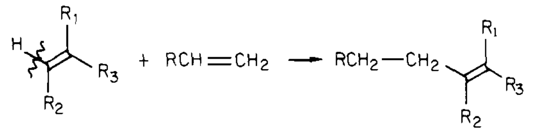
The slower propylene dimerization as compared to ethylene dimerization may be due to a slower olefin insertion step. It is noteworthy that little or no C_9 olefins are produced; this is again a consequence of the lower reactivity of internal olefins toward insertion and/or formation of (μ-hydrido)(μ-alkenyl)dirhenium complexes. Oligomerization thus ceases at dimerization to 2-hexene.

Removal of photodissociated CO from the system by bubbling a stream of propylene through the solution of II during photolysis results in subsequent thermal (25 °C) propylene dimerization. However, only a small quantity (~0.01 equiv, based upon initial II) is generated before activity ceases. As in the analogous experiment involving I and ethylene, loss of activity is associated with decomposition of the photogenerated $(\mu\text{-H})(\mu\text{-alkenyl})Re_2(CO)_7(\text{olefin})$ species. (Here, alkenyl = propenyl, olefin = propylene.) The dimerization product is predominantly *trans*-2-hexene; only a small amount of the cis isomer is generated. This is reasonable in light of the fact that IIb isomerizes rapidly to IIa in the absence of irradiation.[11] Thus, only hydrido propenyl dirhenium species with a trans μ-propenyl ligand geometry (as in IIa) will exist under thermal conditions, giving rise to *trans*-2-hexene (as with IIa in the photochemical reaction).

Conclusion

There has been much discussion in recent years regarding the potential catalytic ability of polynuclear metal compounds.[42] Attention has centered on the possibility of catalytic reactivity different from that of mononuclear complexes, although little has been achieved in this area. Recently, selective catalytic alkyne hydrogenation to internal trans olefins has been achieved by using a dirhodium complex;[6] mononuclear catalysts yield cis olefins. In the present study we have discovered a novel mechanism for olefin dimerization that is specifically dependent on the presence of adjacent metal sites.

The established mechanisms for olefin dimerization at a single metal atom center involve metal hydride species[43] or metallacycle intermediates.[44] By contrast, the dinuclear mechanism we have uncovered accomplishes the transformation in eq 9. That is, the



(9)

vinylic C–H bond of one olefin is cleaved, and a second olefin is inserted in that position. The C–C double bond of the first olefin is thus maintained. Ethylene dimerization yields 1-butene; propylene dimerization (R_1 or R_3 = CH_3 in eq 9) affords 2-hexene. If the two precursor olefins differ, then the product depends upon the order of reaction: vinylic C–H cleavage of propylene followed by insertion of ethylene yields 2-pentene, whereas the reverse gives

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primarily 1-pentene. Polymerization or extended oligomerization does not occur in any of these reactions because the product olefins are less reactive than their precursors toward the dirhenium center, presumably for steric reasons.

We are currently exploring the chemistry of various phosphine-substituted (μ-hydrido)(μ-alkenyl)dirhenium carbonyl compounds, to vary the steric and electronic characteristics of the catalyst and to address the problem of catalyst decomposition. We are also investigating other polynuclear metal systems with respect to similar catalytic activity.

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Registry No. I, 82621-42-9; I-d_4, 88035-65-8; IIa, 82638-69-5; IIb, 88082-36-4; IIIa, 82621-39-4; IIIb, 88082-37-5; IIIc, 82621-43-0; IV, 89958-85-0; V, 90026-98-5; *cis*-V, 89958-86-1; $Re_2(CO)_{10}$, 14285-68-8; C_2H_4, 74-85-1; C_2D_4, 683-73-8; (μ-H)(μ-*trans*-CH=CHPh)$Re_2(CO)_8$, 86244-50-0; ^{13}CO, 1641-69-6; PPh_3, 603-35-0; $HRe(CO)_4(PPh_3)$, 25838-69-1; Re, 7440-15-5; *trans*-4-methyl-2-pentene, 674-76-0; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; 1-pentene, 109-67-1; *cis*-2-butene, 118-03-6; *trans*-2-butene, 624-64-6; 2-hexene, 592-43-8; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; methyl vinyl ether, 107-25-5; 1-hexene, 592-41-6; butene, 25167-67-3; styrene, 100-42-5; 1-butene, 106-98-9; propylene, 115-07-1.

Organoactinide Carbonylation and Carboxylation Chemistry. Structural, Electronic, Bond Energy, and Photochemical Effects on Migratory Insertion in the Tris(cyclopentadienyl)thorium Hydrocarbyl Series

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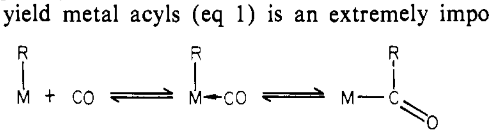
Abstract: This contribution reports a synthetic and kinetic study of CO migratory insertion for the series of thorium hydrocarbyls $Th(\eta^5\text{-}C_5H_5)_3R$, R = *i*-$C_3H_7$, *sec*-$C_4H_9$, neo-$C_5H_{11}$, *n*-$C_4H_9$, $CH_2Si(CH_3)_3$, CH_3, and $CH_2C_6H_5$. Under the conditions employed, the reaction was found to be first order in $Th(C_5H_5)_3R$ and first order in CO. In the above order, the relative rates of migratory insertion were found to be 42:18:1.3:1.0:0.02:0.01:<0.01. In the case of R = CH_3, *i*-C_3H_7, *n*-C_4H_9, neo-C_5H_{11}, and *sec*-C_4H_9, carbene-like (by spectroscopic and chemical properties) η^2-acyl insertion products, $Th(C_5H_5)_3(\eta^2\text{-}COR)$, could be isolated and characterized. In the case of R = *i*-C_3H_7 and $CH_2Si(CH_3)_3$, enolate rearrangement products were isolated and characterized. The relative rates of CO insertion reflect both steric and electronic effects; there is a significant correlation with experimentally determined Th–R bond disruption enthalpies. For $Th(C_5H_5)_3CH_2Si(CH_3)_3$, it was also found that the rate of migratory CO insertion could be significantly accelerated by photolysis. However, secondary reactions of the insertion product are also observed. A comparative study of CO_2 migratory insertion to yield bidentate carboxylates revealed that carboxylation is significantly slower than carbonylation (a factor of 50 for $Th(C_5H_5)_3CH_3$; a factor of 10^5 for $Th(C_5H_5)_3(i\text{-}C_3H_7)$) and that for the above two compounds sensitivity of the rate to the nature of R is considerably altered vis-à-vis CO migratory insertion.

The migratory insertion of carbon monoxide into metal–carbon bonds to yield metal acyls (eq 1) is an extremely important transformation in stoichiometric and catalytic organotransition-metal chemistry.[1] Mechanistically, the process is now reasonably well understood (at least for middle and late transition metals), and factors such as the dependence of rate on the identity of R have been investigated in some detail.[1,2] Of late, it has become evident that organoactinides[3] display an unusual, distinctively nonclassical carbonylation chemistry, which differs from middle and late transition-metal complexes in a number of surprising ways.[4] In view of these dissimilarities, it would be of great interest to investigate migratory insertion reactivity patterns in a structurally well-defined and chemically well-characterized, homologous series of 5f hydrocarbyls.



$$\overset{R}{\underset{M}{|}} + CO \rightleftharpoons \overset{R}{\underset{M}{|}}\!\leftarrow CO \rightleftharpoons M{-}\overset{R}{\underset{\diagdown O}{\overset{|}{C}}} \tag{1}$$

In the present contribution, we report such an investigation of migratory insertion reactivity for the tris(cyclopentadienyl)thorium hydrocarbyls Cp_3ThR (A) Cp = η^5-C_5H_5; a preliminary account was communicated several years ago.[5] This particular series has

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