

(Table III).

There is some ambiguity in the assignment of the lowest energy transitions in the bromide and iodide complexes. Because the Cp orbitals drop in energy and the halide orbitals rise in energy along the series, it is obvious that at some point the two series of orbitals will meet and intertwine with each other; perhaps the halide orbitals will even eventually rise above the Cp orbitals. In our calculation the trend toward the orbitals meeting is clear but the two types of orbitals have not met and are still separate even in the iodide complex. The UV photoelectron spectral results of Green and co-workers,^{11b} however, suggest that in the bromide complex the two types of orbitals are very close in energy and in the iodide complex the iodide orbitals are higher in energy than the Cp orbitals. When the Cp₂TiBr₂ complex is irradiated in its lowest energy electronic absorption band, the Cp-Ti bonds are cleaved.^{8a} On the basis of this result we suggest that a Cp → Ti charge-transfer transition is still lowest in energy in this complex. Adhering to our belief of not using the SCF-X α -SW method for purposes for which it was not intended, we concede that the results of our calculation probably cannot determine which set of orbitals is the higher one in the iodide complex. The point, however, is that the calculation predicts that the Cp and halide orbitals will come closer together along the series. This trend is enough to alert us that the lowest energy excited states of the iodide complex (and possibly the bromide complex) may be different from the earlier members of the series and that the photochemistry of the iodide complex may be different as well. This latter prediction has been borne out; an investigation in our laboratory of the photochemistry of the Cp₂TiI₂ complex shows that the Cp-Ti bonds do not break when this complex is irradiated.³³ Instead, the Ti-I bonds are cleaved.³³ The different photochemistry of the iodide complex is probably a consequence of having a different lowest energy, photochemically active excited state. On the basis

of our experimental results and the trend found in the calculations, we assign the lowest energy transition in the Cp₂TiI₂ complex to an iodide-to-Ti charge transfer (8b₁ → 14a₁; ¹A₁ → ¹B₂). In the absence of detailed spectroscopic data, it makes no sense to assign the other bands in the iodide complex.

The calculational results on the Cp₂Ti(CH₃)₂ complex also support our claim that the SCF-X α -SW method will be useful in identifying LMCT electronic absorption bands. The two lowest energy excited states for this complex are predicted to be 13a₁ → 14a₁ and 9b₁ → 14a₁ (¹A₁ → ¹A₁ and ¹A₁ → ¹B₁, respectively). The 13a₁ and 9b₁ orbitals are Ti-CH₃ bonding orbitals and the 14a₁ orbital is a titanium d orbital (a d_{z²}, d_{x²-y²} mixture) (Figure 5). The important point here is that the lowest energy excited states are not Cp → Ti charge transfer, as in the fluoride, chloride, and bromide complexes, but are transitions involving the Ti-CH₃ σ bond. On the basis of this result we might expect the photochemical behavior of the Cp₂Ti(CH₃)₂ complex to be very different from that of the halide complexes. In fact, the photochemical reactivities of the two types of complexes are very different. Whereas the Cp-Ti bonds are photochemically cleaved in the Cp₂TiX₂ complexes (X = F, Cl, Br), the Ti-CH₃ bonds are cleaved in the Cp₂Ti(CH₃)₂ complex.⁹ (Cleavage of the Ti-CH₃ bond appears not to involve formation of free methyl radicals.⁹ The point is, however, that the Ti-CH₃ bond is ultimately broken.)

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Registry No. Cp₂TiF₂, 309-89-7; Cp₂TiCl₂, 1271-19-8; Cp₂TiBr₂, 1293-73-8; Cp₂TiI₂, 12152-92-0; Cp₂Ti(CH₃)₂, 1271-66-5.

Supplementary Material Available: The exact coordinates for all of the complexes, including outersphere coordinates, and other molecular orbital plots (55 pages). Ordering information is given on any current masthead page.

(33) Bruce, M. R. M.; Tyler, D. R., unpublished results.

Photolysis of Re₂(CO)₁₀ in the Presence of Simple Olefins. Thermal Reactivity of (μ -Hydrido)(μ -alkenyl)dirhenium Octacarbonyl Compounds¹

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Abstract: Photolysis of Re₂(CO)₁₀ at 25 °C in the presence of ethylene, terminal olefins, or 2-butene results in formation of (μ -hydrido)(μ -alkenyl)dirhenium octacarbonyl complexes in high yield. The bridging alkenyl ligand forms a σ bond to one Re and a π bond to the other. The reaction is proposed to proceed through a light-induced radical pathway, producing a 1,2-Re₂(CO)₈(η^2 -olefin)₂ intermediate that undergoes thermal reaction to give the observed product. The μ -alkenyl ligand undergoes a rapid fluxional process at room temperature in which the σ and π bonds of the alkenyl group are interchanged between the bridged rhenium atoms. The μ -hydrido- μ -alkenyl compounds react with a variety of substrates under mild thermal conditions. Treatment with pyridine, P(OMe)₃, or P(OPh)₃ results in elimination of olefin and formation of 1,2-*eq,eq*-Re₂(CO)₈L₂. Kinetics investigations of reactions with pyridine are consistent with a mechanism that begins with intramolecular C-H reductive elimination. Treatment with bis(diphenylphosphino)methane (dppm) affords a dppm-bridged complex, Re₂(CO)₈(dppm); reaction with PPh₃ or P(*n*-Bu)₃ initially generates 1,2-*ax,eq*-Re₂(CO)₈L₂, which thermally isomerizes to 1,2-*ax,ax*-Re₂(CO)₈L₂. Nucleophilic attack of PMe₃ upon the ethenyl ligand of (μ -H)(μ -CH=CH₂)Re₂(CO)₈ results in a dipolar addition product. The μ -hydrido, μ -alkenyl compounds react with ethylene, terminal olefins, or *cis*-2-butene to afford the hydride- and alkenyl-exchanged hydrido-alkenyl species. Reaction with H₂ generates H₂Re₂(CO)₈.

The photochemistry of Mn₂(CO)₁₀ and Re₂(CO)₁₀ has been studied extensively within the past several years, particularly with

respect to substitution by phosphorus² and, to a lesser extent, nitrogen³ ligands. Substitution has also been effected by thermal

Table I. Spectroscopic Data for (μ -Hydrido)(μ -alkenyl)dirhenium Octacarbonyl Compounds, I-VII

compd	$^1\text{H NMR}^a$ δ , ppm	ν_{CO}^b cm^{-1}	M^+ , m/e^c
I	-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); $^3J_{\text{H}_1-\text{H}_2} = 17.2$, $^3J_{\text{H}_2-\text{H}_3} = 10.9$, $^3J_{\text{H}_1-\text{H}_3} = 2.9$ Hz	2117 (vw), 2085 (w), 2021 (s), 1998 (m), 1988 (m), 1978 (mw), 1970 (m)	624
IIa	-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); $^3J_{\text{H}_1-\text{H}_2} = 15.9$, $^3J_{\text{H}_1-\text{CH}_3} = 5.4$ Hz	2114 (vw), 2083 (w), 2017 (s), 1994 (m), 1979 (ms), 1975 (sh), 1967 (m)	638
IIb	-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); $^3J_{\text{H}_2-\text{H}_3} = 11.9$, $^3J_{\text{H}_3-\text{CH}_3} = 6.5$ Hz		
IIIa	-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); $^3J_{\text{H}_1-\text{H}_2} = 16.1$, $^3J_{\text{H}_1-\text{CH}_2} = 5.2$, $^3J_{\text{CH}_2-\text{CH}_3} = 7.3$ Hz	2114 (vw), 2083 (w), 2017 (s), 1995 (m), 1979 (ms), 1976 (sh), 1967 (m)	652
IIIb	-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); $^3J_{\text{H}_2-\text{H}_3} = 11.8$, $^3J_{\text{H}_3-\text{CH}_2} = ^3J_{\text{CH}_2-\text{CH}_3} = 7.2$ Hz		
IIIc	-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, CH_2), 1.31 (t, 3 H, CH_3); $^3J_{\text{H}_1-\text{H}_3} = 2.2$, $^3J_{\text{CH}_2-\text{CH}_3} = 7.4$ Hz		
IVa	-14.44 (s, 1 H, μ -H), 6.51 (d, 1 H, H_2), 5.27 (dt, 1 H, H_1), 2.19 (td, 2 H, allyl CH_2), 1.4-1.6 (m, 4 H, $-\text{CH}_2\text{CH}_2-$), 0.96 (t, 3 H, CH_3); $^3J_{\text{H}_1-\text{H}_2} = 16.0$, $^3J_{\text{H}_1-\text{CH}_2} = 5.8$, $^3J_{\text{CH}_2-\text{CH}_3} = 7.3$ Hz	2114 (vw), 2083 (w), 2017 (s), 1994 (m), 1979 (ms), 1976 (sh), 1967 (m)	680
V	-13.99 (s, 1 H, μ -H), 5.17 (q, 1 H, H_1), 2.99 (s, 3 H, Me_2), 2.04 (d, 3 H, Me_3); $^3J_{\text{H}_1-\text{CH}_3} = 5.8$ Hz	2113 (vw), 2083 (w), 2016 (s), 1992 (s), 1978 (s), 1966 (m)	
VI	-14.21 (s, 1 H, μ -H), 6.85 (d, 1 H, H_1 or H_2), 5.04 (d, 1 H, H_2 or H_1), 3.86 (t, 2 H, OCH_2), 1.72 (m, 2 H, CH_2), 1.44 (m, 2 H, CH_2), 0.96 (t, 3 H, CH_3); $^3J_{\text{H}_1-\text{H}_2} = 13.6$ Hz ^d	2112 (vw), 2083 (w), 2014 (s), 2005 (sh), 1994 (m), 1970 (s), 1964 (sh)	696
VII	-14.16 (s, 1 H, μ -H), 7.53 (d, 1 H, H_1 or H_2), 7.41-7.43 (m, 4 H, $\text{Ph}_\alpha + \text{Ph}_\beta$), 7.28-7.34 (m, 1 H, Ph_γ), 6.22 (d, 1 H, H_2 or H_1); $^3J_{\text{H}_1-\text{H}_2} = 16.6$ Hz	2113 (vw), 2083 (w), 2017 (s), 1996 (m), 1988 (m), 1974 (w, sh), 1969 (m)	700

^a CDCl_3 at 25 °C for I, IIa, IIIa, IIIc, IVa, and VI; CD_2Cl_2 at 25 °C for V and VII; CD_2Cl_2 at -10 °C for V and VII; CD_2Cl_2 at -10 °C for IIb and IIIb. ^b Hexane solution. ^c 70-eV electron impact, $\text{Re}_2 = 372$. ^d Similar to the coupling constant observed for the *trans*-vinyl protons in vinyl *n*-butyl ether itself. 14.3 Hz (CDCl_3).

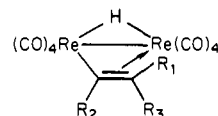
means⁴ and through the use of Me_3NO .⁵ Reactions of these compounds with unsaturated hydrocarbons, e.g., olefins and acetylenes, have received much less attention despite potential relevance to catalytic processes such as isomerization, hydrogenation, oligomerization, etc. Previous investigations involving olefinic substrates have examined reactivity with conjugated polyenes such as 1,3-butadiene,^{3b,6} cycloheptatriene,⁷ and cyclooctatetraene.^{6a} We now describe the first investigation of the reactivity of simple olefins with $\text{Re}_2(\text{CO})_{10}$, in particular under photochemical conditions. We also report a study of the reactivity of the photolysis products, (hydrido)(alkenyl)dirhenium octacarbonyl compounds, with a wide variety of substrates under thermal conditions. A preliminary account of this work has been published.⁸

Results

Photolysis of $\text{Re}_2(\text{CO})_{10}$ in the Presence of Terminal Olefins.

Photolysis of $\text{Re}_2(\text{CO})_{10}$ at 25 °C in the presence of propylene or 1-butene results in formation of (μ -hydrido)(μ -alkenyl)dirhenium octacarbonyl, (μ -H)(μ -CH=CHR) $\text{Re}_2(\text{CO})_8$, where R = Me or Et, respectively.⁹ Spectroscopic data for these compounds are displayed in Table I. Both the (μ -H)(μ -*trans*-

Chart I



- I, $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}$
 IIa, $\text{R}_1 = \text{R}_2 = \text{H}$; $\text{R}_3 = \text{CH}_3$
 IIb, $\text{R}_2 = \text{R}_3 = \text{H}$; $\text{R}_1 = \text{CH}_3$
 IIIa, $\text{R}_1 = \text{R}_2 = \text{H}$; $\text{R}_3 = \text{C}_2\text{H}_5$
 IIIb, $\text{R}_2 = \text{R}_3 = \text{H}$; $\text{R}_1 = \text{C}_2\text{H}_5$
 IIIc, $\text{R}_1 = \text{R}_3 = \text{H}$; $\text{R}_2 = \text{C}_2\text{H}_5$
 IVa, $\text{R}_1 = \text{R}_2 = \text{H}$; $\text{R}_3 = n\text{-C}_4\text{H}_9$
 V, $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{R}_3 = \text{CH}_3$
 VI, $\text{R}_1 = \text{R}_2 = \text{H}$; $\text{R}_3 = \text{O}(\text{CH}_2)_3\text{CH}_3$
 VII, $\text{R}_1 = \text{R}_2 = \text{H}$; $\text{R}_3 = \text{Ph}$

$\text{CH}=\text{CHR})\text{Re}_2(\text{CO})_8$ and (μ -H)(μ -*cis*- $\text{CH}=\text{CHR})\text{Re}_2(\text{CO})_8$ isomers of these products are generated, with the *trans* isomer predominant.¹⁰ The *cis* isomers (IIb and IIIb) are distinguished from the *trans* species (IIa and IIIa) by smaller coupling between the vinyl protons in the NMR spectrum (12 vs. 16 Hz). The *cis* products are thermally unstable with respect to isomerization; 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. The *trans* isomer is thus the sole hydrido-alkenyl product observed after a short period following cessation of photolysis. Overall conversion of $\text{Re}_2(\text{CO})_{10}$ to IIa and IIIa was determined by IR spectroscopy to be greater than 90%. Similarly, IVa was obtained in near-quantitative yield by photolysis in the presence of 1-hexene.

IIa, IIIa, and IVa are light yellow oils at room temperature and are air stable in solution at 25 °C over a period of several hours. However, the purified materials decompose, even under an inert atmosphere, over a period of several weeks.

(10) We have found that the two isomers exist in equilibrium under photochemical conditions. This reactivity, in addition to other aspects of the photochemistry of the (hydrido)(alkenyl)dirhenium compounds, will be discussed in a forthcoming publication.

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

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(9) We observe no reaction with $\text{Mn}_2(\text{CO})_{10}$ under similar conditions.

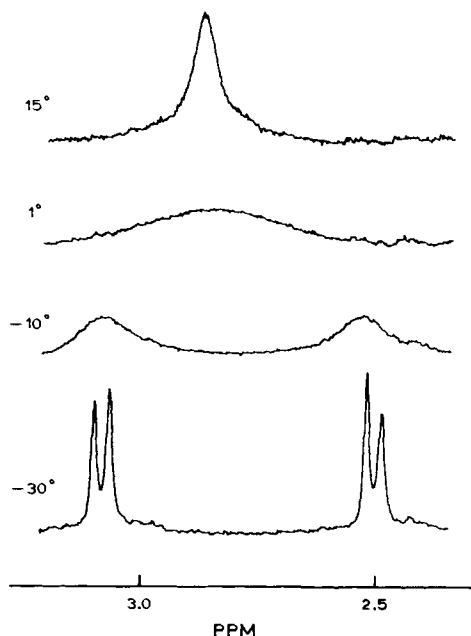


Figure 1. Variable-temperature ^1H NMR spectra of the allyl CH_2 resonance of IIIc with the methyl group (δ 1.34) decoupled.

Photolysis of $\text{Re}_2(\text{CO})_{10}$ in the presence of ethylene results in formation of $(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)\text{Re}_2(\text{CO})_8$, I, as the major product. The hydrido-butenyl complexes IIIa, IIIb, and IIIc are produced as minor products (detected by ^1H NMR). IIIc isomerizes to IIIa in the dark at room temperature with a half-life of ~ 10 h (toluene solution, no excess olefin). After cessation of photolysis the hydrido-butenyl products are slowly converted to I, over a period of 1–2 days, under an ethylene atmosphere at room temperature. I is an air-stable, pale yellow crystalline solid.

Continued photolysis of the reaction solutions after complete disappearance of $\text{Re}_2(\text{CO})_{10}$ results in slow decomposition of the hydrido-alkenyl complex and formation of $[\text{Re}(\text{CO})_3\text{OH}]_4$,¹¹ presumably due to reaction with trace H_2O in solution.^{12,13}

Photolysis in the Presence of 2-Butene. Photolysis of $\text{Re}_2(\text{CO})_{10}$ in the presence of *cis*-2-butene results in production of $(\mu\text{-H})(\mu\text{-C}(\text{CH}_3)=\text{CHCH}_3)\text{Re}_2(\text{CO})_8$, V. Maximum yields obtained were 20%, as determined by ^1H NMR. This complex was not isolated, and the fate of the remaining Re was not determined. Initially, no other hydrido-alkenyl species are produced except for trace amounts of IIIa and IIIb. However, photolysis of the reaction solution over a period of several days results in slow disappearance of V and formation of IIIa and IIIb.

Photolysis of $\text{Re}_2(\text{CO})_{10}$ in the presence of *trans*-2-butene results in slow formation of IIIa and IIIb. No other hydrido-alkenyl species were detected upon complete reaction of the $\text{Re}_2(\text{CO})_{10}$. Production of IIIa and IIIb is several times slower than in the direct photochemical reaction with 1-butene (1 atm). GC analysis of the reaction head gas indicated that *trans*-2-butene is slowly isomerized to 1-butene and *cis*-2-butene during photolysis.

NMR Studies of the (Hydrido)(alkenyl)dirhenium Octacarbonyl Compounds. The ^{13}C NMR spectrum of I in benzene- d_6 was recorded at 20 $^\circ\text{C}$ without ^1H decoupling. Four resonances of equal intensity were observed in the carbonyl region: 185.1 (s), 183.8 (s), 183.0 (s), and 181.9 (s) ppm. Recorded under identical conditions, the ^{13}C NMR spectrum of IIIa also shows four carbonyl peaks of equal intensity: 185.4 (s), 184.4 (s), 183.4 (s), and 182.3 (s) ppm.

The ^1H NMR spectra of I, IIIa, and IIIc in CD_2Cl_2 were monitored as a function of temperature. The ^1H NMR spectrum

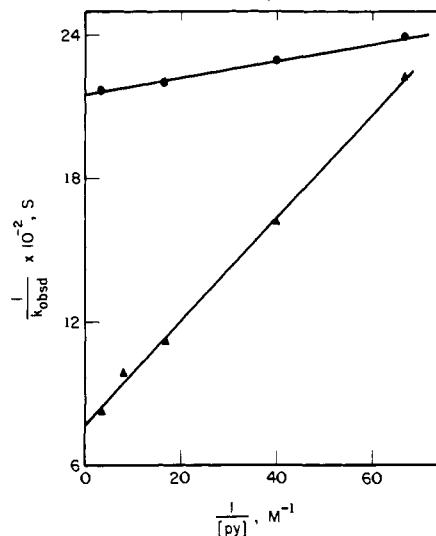


Figure 2. k_{obsd}^{-1} vs. $[\text{pyridine}]^{-1}$ for the reactions of I (\bullet) and IVa (\blacktriangle) with pyridine at 28.5 $^\circ\text{C}$.

of I remains essentially unchanged upon cooling from +25 to -83 $^\circ\text{C}$ except for minor chemical shift changes. The spectra of IIIa and IIIc remain basically unchanged except for the allyl methylene group resonance. The CH_2 group of IIIc appears as a slightly broadened singlet (δ 2.93) at 30 $^\circ\text{C}$ when the methyl group (δ 1.34) is decoupled. As the temperature is lowered (see Figure 1) this resonance broadens and separates into two doublets ($J = 11.3$ Hz). The stopped-exchange region is reached at -40 $^\circ\text{C}$, where the two resonances appear at δ 3.06 and 2.50, respectively. From the observed coalescence temperature (1 $^\circ\text{C}$), the free energy of activation (ΔG^\ddagger_c) for the dynamic process was calculated to be 12.7 kcal/mol.¹⁴ The CH_2 resonance of IIIa shows similar behavior, although at lower temperatures. With the methyl group (δ 1.17) decoupled, the CH_2 resonance (δ 2.33) is a doublet (due to vinyl proton coupling) down to -30 $^\circ\text{C}$. Further cooling results in broadening and eventual separation into two resonances. On the basis of $T_c = -55$ $^\circ\text{C}$ and $\Delta\nu = 180 \pm 10$ Hz (from stopped exchange at -83 $^\circ\text{C}$), ΔG^\ddagger_c for this dynamic process is calculated to be 10.0 kcal/mol.

Thermal Reactions of the Hydrido-Alkenyl Compounds. A. Pyridine. The $(\mu\text{-hydrido})(\mu\text{-alkenyl})\text{dirhenium octacarbonyl}$ compounds I–VII react with excess pyridine in the dark to yield free olefin and 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$, identified by IR spectroscopy^{3d,15} and FDMS. For example, treatment of a toluene solution of IVa with excess pyridine (0.5 M, 100 equiv) yields quantitative production of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$ and 1-hexene¹⁶ within ~ 1 h at room temperature. No intermediates were observed (by IR spectroscopy) during the course of the reaction.

The kinetics of the reactions of I and IVa with pyridine in toluene solution were investigated. The reactions were carried out at 28.5 $^\circ\text{C}$ and monitored by IR spectroscopy. The rate of product formation was determined by monitoring the decrease in IR absorbance at ~ 2085 cm^{-1} due to I or IVa. In all reactions, the pyridine concentration was at least a factor of 20 greater than the initial concentration of hydrido-alkenyl complex. Pseudo-first-order rate plots were found to be linear for at least 3 half-lives. However, the pseudo-first-order rate constant, k_{obsd} , is markedly dependent upon pyridine concentration in the case of IVa. The dependence on pyridine concentration is less marked for I. The results of the kinetics experiments are illustrated in Figure 2 in the form of a $1/k_{\text{obsd}}$ vs. $1/[\text{py}]$ plot.

(14) Activation energy was calculated by using the relations $k_c = \pi(\Delta\nu)/2^{1/2}$ and $k_c = (k_B T_c/h) \exp(-\Delta G^\ddagger_c/RT_c)$, 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.

(15) IR ν_{CO} of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$: 2062 (w), 2006 (m), 1950 (s, br), 1917 (sh), 1905 (m) cm^{-1} (toluene).

(16) Identified and quantitated by GC analysis.

(11) IR ν_{CO} of $[\text{Re}(\text{CO})_3\text{OH}]_4$: 2038 (s), 1939 (vs) cm^{-1} (hexane).

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Table II. Spectroscopic Data for Phosphorus-Donor Reaction Products

compd	^1H NMR, δ , ppm	ν_{CO} , ^a cm^{-1}	FDMS, M^+
$(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$, A	-15.75 (dd, 1 H, $\mu\text{-H}$), 1.55 (m, 1 H, H_a), 1.26 (ddd, 1 H, H_b), 0.71 (td, 1 H, H_c), 0.29 (d, 9 H, PMe_3); $J_{\text{H}_a\text{-H}_b} = 4.9$, $J_{\text{H}_a\text{-H}_c} = 9.9$, $J_{\text{H}_a\text{-(}\mu\text{-H)}} = 2.7$, $J_{\text{H}_b\text{-}^{31}\text{P}} = 8.5$, $J_{\text{H}_c\text{-}^{31}\text{P}} = 14.7$, $J_{(\mu\text{-H})\text{-}^{31}\text{P}} = 6.6$, $J^{31}\text{P-H(Me)} = 11.9$, $J_{\text{H}_a\text{-}^{31}\text{P}} = 4.4$ Hz^b	2089 (vw), 2065 (w), 1988 (s), 1982 (sh), 1965 (m), 1949 (w), 1927 (m), 1920 (sh)	700
$\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$	1.17 (d), $J_{\text{H-}^{31}\text{P}} = 8.6$ Hz^c	2063 (w), 2005 (m), 1959 (s), 1925 (w), 1910 (m)	748
$\text{Re}_2(\text{CO})_8[\text{P(OMe)}_3]_2$	3.23 (d), $J_{\text{H-}^{31}\text{P}} = 11.3$ Hz^c	2077 (w), 2024 (ms), 1986 (s), ~ 1968 (sh), 1946 (w), 1918 (ms)	844
$\text{Re}_2(\text{CO})_8[\text{P(OPh)}_3]_2$		2081 (w), 2032 (m), 1994 (s), ~ 1976 (sh), 1954 (w), 1931 (m)	
$\text{Re}_2(\text{CO})_8(\text{dppm})$	7.30-7.50 (m, 20 H, Ph), 4.40 (t, 2 H, CH_2); $J_{\text{H-}^{31}\text{P}} = 10.0$ Hz^d	2073 (m), 2020 (m), 1980 (s), 1956 (w), 1940 (w), 1915 (m)	980

^a Toluene solution. ^b Toluene- d_8 , 0 °C. ^c Benzene- d_6 , 25 °C. ^d CD_2Cl_2 , 25 °C.

A kinetics study of the reaction of pyridine with $(\mu\text{-D})(\mu\text{-CD}=\text{CD}_2)\text{Re}_2(\text{CO})_8$, I- d_4 , prepared by thermal treatment of IIa with C_2D_4 (vide infra), was performed identically. In this case, k_{obsd} remains relatively constant ($4.4 \times 10^{-4} \text{ s}^{-1} \pm 5\%$) over the pyridine concentration range studied (0.015-0.30 M).

B. Triphenylphosphine. The μ -hydrido- μ -alkenyl compounds all react with excess PPh_3 to give $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ plus free olefin at 25 °C. For example, treatment of I with excess PPh_3 in hexane solution results in formation of an air-stable, pale yellow precipitate within minutes. Complete reaction of I requires ~ 4 h at room temperature. C,H analysis and FDMS (M^+ 1120) of the pale yellow precipitate are consistent with formulation as $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$. The IR spectrum in the carbonyl region of this material, however, is markedly different from that of the known compound, 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$.^{4b,17} In toluene solution, bands occur at 2069 (mw), 2012 (m), 1964 (vs, br), 1934 (m), and 1921 (m) cm^{-1} . At room temperature in the dark these bands diminish and those of 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ appear. The reaction half-life is about 10 h.

A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a CD_2Cl_2 solution of the pale yellow precipitate was obtained. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -7 °C exhibits three resonances: a weak singlet at 16.8 ppm, assigned to 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ by comparison with an authentic sample,¹⁸ and two strong singlets of equal intensity at 15.9 and 0.6 ppm, respectively. When the solution is allowed to stand at 25 °C, the 15.9- and 0.6-ppm singlets slowly and simultaneously decrease in intensity while the 16.8-ppm resonance increases. The 15.9- and 0.6-ppm peaks are thus assigned as the axial¹⁹ and equatorial phosphine resonances, respectively, of a 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ complex, which isomerizes at 25 °C to the known 1,2-*axial,axial* complex.

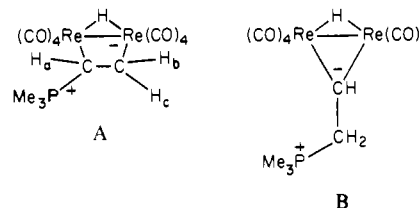
IR and low-temperature ^{31}P NMR indicated that the conversion of I to $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ in hexane is quantitative and that the precipitate is 80-85% 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ and 15-20% 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$. When toluene solvent was employed, IR monitoring of the reaction solution confirmed that the initial product is predominantly 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$.

The UV-vis spectrum (270-500 nm) of the precipitated reaction product in DMF solution was obtained. After subtraction of the absorbance due to the known concentration of 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$, the spectrum shows an absorption maximum at 350 nm ($16\,000 \text{ M}^{-1} \text{ cm}^{-1}$).

Three 0.003 M solutions of the precipitated $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ product were prepared in the presence of CO (1 atm, toluene solution), ^{13}CO (0.6 atm, toluene), and CCl_4 (1:1 $\text{CCl}_4/\text{CH}_2\text{Cl}_2$ by volume), respectively. In all cases, the only process observed by IR is isomerization of 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ to 1,2-

ax,ax- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$. No ^{13}CO incorporation into the product occurs under the ^{13}CO atmosphere.

C. Trimethylphosphine. Treatment of I with excess PMe_3 in hexane solution results in formation of an air-stable, white crystalline precipitate within seconds; the reaction is complete within a few minutes at room temperature. C,H,P analysis and FDMS (M^+ 700) of the crystalline product are consistent with formulation as $(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$, i.e., formal addition of PMe_3 to I. Spectroscopic data for the product are given in Table II. The IR (ν_{CO}) spectrum, similar to that of I but shifted to lower frequencies, suggests two possible structures (A and B) for the reaction product, both of which result from



attack of PMe_3 at an alkenyl carbon to generate a dipolar addition product. The ^1H NMR spectrum is consistent with structure A; structure B is ruled out by the observation that the methylene protons are anisochronous, even at 25 °C. In toluene solution, the product (A) slowly decomposes to I plus other species at ~ 25 °C.

The reaction of I with PMe_3 in toluene solvent rapidly generates the dipolar addition product, A, in solution. This species then slowly decomposes over a 15-h period at room temperature to produce a clear yellow solution that exhibits IR absorptions at 2072 (w), 2063 (sh), 2005 (w), 1959 (s, br), 1925 (w), 1910 (mw), 1890 (vw), 1873 (w), and 1843 (mw) cm^{-1} . The major product of this reaction solution is $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$, an air-stable, pale yellow solid, isolated by TLC and characterized spectroscopically (Table II). The IR spectral pattern is very similar to those of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8\text{L}_2$ (L = py,¹⁵ CH_3CN ¹³) but markedly different from the spectrum of 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8\text{L}_2$ (L = PPh_3).¹⁷ The major product is thus assigned as 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$. A solution of this complex (toluene solvent) shows no change in IR spectrum over a 1-day period, indicating little or no tendency toward isomerization. Because of decomposition on chromatographic supports (silica), the species responsible for the other IR bands of the reaction solution of I with PMe_3 (15 h, toluene) were not isolated or identified.

Reaction of IIa with excess PMe_3 in hexane does not produce a precipitate. IR monitoring of the reaction indicated only formation of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$ in near-quantitative yield; no intermediates were observed. Complete reaction requires 2-3 h at room temperature.

D. P(*n*-Bu)₃. Treatment of a hexane solution of I with excess $\text{P}(n\text{-Bu})_3$ does not result in precipitate formation. IR data indicate a similar reaction sequence when L = PPh_3 , i.e., initial formation of 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8[\text{P}(n\text{-Bu})_3]_2$ within a few hours, followed

(17) IR ν_{CO} of 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$: 2012 (w), 1985 (w, sh), 1960 (vs) cm^{-1} (toluene).

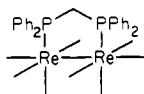
(18) Prepared by the method of ref 5.

(19) The ^{31}P chemical shifts of *ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ and 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ in chloroform solution are 14.9 and 17.5 ppm, respectively: Fawcett, J. P.; Poë, A. J.; Twigg, M. V. *J. Organomet. Chem.* 1973, 61, 315.

by isomerization to the 1,2-axial,axial species (isomerization half-life of 1–2 days at 25 °C). Carbonyl stretching bands at 2068 (mw), 2006 (m), 1971 (s), 1928 (s), and 1917 (s) cm^{-1} (hexane solution) were assigned to the 1,2-axial,equatorial isomer; 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8[\text{P}(n\text{-Bu})_3]_2$ exhibits a very strong absorption at 1956 cm^{-1} . Both products are colorless.

E. P(OMe)₃ and P(OPh)₃. I reacts with excess P(OMe)₃ in toluene solution to afford $\text{Re}_2(\text{CO})_8[\text{P}(\text{OMe})_3]_2$ in essentially quantitative yield (by IR and ¹H NMR spectroscopy) after 12 h at room temperature. Similar treatment with P(OPh)₃ yields $\text{Re}_2(\text{CO})_8[\text{P}(\text{OPh})_3]_2$. Spectroscopic data for both compounds are contained in Table II. No intermediates were observed by IR spectroscopy during the course of the reactions. The geometry of the two products is assigned as 1,2-equatorial,equatorial on the basis of the ¹H NMR (for $\text{Re}_2(\text{CO})_8[\text{P}(\text{OMe})_3]_2$) and the strong similarity of the IR spectra to the pattern observed for 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$.¹⁵ Both products are colorless and stable in toluene solution (under argon) over a period of at least a day at room temperature.

F. Bis(diphenylphosphino)methane (dppm). IVa reacts with dppm (1.5 equiv) in CH_2Cl_2 solution to yield $\text{Re}_2(\text{CO})_8(\text{dppm})$, isolated as a pale yellow, air-stable solid in 90% yield after a 3-day reaction period at room temperature. The ¹³C NMR (CDCl_3) of the product exhibits three resonances in the carbonyl region: 200.7 (s, 4 C), 193.9 (t, 2 C, $J = 28.0$ Hz), and 189.8 (s, 2 C) ppm. (Other spectroscopic data are contained in Table II). On the basis of the IR spectral pattern, similar to that of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$,¹⁵ and the ¹³C NMR spectrum it is concluded that the dppm ligand bridges the two rhenium atoms, with each P occupying an equatorial site:



³¹P–¹³C coupling in the ¹³C NMR is observed only for the carbonyls trans to phosphorus²⁰ (193.9 ppm); virtual coupling is probably responsible for the triplet structure of this resonance.

G. Olefins. I–V all react with excess olefin at room temperature to afford the alkenyl-exchanged (μ -hydrido)(μ -alkenyl)dirhenium octacarbonyl complex. For example, IIIa reacts with ethylene (1 atm, toluene solution) to yield I and 1-butene in near-quantitative yield within 1 day. Treatment of a solution of I with 1 atm of 1-butene generates IIIa; no IIIb or IIIc is observed (by ¹H NMR) even after very short reaction periods (~10 min at 25 °C). Similarly, dissolution of I in neat 1-hexene results in quantitative production of IVa within several hours.

Exchange occurs with *cis*-2-butene, although more slowly than for ethylene or terminal olefins. Reaction of IIa with *cis*-2-butene (1 atm, toluene) at room temperature results in 50% conversion to V after 2 days. No reaction is observed with *trans*-2-butene even after several days.

IIa reacts with C_2D_4 (1 atm) in toluene solution to yield (μ -D)(μ -CD=CD₂) $\text{Re}_2(\text{CO})_8$, I-d₄. Treatment of a heptane solution of IVa with excess vinyl *n*-butyl ether affords VI, (μ -H)(μ -*trans*-CH=CHO-*n*-Bu) $\text{Re}_2(\text{CO})_8$, isolated as an air-stable, colorless oil by TLC. Dissolution of I in neat styrene yields VII, (μ -H)(μ -*trans*-CH=CHPh) $\text{Re}_2(\text{CO})_8$, in essentially quantitative yield within 5–6 h, isolated as an air-stable, pale yellow oil. Spectroscopic data for VI and VII are given in Table I.

IIIa reacts with excess acrylonitrile in toluene solution to yield only $\text{Re}_2(\text{CO})_8(\text{NCCH}=\text{CH}_2)_2$, isolated as an air-stable yellow solid after complete reaction: IR ν_{CO} (toluene) 2070 (w), 2019 (m), 1970 (s), 1933 (sh), 1917 (m) cm^{-1} ; FDMS, M⁺ 702. The geometry is assigned as 1,2-equatorial,equatorial on the basis of the similarity of the IR spectrum to the patterns observed for

1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$ ¹⁵ and 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2$.¹³ The acrylonitrile ligands are probably N-coordinated as in the bis-acetonitrile complex.

Treatment of a heptane solution of I with 1 atm of 1,3-butadiene results in quantitative production in 30–40 h of $\text{Re}_2(\text{CO})_8(\text{butadiene})$, identified by IR spectroscopy.^{6a}

H. Hydrogen. I reacts with H₂ (1 atm, toluene solution) over 3 days to initially generate $\text{H}_2\text{Re}_2(\text{CO})_8$, identified by IR²¹ and ¹H NMR spectroscopy ($\delta -9.04$ in CDCl_3). In a slow subsequent reaction, $\text{H}_2\text{Re}_2(\text{CO})_8$ is converted to $\text{H}_3\text{Re}_3(\text{CO})_{12}$, identified by IR²² and ¹H NMR spectroscopy ($\delta -17.2$ in CDCl_3). After a reaction period of a few weeks, essentially complete conversion to $\text{H}_3\text{Re}_3(\text{CO})_{12}$ occurs, some of which precipitates out as a white crystalline material.

Reaction of IIIa with H₂ follows a similar course. GC analysis of the reaction solution head gas after 12 h (<10% reaction) indicated liberation of 1-butene and minor amounts of 2-butene and butane.

I. Other Substrates. Dissolution of I in neat CH_3CN results in complete conversion to 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2$ within 5 h at room temperature. The product was identified by IR spectroscopy: 2072 (w), 2017 (m), 1971 (s, br), 1906 (m) cm^{-1} in CH_2Cl_2 solution.¹³

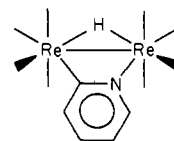
I–V all react with CO (1 atm) to generate $\text{Re}_2(\text{CO})_{10}$. The room-temperature reaction of IVa in toluene solution has a half-life of 3–4 days.

Dissolution of I in wet THF (2% H₂O by volume) eventually results in formation of $[\text{Re}(\text{CO})_3\text{OH}]_4$, identified by IR spectroscopy.^{11,12} This process is slow, and the IR spectrum is complex in the carbonyl region during the first 2 days of reaction. After 3 days, the predominant species in solution is $[\text{Re}(\text{CO})_3\text{OH}]_4$.

The major product of the reaction of I with H₂S (1 atm, toluene solution) is $\text{Re}_2(\text{CO})_8(\text{SH})_2$, identified by IR spectroscopy.²³ Complete reaction of I requires about 6 h. No hydridic species were detected in the ¹H NMR spectrum of the reaction product solution.

Discussion

Structure of the (Hydrido)(alkenyl)dirhenium Octacarbonyl Compounds. The spectroscopic data (Table I) for I–VII indicate a structure analogous to that of the (μ -hydrido)(μ -pyridyl)dirhenium octacarbonyl complex,^{3d} the structure



of which has been determined by X-ray crystallography.²⁴ The IR spectra in the carbonyl region of I–VII and the hydrido-pyridyl compound²⁵ are very similar, particularly above 2010 cm^{-1} . The complexity of the spectra (6–8 bands) indicates little or no structural symmetry; band frequencies are consistent with terminal carbonyl ligands. The bridging pyridyl or alkenyl ligand is responsible for the structural asymmetry, forming a σ bond to one Re and a dative bond (N lone pair or π -olefinic interaction) to the other. In the X-ray structure determination, the hydride ligand of the pyridyl-bridged complex was located in a bridging position opposite the pyridyl moiety. The hydride of the alkenyl complexes also bridges the two metals, as evidenced by high-field hydride NMR chemical shifts similar to the chemical shifts of the pyridyl compound ($\delta -14.52$, CD_2Cl_2) and bridging hydrides in rhenium carbonyl clusters.²⁶ The crystal structure determination of the

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(22) Huggins, D. K.; Fellmann, W.; Smith, J. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1964**, *86*, 4841.

(23) Küllmer, V.; Vahrenkamp, H. *Chem. Ber.* **1976**, *109*, 1560.

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

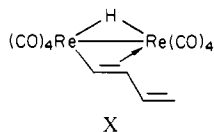
(25) IR spectral data for (μ -H)(μ -NC₅H₄) $\text{Re}_2(\text{CO})_8$: 2112 (vw), 2086 (w), 2015 (s), 2006 (m), 1994 (m), 1979 (w), 1960 (ms), 1958 (sh) cm^{-1} (hexane).

(20) The ¹³C NMR spectrum of 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ in the carbonyl region shows only a singlet at 200.3 ppm (CDCl_3). Thus, ³¹P–¹³C coupling is essentially absent in this complex, in which all carbonyls are *cis* to ³¹P. We also note that *trans* ³¹P–¹³C coupling is generally larger than *cis* ³¹P–¹³C coupling: Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

hydrido-pyridyl complex revealed a Re-Re single bond and a distorted octahedral geometry about each metal. These structural features are also very likely characteristic of I-VII.

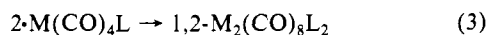
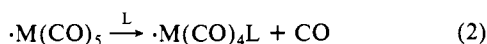
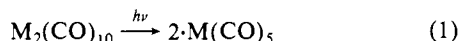
Unlike the hydrido-ethenyl complex (I), isomeric products are observed for species derived from 1-enes (II and III). These differ in the R group position relative to the Re-C σ bond. Isomers with R in a trans position are thermodynamically most stable. Only one isomer is observed of the product derived from *cis*-2-butene, V. Reactions with *trans*-2-butene do not yield hydrido-2-butenyl complexes; photochemical reaction with $\text{Re}_2(\text{CO})_{10}$ results in slow production of IIIa,b; thermal reaction (alkenyl ligand exchange) with I does not proceed. The lack of reactivity of *trans*-2-butene strongly suggests that V possesses a *cis*- as opposed to *trans*-2-butenyl ligand; the two possibilities are indistinguishable by NMR.

Analogues to the dirhenium hydrido-alkenyl compounds exist in osmium cluster chemistry; reactions of simple olefins with tri- and tetraosmium carbonyl compounds yield (μ -hydrido)(μ -alkenyl)triosmium²⁷ and -tetraosmium²⁸ products, respectively. Low-temperature photolysis of $\text{Re}_2(\text{CO})_{10}$ in the presence of 1,3-butadiene has been shown to yield (μ -H)(μ - η^2 -CH=CHCH=CH₂) $\text{Re}_2(\text{CO})_8$,^{6b} X. Recently, photochemical reactions

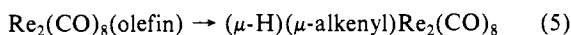
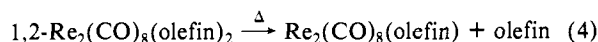


of $\text{Re}_2(\text{CO})_{10}$ with cyclic mono- and polyolefins have been found to yield complexes analogous to I-VII.²⁹

Mechanism of the Photochemical Reaction of $\text{Re}_2(\text{CO})_{10}$ with Olefins. UV photolysis of $\text{M}_2(\text{CO})_{10}$ (M = Mn or Re) in the presence of phosphine or phosphite ligands results in formation of disubstituted dinuclear compounds, 1,2- $\text{M}_2(\text{CO})_8\text{L}_2$.² The reaction is believed to occur via thermal substitution of photo-generated $\cdot\text{M}(\text{CO})_5$ radicals (eq 1-3). In the photochemical



reaction of $\text{Re}_2(\text{CO})_{10}$ with olefins, we propose the initial formation of a 1,2- $\text{Re}_2(\text{CO})_8(\eta^2\text{-olefin})_2$ intermediate via this mechanism. Thermal loss of one olefin from this species provides a site for oxidative addition of a vinylic C-H of the olefin coordinated to the adjacent Re (eq 4 and 5). This type of reaction sequence

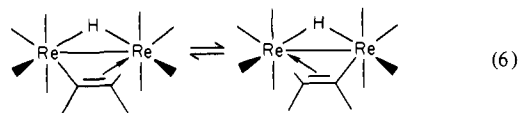


has been observed for 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$, which undergoes reaction in refluxing benzene to give (μ -H)(μ -NC₅H₄) $\text{Re}_2(\text{CO})_8$ and pyridine.³⁴ Reaction of 1,2- $\text{Re}_2(\text{CO})_8(\text{olefin})_2$ probably occurs readily at room temperature due to the greater lability of the olefin ligands (relative to pyridine).

The formation of hydrido-butenyl compounds (III) in the photochemical reaction of $\text{Re}_2(\text{CO})_{10}$ with ethylene and related olefin dimerization processes will be discussed in a forthcoming publication.

Fluxional Behavior of the μ -Alkenyl Ligand. Shapley and co-workers³⁰ have established that the alkenyl ligand of (μ -H)(μ -CH=CHR) $\text{Os}_3(\text{CO})_{10}$ undergoes a rapid, fluxional process at room temperature in which the σ and π bonds of the μ -alkenyl group are rapidly interchanged between the bridged osmium

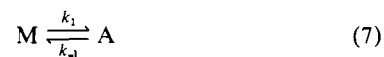
atoms. We find, on the basis of NMR studies, evidence for similar fluxional behavior in the (hydrido)(alkenyl)dirhenium complexes.



The observation of only four carbonyl signals (equal intensity) for I and IIIa in the ¹³C NMR at 20 °C is consistent with the proposed rapid fluxional mechanism. A similar ¹³C NMR is observed for (μ -H)(μ - η^2 -CH=CHCH=CH₂) $\text{Re}_2(\text{CO})_8$.^{6b} Our variable-temperature ¹H NMR results are also consistent with fluxional behavior. In a static structure, the allyl methylene protons of IIIa-c are diastereotopic; chemical shift equivalence would result if the fluxional σ -, π -interchange process is fast on the NMR time scale. The temperature dependence of the methylene resonances of IIIa and IIIc yielded ΔG^\ddagger values of 10.0 and 12.7 kcal/mol, respectively, for the fluxional process. These are quite similar to the values calculated via ¹³C NMR methods for (μ -H)(μ -CH=CH₂) $\text{Os}_3(\text{CO})_{10}$ ^{30a} (10.3 kcal/mol) and (μ -H)(μ -CPh=CHPh) $\text{Os}_3(\text{CO})_{10}$ ^{30b} (11.3 kcal/mol). The somewhat larger activation energy for IIIc (as compared to that for IIIa) is probably a consequence of greater steric interaction of the R (ethyl) group with carbonyl ligands.

Thermal Reactions of the Hydrido-Alkenyl Compounds. The (μ -hydrido)(μ -alkenyl)dirhenium octacarbonyl compounds react with a variety of substrates under mild thermal conditions. In most cases, elimination of olefin occurs with concomitant production of a substituted dirhenium octacarbonyl complex. The high yields observed make the general reaction attractive for the synthesis of a number of different dirhenium compounds. This reactivity contrasts with that of (μ -H)(μ -NC₅H₄) $\text{Re}_2(\text{CO})_8$, which does not eliminate pyridine upon treatment with nitrogen and phosphorus nucleophiles at temperatures up to 80 °C.²⁴

A. Pyridine. The results of the kinetics investigations of the reactions of I and IVa with pyridine (Figure 2) indicate a reaction mechanism of the form

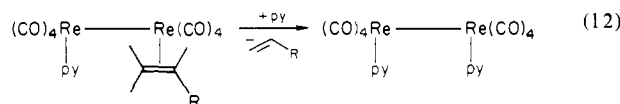
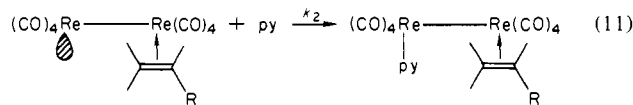
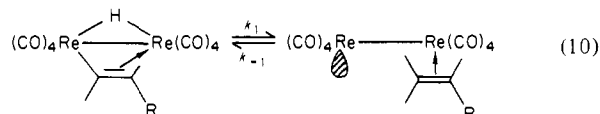


The rate expression for this scheme³¹ is of the form:

$$\frac{1}{k_{\text{obsd}}} = \frac{k_{-1}}{k_1 k_2} \left(\frac{1}{[\text{L}]} \right) + \frac{1}{k_1} \quad (9)$$

(L = pyridine). As determined from the results displayed in Figure 2, $k_1 = 1.3 \times 10^{-3} \text{ s}^{-1}$ and $k_{-1}/k_2 = 2.8 \times 10^{-2} \text{ M}$ for reaction of IVa with pyridine at 28.5 °C (toluene solution); $k_1 = 4.6 \times 10^{-4} \text{ s}^{-1}$ and $k_{-1}/k_2 = 1.7 \times 10^{-3} \text{ M}$ for reaction of I. Essentially the same intercept, corresponding to a nearly identical value for k_1 , was observed for I-d₄.

The following scheme is proposed to account for the observed kinetics:



(26) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.

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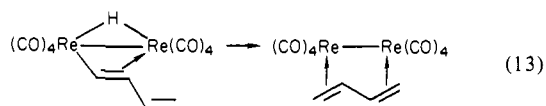
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The first step (eq 10) is an intramolecular C–H reductive elimination to produce an intermediate with a vacant site at one Re and coordinated olefin at the other. This species can undergo either intramolecular oxidative addition (k_{-1}) or reaction with pyridine. The end product, 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$, is obtained by rapid substitution of coordinated olefin by a second pyridine (eq 12). The slowest step in the scheme is k_1 ; the observed kinetics behavior results from the competition of two rapid reaction pathways (k_{-1} and $k_2[\text{py}]$) for the intermediate generated in eq 10.

Indirect evidence for the proposed initial step (eq 10) is provided by the observation that IIIb and IIIc isomerize thermally to IIIa. (Also, IIb isomerizes to IIa.) The most plausible mechanism for these isomerizations is C–H reductive elimination, giving an intermediate as in eq 10, followed by rotation of the coordinated olefin about the Re–olefin bond and oxidative addition of the vinylic C–H trans to R. Franzreb and Kreiter^{6b} report that the hydrido–butadienyl complex, $(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH=CHCH=CH}_2)\text{-Re}_2(\text{CO})_8$, is unstable at room temperature in solution and rearranges to $\text{Re}_2(\text{CO})_8(1,2\text{-}\eta^2,\eta^2\text{-butadiene})$:



This reaction provides further evidence for an initial reductive elimination step (k_1), in this case followed by intramolecular π coordination of butadiene. Interestingly, we find that the butadiene-coordinated end product of this reaction does not react with pyridine at room temperature over a period of 1 day.

Comparison of the results for I and I-*d*₄, $(\mu\text{-D})(\mu\text{-CD=CD}_2)\text{Re}_2(\text{CO})_8$, indicate a very small k_1 isotope effect: $k_1^{\text{H}}/k_1^{\text{D}} = 1.05 \pm 0.05$ (at 28.5 °C). Mechanistic conclusions are precluded by the scarcity of data in the literature concerning isotope effects in C–H reductive elimination reactions, particularly involving a bridging metal–hydrogen bond. However, our value is markedly smaller than that which Halpern et al. obtained for methane elimination from *cis*-PtH*(CH₃)(PPh₃)₂, $k_{\text{H}}/k_{\text{D}} = 3.3 \pm 0.3$.³²

Intramolecular reductive elimination is considerably faster for IVa than I ($k_1 = 1.3 \times 10^{-3}$ and 4.6×10^{-4} s⁻¹, respectively), perhaps due to steric effects of the alkenyl ligand. We also note that the (hydrido)(alkenyl)triosmium complex $(\mu_2\text{-H})(\mu_2\text{-CH=CH}_2)\text{Os}_3(\text{CO})_{10}$, does not react with pyridine at room temperature.³³ This indicates a much greater stability with respect to reductive elimination than in the dirhenium analogues.

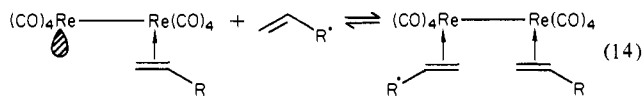
B. Phosphines and Phosphites. With the exception of the reaction of I with PMe_3 , the (hydrido)(alkenyl)dirhenium compounds react with all phosphorus nucleophiles studied to yield olefin and 1,2- $\text{Re}_2(\text{CO})_8\text{L}_2$, where L = phosphorus ligand. The geometry of the disubstituted dirhenium product is dependent upon the steric bulk of the phosphorus ligand. Relatively small phosphorus ligands such as PMe_3 , P(OMe)_3 , and P(OPh)_3 yield a stable 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8\text{L}_2$ species, the geometry preferred electronically (L trans to CO) in the absence of steric effects. With the larger ligands PPh₃ and $\text{P}(n\text{-Bu})_3$ the predominant initial product is 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8\text{L}_2$, which slowly isomerizes thermally in solution to 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8\text{L}_2$.

The 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8\text{L}_2$ species are the first examples of such a geometry among $\text{M}_2(\text{CO})_8\text{L}_2$ (M = Mn or Re) compounds. Our results that the isomerization of 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ to the 1,2-*axial,axial* species is completely unaffected by the presence of CO, ¹³CO, or CCl₄ indicate a nondissociative isomerization pathway.³⁴

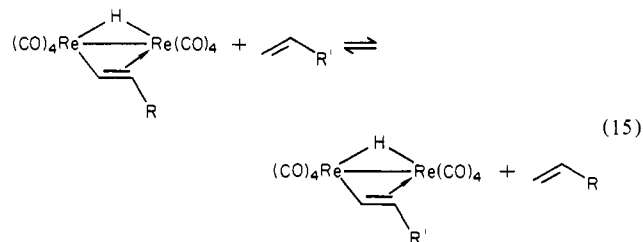
The reaction of IVa with bis(diphenylphosphino)methane to give the dppm-bridged complex, $\text{Re}_2(\text{CO})_8(\text{dppm})$, in 90% yield illustrates the synthetic utility of these compounds. Other ligand-bridged dirhenium complexes are accessible via this route.³⁵

Formation of the dipolar addition product (A) in the reaction of I with PMe_3 is similar to the reactivity of $(\mu\text{-H})(\mu\text{-CH=CH}_2)\text{Os}_3(\text{CO})_{10}$ toward PMe_2Ph .^{33,36} The osmium product, however, is an addition product analogous to structure B, resulting from phosphine attack at the vinyl β carbon. The difference may be due to the greater steric bulk of PMe_2Ph . (The triosmium complex does not react at 25 °C with PPh_3 .³³) Attack of P, N, and C nucleophiles upon μ -acetylide ligands, particularly in $\text{Fe}_2(\text{CO})_6(\mu\text{-C}\equiv\text{CR})(\mu\text{-PPh}_2)$, has been studied extensively by Carty and co-workers.³⁷ The dirhenium addition product undergoes slow PMe_3 dissociation in solution; slow formation of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$ plus other species occurs in the presence of excess phosphine. Formation of the addition product is severely constrained by steric factors in the alkenyl ligand (no addition product observed in the reaction of IIa with PMe_3) as well as in the phosphine (no addition product observed from the reaction of I with $\text{P}(n\text{-Bu})_3$, a more basic but larger nucleophile than PMe_3). Nucleophilicity of the phosphorus ligand is also important; the reaction of I with P(OMe)_3 , a smaller but weaker nucleophile than PMe_3 , yields only a $\text{Re}_2(\text{CO})_8\text{L}_2$ product with no detectable dipolar addition species.

C. Olefins. Reaction of IIa with $\text{CD}_2=\text{CD}_2$ to yield I-*d*₄ demonstrates that exchange of alkenyl ligand and hydride occurs in reactions with olefins. This is consistent with a mechanism which begins with intramolecular C–H reductive elimination (eq 10), as proposed for the reaction with pyridine. Coordination of a new olefin, eq 14, affords a bis-olefin intermediate, loss of either



olefin from which provides a site for intramolecular oxidative addition. The hydride- and alkenyl-exchanged (hydrido)(alkenyl)dirhenium product can thus be obtained in essentially quantitative yield by using a large excess of one olefin to shift the equilibrium, eq 15, far to one side.



In exchange reactions employing terminal olefins, only isomers with alkenyl group R trans to the Re–C σ bond are produced, even at short reaction times. This indicates a strong steric preference for oxidative addition of vinylic C–H trans to the alkyl group of the coordinated 1-ene. Steric hindrance in olefin coordination and/or oxidative addition is likely responsible for the sluggishness of exchange with *cis*-2-butene and the lack of reaction with *trans*-2-butene.

Exchange with vinyl *n*-butyl ether and styrene proceeds as with simple terminal olefins, yielding a *trans* hydrido–alkenyl product (VI and VII). Reaction with acrylonitrile, however, affords N-coordinated 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{NCCH=CH}_2)_2$. Treatment of I with 1,3-butadiene gives the butadiene-bridged complex, $\text{Re}_2(\text{CO})_8(1,2\text{-}\eta^2,\eta^2\text{-butadiene})$.

D. Hydrogen and Other Substrates. Reaction of I with H₂ is probably initiated by intramolecular reductive elimination (eq 10). Oxidative addition of H₂ at the vacant site is followed by dissociation of olefin, leading to H₂ $\text{Re}_2(\text{CO})_8$ formation.

The reactions of I with CH₃CN and CO likely proceed via the mechanism proposed for L = pyridine. As with pyridine and small phosphorus donor ligands, acetonitrile generates a 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8\text{L}_2$ product.

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Treatment of I with H_2O (wet THF) may lead to formation of an unstable $\text{Re}_2(\text{CO})_8(\text{OH})_2$ intermediate, as proposed in the photochemical reaction of $\text{Re}_2(\text{CO})_{10}$ with water,¹³ which decomposes to eventually yield $[\text{Re}(\text{CO})_3\text{OH}]_4$. The decomposition pathway has been suggested to involve a $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_8$ intermediate.¹³

Experimental Section

General. Dirhenium decacarbonyl was purchased from Pressure Chemical Co. and used without further purification. Hexane, heptane, benzene, and toluene were treated with concentrated H_2SO_4 , rinsed with aqueous NaHCO_3 , dried over MgSO_4 , and distilled from CaH_2 under argon. Pyridine was predried over KOH, distilled under argon, and stored over 3A molecular sieves (Linde). THF was refluxed over CuCl for several hours to remove peroxides and then distilled under argon. 1-Hexene was distilled from CaH_2 under argon. Reagent grade acetonitrile, methylene chloride, CCl_4 , and DMF were degassed prior to use. Acrylonitrile (99+%) styrene (99%), and *n*-butyl vinyl ether (98%) were obtained from Aldrich and degassed prior to use.

CP grade CO, ethylene, propylene, 1-butene, *trans*-2-butene, 1,3-butadiene, H_2 , and H_2S were obtained from Linde and used directly. *cis*-2-Butene (99%) was also obtained from Linde. ^{13}C (99% ^{13}C enriched) was obtained from Monsanto Research Corp., Mound Facility (Miamisburg, OH). C_2D_4 (99 atom % D) was purchased from KOR Isotope.

Triphenylphosphine, trimethylphosphine, tri-*n*-butylphosphine, trimethylphosphite, triphenylphosphite, and bis(diphenylphosphino)methane (dppm) were purchased from Strem Chemicals, Inc. PPh_3 was recrystallized twice from ethanol; dppm was used without further purification. Phosphite reagents were degassed prior to use. PMe_3 and $\text{P}(n\text{-Bu})_3$ were used as obtained and handled in an inert-atmosphere box.

Reagent grade solvents (hexane, toluene, CH_2Cl_2 , and ethyl acetate) 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 UV₂₅₄ fluorescent indicator) were obtained from Brinkmann Instruments, Inc.

Infrared spectra were obtained with a Beckman IR-4240 spectrophotometer. Electronic spectra were recorded on a Cary-219 spectrophotometer using matched 1.0-cm quartz cells. Field desorption mass spectra (FDMS) were obtained with a Varian MAT 731 spectrometer equipped with a field desorption source; electron impact spectra (EI) were recorded at 70 eV with a Varian MAT CH-5 instrument. All *m/e* values are reported relative to $\text{Re}_2 = 372$. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. ^1H NMR spectra were obtained with a Nicolet NT-360 instrument at 360.06 MHz. Spectra were recorded at ambient temperature except where indicated otherwise. ^{13}C NMR spectra were obtained with the same instrument at 90.55 MHz. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian XL-100 spectrometer at 40.50 MHz using broad-band proton decoupling. Chemical shifts are reported relative to H_3PO_4 , with positive defined as downfield of the H_3PO_4 resonance.

Gas chromatographic analysis for olefins was performed using a Varian Aerograph Series 2700 gas chromatograph equipped with a 12 ft \times $1/4$ 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: *n*-butane, 8.0; 1-butene, 10.0; *trans*-2-butene, 12.0; *cis*-2-butene, 13.0. With the column at 81 °C and injection port at 200 °C, the following C_6 retention times were observed: *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.

Photolyses of $\text{Re}_2(\text{CO})_{10}$ in the Presence of Olefin. Photochemical reactions employed a General Electric 275-W sunlamp as the irradiation source.³⁸ Reaction vessels (50-mL Pyrex Schlenk flasks equipped with septum inlets) were placed ~5 cm from the lamp. The Pyrex-filtered radiation consists primarily of 366-nm wavelength; significant emission is also observed at 313, 334, 406, and 436 nm.¹³ Solutions were maintained at room temperature (~25 °C) during photolysis by forced-air cooling of the reaction vessels.

A. Propylene. $\text{Re}_2(\text{CO})_{10}$ (0.30 g, 0.46 mmol) was dissolved in 10 mL of toluene under argon. The solution was then vacuum degassed and saturated with propylene (1 atm). Photolysis for a 15–20-h period resulted in near-complete (~90%) reaction of the $\text{Re}_2(\text{CO})_{10}$, as determined by IR spectroscopy. Reaction of the remaining $\text{Re}_2(\text{CO})_{10}$ was effected by vacuum degassing the reaction solution to remove evolved

CO, resaturating with 1 atm of propylene, and photolyzing an additional 2–3 h. Vacuum removal of solvent after photolysis left a yellow oily residue. IIa, a pale yellow oil, was isolated by column chromatography (4:1 hexane/ CH_2Cl_2) and subsequent sublimation 50 °C (0.1 mm) of the chromatographed product. Yield: 0.20–0.24 g (70–80%). Anal. Calcd for $\text{C}_{11}\text{H}_6\text{O}_8\text{Re}_2$: C, 20.69; H, 0.95. Found: C, 21.05; H, 0.98.

Reactions of smaller scale were performed in the identification and characterization (by ^1H NMR) of isomer IIb: $\text{Re}_2(\text{CO})_{10}$ (0.015 g, 0.023 mmol) was dissolved in 1–2 mL of toluene- d_6 under 1 atm of propylene, and the solution was photolyzed for 30–60 min. Immediately following cessation of photolysis the reaction solution was transferred via gas-tight syringe to an NMR tube immersed in a –78 °C $\text{CO}_2/2$ -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 –10 to –20 °C. Alternatively, a hexane solution (2 mL) of $\text{Re}_2(\text{CO})_{10}$ (0.015 g) under 1 atm of propylene was photolyzed 30–60 min; solvent was removed rapidly (within 2 min) under vacuum at room temperature after photolysis. The residue was dissolved in CD_2Cl_2 , and the resulting solution was immediately chilled to –78 °C as above. The ^1H NMR was obtained at low temperature as described above. Isomer IIb was not isolated.

B. 1-Butene. IIIa, a pale yellow oil, was prepared in similar yield (70–80%) from $\text{Re}_2(\text{CO})_{10}$ (0.30 g, 0.46 mmol) by the above-described procedure (for IIa) employing 1 atm of 1-butene instead of propylene. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{O}_8\text{Re}_2$: C, 22.09; H, 1.24. Found: C, 22.27; H, 1.25. Reactions of smaller scale, as previously described, were employed in the identification and characterization of IIIb, which was not isolated.

C. 1-Hexene. $\text{Re}_2(\text{CO})_{10}$ (0.30 g, 0.46 mmol) was dissolved in 10 mL of a toluene/1-hexene solution (3:1 by volume) under argon and photolyzed 15–20 h. The solution was then vacuum degassed and photolyzed an additional 2–3 h under an argon atmosphere. IVa, a pale yellow oil, was isolated in 70–80% yield by column chromatography (4:1 hexane/ CH_2Cl_2) and subsequent sublimation 65 °C (0.1 mm) of the chromatographed product. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_8\text{Re}_2$: C, 24.71; H, 1.78. Found: C, 24.73; H, 1.63.

D. Ethylene. $\text{Re}_2(\text{CO})_{10}$ (0.30 g, 0.46 mmol) was dissolved in 10 mL of toluene under argon. The solution was saturated with 1 atm of ethylene, photolyzed 15–20 h, degassed, resaturated with ethylene, and photolyzed an additional 2–3 h. The solution was then allowed to stand at room temperature for 1 day under an ethylene atmosphere, after which it was degassed, resaturated with ethylene, and allowed to stand for another 1-day period. I, a pale yellow crystalline solid, was isolated in 70–80% yield from the reaction solution by column chromatography (4:1 hexane/ CH_2Cl_2) and subsequent sublimation 70 °C (0.1 mm) of chromatographed product. Anal. Calcd for $\text{C}_{10}\text{H}_4\text{O}_8\text{Re}_2$: C, 19.23; H, 0.65. Found: C, 19.46; H, 0.77. Smaller scale reactions, previously described, were employed in the ^1H NMR identification and characterization of products IIIa–c, which were not isolated.

E. 2-Butene. $\text{Re}_2(\text{CO})_{10}$ (0.30 g, 0.46 mmol) was dissolved in 10 mL of toluene and saturated with 1 atm of *cis*- or *trans*-2-butene. The solution was photolyzed 15–20 h; products were identified by IR spectroscopy and ^1H NMR and were not isolated.

NMR Studies. A solution of I, IIIa, and IIIc for variable-temperature ^1H NMR studies was prepared by photolysis of a hexane solution (4 mL) of $\text{Re}_2(\text{CO})_{10}$ (0.020 g, 0.031 mmol) under 1 atm of ethylene for 90 min, vacuum removal of solvent (at ~25 °C), and dissolution of the residue in CD_2Cl_2 at room temperature. NMR studies were conducted immediately thereafter.

Thermal Reactions of the Hydrido-Alkenyl Compounds. All reactions of the (hydrido)(alkenyl)dirhenium compounds were performed by using purified solvents and Schlenk reaction vessels equipped with septum inlets. Except where indicated, reactions were performed at room temperature (~25 °C) and the initial concentration of the reactant dirhenium compound was $(0.5\text{--}1.0) \times 10^{-2}$ M. Reactions were generally conducted under an inert (argon) atmosphere, although in many cases (reactions with pyridine, PPh_3 , and olefins) the presence of air was observed to have little or no effect. Exclusion of room light had no effect upon any of the reactions studied.

A. Pyridine. Kinetics experiments involving the reactions of I, I-*d*₄, and IVa with pyridine were performed with an initial dirhenium reactant concentration of 6.4×10^{-4} M. Pyridine concentrations employed were at least a factor of 20 greater than this. Solution IR cells of 1.0-mm path length with NaCl windows were employed. The empty cells were mounted into the IR spectrometer within a temperature-controlled box³⁹ (maintained at 28.5 °C by a stream of dry thermostated air). After the reactants were mixed, solutions were injected into the thermostated IR cell. Pseudo-first-order rate plots were found to linear (correlation

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coefficient ≥ 0.998) for at least 3 half-lives for all reactions.

B. Triphenylphosphine. I (0.030 g, 0.048 mmol) and PPh_3 (0.10 g, 0.38 mmol) were dissolved in 2 mL of hexane. The solution was stirred at room temperature for 5 h, after which the precipitate product, $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$, was isolated by filtration and washed with hexane. Anal. Calcd for $\text{C}_{44}\text{H}_{30}\text{O}_8\text{P}_2\text{Re}_2$: C, 47.14; H, 2.70. Found: C, 47.53; H, 2.74. A DMF solution of some of the product was prepared rapidly and its UV-Vis spectrum was recorded immediately thereafter so as to minimize 1,2-axial, equatorial to 1,2-axial, axial isomerization. For ^{31}P NMR, 20–30 mg of the precipitate product was dissolved in 3 mL of CD_2Cl_2 in an NMR tube, and the solution was immediately chilled to -7°C in the NMR probe.

C. Trimethylphosphine. I (0.030 g, 0.048 mmol) was dissolved in 2 mL of hexane under argon. PMe_3 (0.1 g, 1.3 mmol) was added via syringe, and the solution was stirred for 5 min at room temperature. The precipitated product, $(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$, was collected by filtration and washed with hexane. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{O}_8\text{PRe}_2$: C, 22.29; H, 1.87; P, 4.42. Found: C, 22.22; H, 1.70; P, 4.49.

I (0.015 g, 0.024 mmol) was dissolved in 3 mL of toluene under argon. PMe_3 (0.03 g, 0.4 mmol) was added and the solution was stirred at room temperature for 15 h. Vacuum removal of solvent from the clear yellow reaction solution afforded a yellow oil. $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$ was isolated from this oil as a pale yellow solid by preparative TLC (2:1 hexane/ CH_2Cl_2).

IIa (0.030 g, 0.047 mmol) was dissolved in 2 mL of hexane; PMe_3 (0.1 g, 1.3 mmol) was added, and the reaction solution was monitored by IR spectroscopy.

D. P(*n*-Bu) $_3$. I (0.012 g, 0.019 mmol) was dissolved in 3 mL of hexane under argon. $\text{P}(n\text{-Bu})_3$ (0.1 g, 0.5 mmol) was added via syringe, and the solution was stirred at room temperature. The reaction was monitored by IR spectroscopy; $\text{Re}_2(\text{CO})_8[\text{P}(n\text{-Bu})_3]_2$ products were not isolated.

E. P(OMe) $_3$ and P(OPh) $_3$. I (0.012 g, 0.019 mmol) was dissolved in 3 mL of toluene under argon. $\text{P}(\text{OMe})_3$ (0.047 g, 0.38 mmol) or $\text{P}(\text{OPh})_3$ (0.12 g, 0.39 mmol) was added via syringe, and the solution was stirred at room temperature. Reactions were monitored by IR spectroscopy; products were not isolated.

F. Bis(diphenylphosphino)methane, dpmm. IVa (1.0 g, 1.5 mmol) and dpmm (0.88 g, 2.3 mmol) were dissolved in 100 mL of CH_2Cl_2 . The solution was stirred at room temperature for 3 days. Following vacuum removal of solvent, $\text{Re}_2(\text{CO})_8(\text{dpmm})$ was isolated as a pale yellow solid by column chromatography (7:7:2 toluene/hexane/ethyl acetate) and subsequent recrystallization of the chromatographed product from CH_2Cl_2 /hexane (slow evaporation). Yield: 1.3 g (90%). Anal. Calcd for $\text{C}_{33}\text{H}_{22}\text{O}_8\text{P}_2\text{Re}_2$: C, 40.41; H, 2.26. Found: C, 40.24; H, 2.07.

G. Olefins. IIa (0.23 g, 0.36 mmol) was dissolved in 10 mL of toluene. The solution was vacuum degassed, saturated with 1 atm of C_2D_4 , and stirred for 10 h at 40°C . The solution was then degassed (at 25°C), resaturated with C_2D_4 , and stirred at 40°C an additional 10 h. The degas/ C_2D_4 -treatment procedure was repeated, after which conversion of IIa to I- d_4 was complete (by IR spectroscopy, ^1H NMR). I- d_4 , a pale

yellow crystalline solid, was isolated by column chromatography (4:1 hexane/ CH_2Cl_2) and subsequent sublimation (70°C (0.1 mm)) of the chromatographed product. Yield: 0.14 g (62%). Anal. Calcd for $\text{C}_{10}\text{D}_4\text{O}_8\text{Re}_2$: C, 19.11; D, 1.27. Found: C, 19.19; D, 1.14. Mass spectrometric analysis (EI, 70 eV) indicates actual isotopic distribution to be 97% $\text{D}_4\text{C}_{10}\text{O}_8\text{Re}_2$ and 3% $\text{D}_3\text{HC}_{10}\text{O}_8\text{Re}_2$, consistent with the C_2D_4 isotopic enrichment (99% D atom).

IVa (0.010 g, 0.015 mmol) was dissolved in 3 mL of heptane. Vinyl *n*-butyl ether (0.15 g, 1.5 mmol) was added via syringe, and the solution was allowed to stand at room temperature for 50 h. ^1H NMR indicated near-complete conversion of IVa to VI at this point; VI was isolated as a colorless oil by preparative TLC (hexane) and subsequent removal of solvent under vacuum.

I (0.010 g, 0.016 mmol) was dissolved in 2 mL of styrene, and the solution was allowed to stand at room temperature for 6 h. IR and ^1H NMR spectroscopy indicated complete conversion of I to VII at this point. VII was isolated as a pale yellow oil by preparative TLC (10:1 hexane/ CH_2Cl_2) and subsequent removal of solvent under vacuum.

IIIa (0.030 g, 0.046 mmol) was dissolved in 8 mL of toluene. Acrylonitrile (0.32 g, 6.0 mmol) was added and the solution was stirred at room temperature. Complete reaction of IIIa was observed (by IR spectroscopy) after 3 h; $\text{Re}_2(\text{CO})_8(\text{NCCH}=\text{CH}_2)_2$ was isolated as a yellow solid by vacuum removal of solvent.

H. Hydrogen. I (0.015 g, 0.024 mmol) was dissolved in 3.5 mL of toluene. The solution was vacuum degassed, saturated with 1 atm of H_2 , and stirred at room temperature. Products were identified by IR and ^1H NMR spectroscopy. The reaction of IIIa (0.008 g, 0.012 mmol) with 1 atm of H_2 in toluene solution (1 mL) was performed similarly.

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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; IVa, 82621-40-7; V, 82621-41-8; VI, 88035-61-4; VII, 86244-50-0; $(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$, 88035-62-5; 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{PMe}_3)_2$, 88035-63-6; 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8[\text{P}(\text{OMe})_3]_2$, 88035-64-7; 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8[\text{P}(\text{OPh})_3]_2$, 88082-38-6; $\text{Re}_2(\text{CO})_8(\text{dpmm})$, 82292-83-9; 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$, 27770-64-5; 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{NCCH}=\text{CH}_2)_2$, 88035-66-9; 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{py})_2$, 88154-71-6; 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$, 88082-39-7; 1,2-*ax,eq*- $\text{Re}_2(\text{CO})_8[\text{P}(n\text{-Bu})_3]_2$, 88035-67-0; 1,2-*ax,ax*- $\text{Re}_2(\text{CO})_8[\text{P}(n\text{-Bu})_3]_2$, 88082-40-0; C_2D_2 , 683-73-8; $\text{Re}_2(\text{CO})_8(\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2)$, 77727-59-4; $\text{HzRe}_2(\text{CO})_8$, 38887-05-7; $\text{H}_3\text{Re}_3(\text{CO})_{12}$, 73463-62-4; 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2$, 88082-41-1; $[\text{Re}(\text{CO})_3\text{OH}]_4$, 56553-73-2; $\text{Re}_2(\text{CO})_8(\text{SH})_2$, 59390-74-8; dirhenium decacarbonyl, 14285-68-8; ethylene, 74-85-1; propylene, 115-07-1; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; 1,3-butadiene, 106-99-0; *cis*-2-butene, 590-18-1; 1-hexene, 592-41-6; pyridine, 110-86-1; tributylphosphine, 998-40-3.