Mechanism of (*μ*-H)(*μ*-alkenyl)Re₂(CO)₈ Formation in 350 nm Flash Irradiations of Re₂(CO)₁₀

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The mechanism of (*μ*-H)(*μ*-alkenyl)Re₂(CO)₈ formation upon UV irradiations of Re₂(CO)₁₀ in presence of olefin (styrene, *trans*-stilbene, 4-methyl-1-cyclohexane, and ethylene) was investigated by laser flash photolyses. Such photoproducts result from reactions of the olefin with *eq*-Re(CO)₉. No reactions of Re(CO)₅ leading to hydride alkenyl products were observed. Dependences of the reaction rate on olefin concentration and solvent revealed an additional intermediate formed after the addition of the olefin to *eq*-Re(CO)₉ and before the appearance of the *μ*-hydrido−*μ*-alkenyl products.

Introduction

The photochemistry of metal−metal bonded carbonyl complexes $M_2(CO)_{10}$, M = Re or Mn, has received considerable attention.[1−4] Two primary photoprocesses, the homolytic dissociation in pentacarbonyl radicals, eq 1, and the photoelimi-

$$M_2(CO)_{10} + h\nu \rightarrow 2M(CO)_5 \quad (1)$$

nation of CO, eq 2, have been reported for these complexes.

$$M_2(CO)_{10} + h\nu \rightarrow M_2(CO)_9 + CO \quad (2)$$
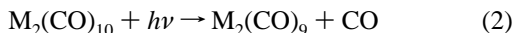
When appropriate scavengers of these coordinately unsaturated products are not available, they regenerate the decacarbonyl complex via termination reactions, eqs 3, 4.

$$2M(CO)_5 \xrightarrow{k_R} M_2(CO)_{10} \quad (3)$$

$$M_2(CO)_9 + CO \rightarrow M_2(CO)_{10} \quad (4)$$
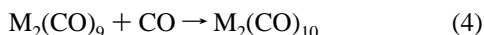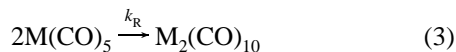
Two isomers of the nanocarbonyl photoproduct, *eq*-Re₂(CO)₉ and *ax*-Re₂(CO)₉, were characterized by using matrix isolation and liquid-noble-gas techniques.[5] Moreover, 366 nm photolyses of Re₂(CO)₁₀ in solutions of olefin yield hydridoalkenyldirhenium octacarbonyl complexes, (*μ*-H)(*μ*-alkenyl)Re₂(CO)₈, as major photoproducts.[6,7] Carbonyls with semibridging CO have been generated under various conditions;[8] the equivalent Re complex, (b) b-Re₂(CO)₉, has not been observed, however, in the photochemistry of Re₂(CO)₁₀.

The roles of the primary products, eqs 1 and 2, in the (*μ*-H)(*μ*-alkenyl)Re₂(CO)₈ formation have not been unquestionably established. A mechanism in the literature assigned the forma-
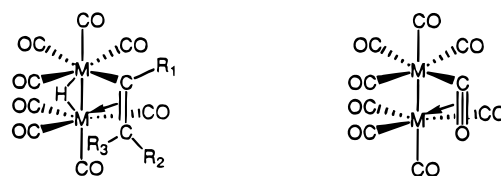
(a) (*μ*−hybrido)(*μ*-alkenyl)M₂(CO)₈　　(b) b−M₂(CO)₉

tion of the hydride alkenyl products to a reaction of the pentacarbonyl radical with the olefin.[7] Since a later study has demonstrated that tributyltin hydride reacts with Mn₂(CO)₉ and not with Mn(CO)₅,[3] doubts were fostered with regard to the participation of Re(CO)₅ in the formation of hydride alkenyl products. In this paper, such concerns were addressed by using flash photochemical techniques for the investigation of the intermediates and the kinetics of their reactions.

Experimental Section

Photochemical Procedures. The flash photolysis apparatuses with 10 ns and with 30 μs time responses were described elsewhere.[9] Laser pulses of 351 nm and 355 nm, for measurements in the nanosecond−microsecond time domain, were respectively generated with an excimer laser (Lambda Physik) and with a Nd-YAG laser (Quanta Ray). In conventional flash photolysis, two FP-100C (Xenon Corp.) flash lamps were used as sources of 30 μs polychromatic light pulses. The spectral region, i.e., $\lambda_{exc} \geq 320$ nm, for the irradiation of the photolyte was selected with appropriate cutoff filters. Solutions from which Re₂(CO)₁₀ was absent were used as blanks to verify that transients related to the irradiation of other solutes and from biphotonic processes were not generated in flash photochemical experiments. Laser powers were kept sufficiently low to prevent secondary photolyses of Re₂(CO)₉ and Re(CO)₅.

Solutions for flash photolysis studies were prepared in a glovebox and bubbled for 40 min with Ar (high purity grade). Liquids were handled in a gastight cell. The samples were stirred after each irradiation an refreshed after 10 consecutive experiments.

Materials. Re₂(CO)₁₀ was obtained 99.99% pure from Jansen Chemicals. This material and samples purified by sublimation under vacuum exhibited the same chemical behavior. Hexane (Fisher, Certified ACS) was purified by a literature procedure.[4] Solvents, i.e., cyclohexane and acetonitrile, were dried over molecular sieves and/or Na₂SO₄. Other compounds were commercially available and were used without further purification.

Results

Characteristic absorption bands of the nanocarbonyl, Re₂(CO)₉, and pentacarbonyl, Re(CO)₅, complexes, Figure 1, were ob-

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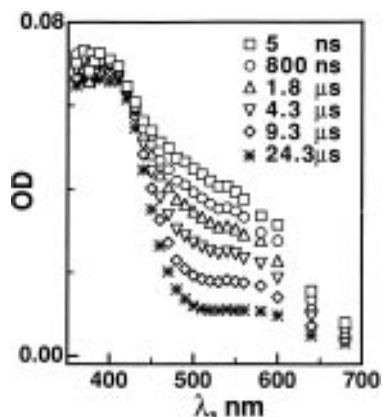(8) Zhang, S.; Brown, T. L. *Inorg. Chem.* **1995,** *34,* 1164.

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Figure 1. Spectral changes following 350 nm laser irradiations of 4 × 10^{-3} M Re$_2$(CO)$_{10}$ in Ar-deaerated cyclohexane. Spectral changes for $t \leq 20$ μs (key in the insert) due to Re(CO)$_5$ recombination. Absorptions recorded at $t \approx 20$ μs are mostly related to the Re$_2$(CO)$_{10}$ spectrum.
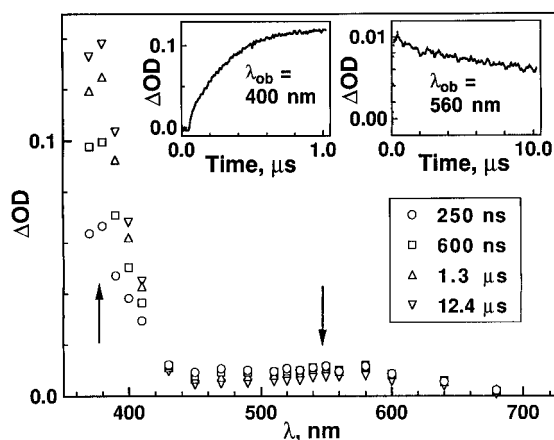

Figure 2. Time-resolved spectra for the formation of (μ-hydride)(μ-styrenyl)Re(CO)$_8$ in 350 nm laser irradiations of 4.0 × 10^{-3} M Re$_2$(CO)$_{10}$, 1.0 × 10^{-2} M styrene in Ar-deaerated cyclohexane. The inserts show oscillographic traces for the hydride alkenyl product formation (λ_{ob} 400 nm) and Re(CO)$_5$ recombination (λ_{ob} 560 nm).

served after the 30 ns laser flash irradiation of Re$_2$(CO)$_{10}$ (4 × 10^{-3} M) and olefin (concentrations between 10^{-2} and 10^{-4} M) in cyclohexane. Time-resolved spectra showed Re$_2$(CO)$_9$ to be stable for periods longer than a ms in the absence of olefin and less than 10^{-5} M flash photochemically generated CO. In the presence of styrene or *trans*-stilbene, however, a growth of the optical density below 425 nm, Figure 2, revealed the formation of new products. When these olefins were replaced by 4-methyl-1-cyclohexene, the corresponding reaction products absorb at shorter wavelengths and the growth of the optical density was followed at 370 or 380 nm. No absorptions above 360 nm were observed for the ethylene product; the reaction had to be followed by the disappearance of Re$_2$(CO)$_9$ at 400 nm.

The spectrum of the terminal products, determined by conventional flash photolysis, persisted without changes, i.e. the products were stable, for almost 0.5 s. Formation of these products was averted when cyclohexane was replaced by acetonitrile, a scavenger of Re$_2$(CO)$_9$.

(1) Reactions of Re(CO)$_5$. No changes on the rate of Re(CO)$_5$ decay (480 nm $\leq \lambda_{obs} \leq$ 600 nm) were detected in the presence of olefin under the conditions of the experiments described above, Figure 3. This result rules out any reaction between Re(CO)$_5$ species and olefin. Recombination of the radicals, eq 3, accounts for the second-order dependence of the rate on the Re(CO)$_5$ concentration. The measured rate constant,
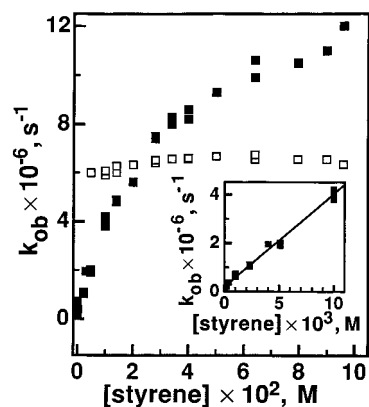

Figure 3. Typical dependence of the overall rate constant, $k_{ob} = 0.693/t_{1/2}$, for the formation of (μ-hydride)(μ-alkenyl)Re$_2$(CO)$_8$ (■) and Re(CO)$_5$ recombination (□) on olefin concentration. Data were recorded for the formation of (μ-hydride)(μ-styrenyl)Re$_2$(CO)$_8$ in 350 nm laser irradiations of 4.0 × 10^{-3} M Re$_2$(CO)$_{10}$ and various concentrations of styrene in Ar-deaerated cyclohexane. The insert shows the linear segment of the plot for [styrene] $\leq$ 10^{-2} M.

Table 1. Second-Order Rate Constants for Reactions of Re(CO)$_5$ with Various Reactants

reactant	k, (M^{-1} s^{-1})	solvent
Re(CO)$_5$	5.4 × 10^9 [a]	ethanol
	3.6 × 10^9 [b]	cyclohexane
CCl$_4$	3.9 × 10^7 [a]	ethanol
	5.5 × 10^7 [c]	cyclohexane
Cl$_3$CCCl$_3$	1.0 × 10^8	cyclohexane

[a] Reference 2. [b] Reference 1. [c] This work and ref 1.

$k_R = (4.5 \pm 0.5) \times 10^9$ M^{-1} s^{-1}, agreed with a literature value for the disappearance of the radical in the absence of olefin.[2] That Re(CO)$_5$ does not participate in the formation of (μ-H)-(μ-alkenyl)Re$_2$(CO)$_8$ was further investigated by trapping the radical with hexachloroethane, Cl$_3$CCCl$_3$. Flash irradiations of Re$_2$(CO)$_{10}$ in the presence of 10^{-1} M Cl$_3$CCCl$_3$ and 10^{-2} M styrene showed Re(CO)$_5$ disappearing according to eq 5, with

$$Re(CO)_5 + Cl_3CCCl_3 \rightarrow Re(CO)_5Cl + Cl_3C(C^\bullet)Cl_2 \quad (5)$$
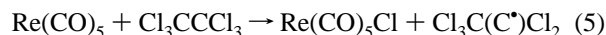
a rate that exhibited a first-order dependence in Cl$_3$CCCl$_3$ concentration, Table 1. Similar observations were made with 1 × 10^{-2} to 5 × 10^{-3} M CCl$_4$ instead of Cl$_3$CCCl$_3$, Table 1. Although the radical was almost completely trapped by 10^{-1} M Cl$_3$CCCl$_3$, the same (μ-H)(μ-alkenyl)Re$_2$(CO)$_8$ concentrations (per flash) were generated with and without halocarbon.

(2) Concentration Dependence of the Reaction Rate. The mechanism of hydride alkenyl product formation was flash photochemically investigated as a function of olefin concentration. In a range of styrene or *trans*-stilbene concentration between 10^{-4} and 10^{-2} M, the (μ-H)(μ-alkenyl)Re$_2$(CO)$_8$ formation, followed at 380 or 400 nm, appeared to be kinetically of a pseudo-first-order dependence on Re$_2$(CO)$_9$ concentration. Indeed, the overall rate constant, k_{ob}, exhibited a linear dependence in olefin concentration, eq 6, for [olefin] $\leq$ 10^{-2}

$$k_{ob} = k_I + k_{II}[\text{olefin}] \quad (6)$$

M, Figure 3. Second-order rate constants, k_{II}, were calculated from the slope of the line, Table 2. The inset to Figure 3 shows that the intercept, namely k_I in eq 6, is not negligible. The value of k_I remained the same after cyclohexane solvent was purified to eliminate the potential presence of olefin and water contaminants in various concentrations. A large reproducibility of the intercept value, when measured with samples handled in a
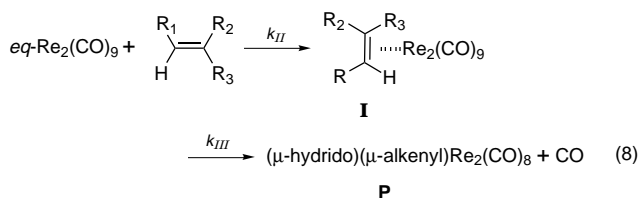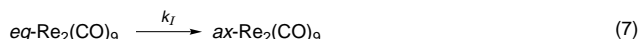
Table 2. Rate Constants for Reactions of $Re_2(CO)_9{}^a$

olefin	k_I, s^{-1}	k_{II}, M^{-1} s^{-1}	k_{III}, s^{-1}	solvent
styrene	2.0×10^5	3.9×10^8	2.0×10^7	cyclohexane
	1.6×10^6	8.6×10^8	2.4×10^7	*n*-hexane
	b	3.6×10^5	b	toluene
trans-stilbene	1.7×10^5	4.1×10^8	1.6×10^6	cyclohexane
4-methyl-1-cyclohexane	1.8×10^5	5.0×10^8	b	cyclohexane
ethylene	1.8×10^5	1.6×10^8	b	cyclohexane
	b	4.6×10^5	b	toluene

^{a} Errors in the rate constants equal to or less than 10%. ^{b} Unreliable estimates due to limited experimental conditions.

different manner, signals that it is not a consequence of randomly introduced impurities, e.g., H_2O. It is indeed a feature of the reaction mechanism. It must also be noted that $Re(CO)_5$ is a stable product on the time scale of these experimental observations, i.e., the intercept cannot be associated with the decay of such a species.

Equation 6 can be interpreted in terms of two parallel reactions: a transformation of *eq*-$Re_2(CO)_9$ into another intermediate, i.e., *ax*-$Re_2(CO)_9$ with rate constant k_I, eq 7, and the olefin trapping of *eq*-$Re_2(CO)_9$ with rate constant k_{II}, eq 8. It

$$eq\text{-}Re_2(CO)_9 \xrightarrow{\;k_I\;} ax\text{-}Re_2(CO)_9 \quad (7)$$

$$eq\text{-}Re_2(CO)_9 + \underset{H}{\overset{R_1}{\diagup}}=\underset{R_3}{\overset{R_2}{\diagdown}} \xrightarrow{\;k_{II}\;} \underset{\substack{| \\ R-\overset{H}{\underset{}{C}}}}{\overset{R_2 \diagdown \diagup R_3}{\underset{\cdots\cdots Re_2(CO)_9}{}}}$$

I

$$\xrightarrow{\;k_{III}\;} (\mu\text{-hydrido})(\mu\text{-alkenyl})Re_2(CO)_8 + CO \quad (8)$$

P

must be noted that reversibility in eqs 7 and 8 could not be observed under the conditions of the flash photochemical experiments and back-reactions were consequently ignored in the kinetic analysis.

The kinetics of the parallel reactions, eq 7,8, was also investigated by means of the efficiency of hydride alkenyl product formation, eq 9. The superscript, lim, denotes values

$$\xi = \frac{[\mathbf{P}]_{t\to\infty}}{[\mathbf{P}]_{t\to\infty}^{lim}} = \frac{\Delta OD_{t\to\infty}}{\Delta OD_{t\to\infty}^{lim}} = \frac{k_{II}[\text{olefin}]}{k_I + k_{II}[\text{olefin}]} \quad (9)$$

of the optical density change, ΔOD, or the hydride alkenyl concentration, [P], measured at such olefin concentrations, i.e., above 10^{-1} M, that all photogenerated *eq*-$Re_2(CO)_9$ was trapped by the olefin. Flash photogenerated concentrations of hydride alkenyl were investigated by means of the ΔOD values, λ_{ob} 380 nm, several μs after the laser irradiation, Figure 4. In such an interval, ΔOD reach a constant value independent of time, a condition that is indicated by the subscript $t \to \infty$ in ΔOD and [P], eq 9. Values of k_I and k_{II} from eq 6 provide a good fitting of eq 9 to the experimental data, i.e., the solid line in Figure 4.

When concentrations of the olefin, styrene, or *trans*-stilbene, were above 10^{-2} M, departures from the functional behavior of eq 6 were appreciable, Figure 3. Plots of k_{ob} vs olefin concentration approach to a limit where the rate of hydride alkenyl formation becomes independent of olefin concentration. The departures from eq 6 were attributed to one additional reaction, i.e. one more reaction intermediate (**I**) in eq 8, after the trapping of $Re_2(CO)_9$. The conversion of this intermediate to the hydride alkenyl product with a rate constant k_{III}, eq 8, makes k_{ob} independent of the olefin concentration at the limit of high concentrations.
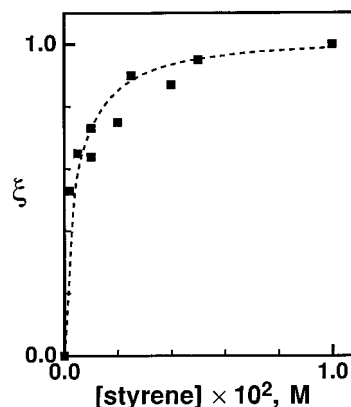

Figure 4. Dependence of the efficiency of $(\mu\text{-hydride})(\mu\text{-styrenyl})$-$Re_2(CO)_8$ formation on styrene concentration. The curve is the fitting of eq 9 to the experimental data with rate constants in Table 2. Other conditions are as in Figure 3.

It is possible to describe the functional dependence of k_{ob} on olefin concentration by solving eqs 10 and 11, for the rates of $Re_2(CO)_9$ and the intermediate **I** in eq 8.[10] A combination of

$$\frac{d[eq\text{-}Re_2(CO)_9]}{dt} =$$
$$-k_I[eq\text{-}Re_2(CO)_9] - k_{II}[eq\text{-}Re_2(CO)_9][\text{olefin}] \quad (10)$$

$$\frac{d[\mathbf{I}]}{dt} = -k_{III}[\mathbf{I}] + k_{II}[Re_2(CO)_9][\text{olefin}] \quad (11)$$

the integrated laws for the reactants and product, **P**, leads to eq 17,[10] where $t_{1/2} = 0.693k_{ob}^{-1}$. The rate constant k_{III}, Table 2,

$$\frac{k_I + k_{II}[\text{olefin}] - k_{III}}{2} + k_{III}e^{(-k_I+k_{II}[\text{olefin}])t_{1/2}} =$$
$$(k_I + k_{II}[\text{olefin}])e^{-k_{III}t_{1/2}} \quad (17)$$

was calculated by solving eq 17 after replacing in it estimates of k_I, k_{II} (above) and experimental values of $t_{1/2}$ and [olefin], olefin = styrene, *trans*-stilbene. A further mathematical treatment of the integrated rate laws gives an expression for the oscillographic traces containing the unknown ϵ_I/ϵ_P, i.e., the ratio of the **I** and **P** extinction coefficients, eq 22. A value $\epsilon_I/\epsilon_P \approx$ 0.6 was determined by fitting eq 21 to oscillographic traces recorded at 400 nm with [styrene] = 1.0 M. Similarities between the spectra of the intermediate **I** and the hydride styrenyl product from 350 and 700 nm, i.e., the observation window, impeded the recording of the spectrum of **I** in the flash photolysis experiment.

Rate constants k_I, k_{II}, and k_{III} were determined in various hydrocarbon solvents, Table 2, by the procedure described above. While k_I and k_{II} are dependent on the nature of the solvent, k_{III} only depends on the olefin.

$$\frac{\Delta OD_t}{\Delta OD_{t\to\infty}} = \frac{\Delta OD_{t=0}}{\Delta OD_{t\to\infty}}(e^{-(k_I+k_{II}[\text{olefin}])t}) +$$
$$\frac{k_I + k_{II}[\text{olefin}]}{k_I + k_{II}[\text{olefin}] - k_{III}}(e^{-k_{III}t} - e^{-(k_I+k_{II}[\text{olefin}])t}) +$$
$$\frac{k_{III}(k_I + k_{II}[\text{olefin}])}{k_I + k_{II}[\text{olefin}] - k_{III}}\left(\frac{(1 - e^{-k_{III}t})}{k_{III}} - \frac{1 - e^{-(k_I+k_{II}[\text{olefin}])t}}{k_I + k_{II}[\text{olefin}]}\right) \quad (22)$$

Discussion

The results show that $(\mu\text{-}H)(\mu\text{-alkenyl})Re_2(CO)_8$ complexes are solely produced by reaction of olefin with $Re_2(CO)_9$. That

(10) Supporting Information.

Re(CO)$_5$ plays no role in the formation of such hydride alkenyl products is demonstrated by the following experimental observations. Reactions between olefin and Re(CO)$_5$ must be too slow to compete with the dimerization of Re(CO)$_5$, eq 3, and the rate of pentacarbonyl does not change with olefin concentration, Table 1. In addition, a complete scavenging of Re(CO)$_5$ by Cl$_3$CCCl$_3$ did not change the yield of (μ-H)(μ-alkenyl)-Re$_2$(CO)$_8$. The reactive Re$_2$(CO)$_8$ species, a proposed precursor of hydride alkenyl products, was not produced, therefore, in a recombination of Re(CO)$_5$ radicals. It must be inferred that photogenerated nanocarbonyl, eq 2, is the only precursor of the hydride alkenyl products. This proposition is also in accordance with results from selectively trapping the nanocarbonyl (but not the pentacarbonyl) with appropriate scavengers, e.g., CH$_3$CN. Indeed, it has been shown that coordinating solvents, e.g., S = CH$_3$CN or 2-MeTHF, react with Mn$_2$(CO)$_9$ to give Mn$_2$-(CO)$_9$S.[11] Formation of the Re analog, Re$_2$(CO)$_9$CH$_3$CN, where CH$_3$CN intercepts Re$_2$(CO)$_9$, prevents the formation of the hydride alkenyl product.

Formation of the hydride alkenyl products from reactions of olefin with nanocarbonyl is a multistepped mechanism reflected in the rate of product formation. In the limit of low olefin concentration, Figure 3, the reaction kinetics approaches that of a competition between two parallel processes. While these reactions are kinetically of a first order in Re$_2$(CO)$_9$ concentration, only one of them exhibits an additional first-order dependence on the concentration of olefin. The intercept in Figure 3 and the value of k_I can be considered as evidence for an unimolecular conversion of the primary nanocarbonyl product, eq 2, to a reactive isomer, *eq*-Re$_2$(CO)$_9$, in competition with an interception of Re$_2$(CO)$_9$ by styrene, eqs 7 and 8.

The proposition of a nanocarbonyl complex with CO coordinated to both metal centers, (**b**) b-Re$_2$(CO)$_9$, was previously advanced for the photochemistry of Mn$_2$(CO)$_{10}$.[12,13] While species with semibridging CO have been characterized in photolyses of MnRe(CO)$_{10}$,[8] the experimental evidence rules out the formation of **b** as a relevant photoproduct of Re$_2$(CO)$_{10}$.[5] In this regard, the nanocarbonyl species *eq*-Re$_2$(CO)$_9$ and *ax*-Re(CO)$_9$ are most likely the solvent-stabilized species detected in low temperature experiments. Competition between such a linkage isomerization and trapping of the primary nanocarbonyl, *eq*-Re$_2$(CO)$_9$, accounts for the dependence of the efficiency, ξ, of (μ-H)(μ-alkenyl)Re$_2$(CO)$_8$ formation on olefin concentration. An expression for ξ in terms of the rate constants k_I and k_{II}, eq 9, agreed with the kinetics represented in eq 6. It must be noted, however, that a mechanism based only on the competition between eqs 7 and 8 does not predict the tendency of the of the overall rate constant, k_{ob}, to reach a limiting value at large olefin concentrations, Figure 3. The interpretation of the functional dependence of k_{ob} on olefin concentration requires the insertion of an additional intermediate after the scavenging of Re$_2$(CO)$_9$ by olefin, eq 7, and before the formation of the hydride alkenyl product, eq 8. It is possible that such an intermediate undergoes an intramolecular reorganization, i.e., coordination of olefin to both Re centers and displacement of CO, for the formation of the hydride alkenyl product. This reorganization will explain the dependence of k_{III} on the olefin. Some attachment of the primary nanocarbonyl to the solvent accounts for the dependence of k_I and k_{II} on the solvent, an observation in agreement with literature reports.[14,15] The magnitude of the rate constants variation with saturated hydrocarbon solvents, Table 2, can be expected for hydrogen bonding and/or van de Waals interactions between the metallocarbonyl and a solvent molecule. A weak π-bond between toluene and *eq*-Re$_2$(CO)$_9$ may be further diminishing the values of k_I and k_{II}.

Supporting Information Available: Text giving eqs 12−16 and 18−21 in the mathematical treatment leading to eqs 17 and 22 (3 pages). Ordering information is given on any current masthead page.

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