Preparation and Reactivity of (μ-Hydrido)(μ-phenylacetylido)dirhenium Octacarbonyl, (μ-H)(μ-C≡CPh)$Re_2(CO)_8$[1]

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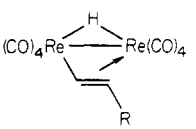
(μ-Hydrido)(μ-phenylacetylido)dirhenium octacarbonyl, I, is prepared by the room-temperature reaction of phenylacetylene with (μ-hydrido)(μ-propenyl)dirhenium octacarbonyl. I undergoes remarkably facile CO substitution by pyridine, triphenylphosphine, or triisobutylphosphine. Kinetics results for the reaction with pyridine are consistent with a CO dissociative mechanism; the first-order rate constant at 26 °C is 4.9×10^{-4} s^{-1}. Structures for the mono- and disubstituted derivatives of I are proposed on the basis of IR data. The bridging acetylide ligand of I and its derivatives undergoes a rapid fluxional process at 20 °C in which the σ and π bonds are interchanged between the bridged rhenium atoms. Treatment of I with trimethylphosphine rapidly generates a dipolar addition product via nucleophilic attack of PMe_3 at the μ-acetylide ligand. This reactivity is not observed with the larger phosphines, PPh_3 and $P(i\text{-}Bu)_3$.

Introduction

We recently reported the synthesis of (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl complexes via the photochemical reaction of $Re_2(CO)_{10}$ with simple olefins.[2] The μ-hydrido μ-alkenyl compounds react with a variety of substrates under mild thermal conditions, including pyridine, P donors, olefins, and H_2.[3] With nucleophiles such as pyridine and PPh_3, elimination of olefin occurs with concomitant production of 1,2-$Re_2(CO)_8L_2$ in quantitative yield. We now describe the preparation of (μ-hydrido)(μ-phenylacetylido)dirhenium octacarbonyl, (μ-H)(μ-C≡CPh)$Re_2(CO)_8$, I, via the reaction of the μ-hydrido μ-alkenyl compounds with phenylacetylene. We also report studies of the thermal reactivity of I with simple nucleophiles, principally pyridine and phosphines.

Results

Preparation of (μ-H)(μ-C≡CPh)$Re_2(CO)_8$, I. Treatment of (μ-H)(μ-*trans*-CH=CHCH$_3$)$Re_2(CO)_8$, IIa, with excess phenylacetylene at room temperature affords I in 85% yield (by ^1H NMR) within 5–10 h. Spectroscopic



IIa, R = CH_3

data for the product are given in Table I. I is stable in solution in the presence of air but tends to decompose on silica chromatographic supports. Similarly, reaction of IIa with (*p*-methoxyphenyl)acetylene yields (μ-H)(μ-*p*-C≡CC$_6$H$_4$OCH$_3$)$Re_2(CO)_8$.

^{13}C NMR Spectrum of I. Without ^1H decoupling, the ^{13}C NMR spectrum of I (C_6D_6, 20 °C) exhibits three resonances in the carbonyl region: 181.6 (s), 182.1 (s), and 184.6 ppm (d, J = 3.5 Hz) of relative intensity 2:1:1. The doublet at 184.6 ppm collapses to a singlet when broadband ^1H decoupling (centered at δ −14) is employed.

Reaction of I with Pyridine. Treatment of a CH_2Cl_2 or hexane solution of I with excess pyridine affords a single isomer of (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(py), III, in near quantitative yield within 1–2 h at room temperature. Spectroscopic data for III are contained in Table I. No other isomers of this complex were detected (by ^1H NMR) during the course of the reaction. This monosubstituted compound reacts slowly with excess pyridine to yield a single isomer of a disubstituted species, (μ-H)(μ-C≡CPh)$Re_2(CO)_6(py)_2$, IV (see Table I). A trace of this product is detected after 1–2 h in the reaction of I with pyridine, but a 10-day period (CH_2Cl_2 solution) is required for essentially complete (~95%) conversion. Both III and IV are air-stable in solution.

The rate of the reaction of I with pyridine was studied under condition of excess pyridine. Reactions were carried out at 26 °C using toluene solvent. The rate of product formation was determined by monitoring the decrease in IR absorbance at 2119 cm^{-1} due to I. Log plots of I concentration vs. time were found to be linear ($R > 0.998$) for 3 half-lives. The observed pseudo-first-order rate constant, k_{obsd}, is 4.9×10^{-4} s^{-1} for initial pyridine concentrations of 0.107 and 0.537 M, indicating the reaction to be zeroeth order in pyridine.

(μ-H)(μ-*p*-C≡C-C$_6$H$_4$OCH$_3$)$Re_2(CO)_8$ also undergoes CO substitution by pyridine, yielding (μ-H)(μ-*p*-C≡CC$_6$H$_4$OCH$_3$)$Re_2(CO)_7$(py): IR ν_{CO} (toluene) 2101 (w), 2030 (s), 2005 (s), 1987 (s), 1960 (s), 1934 (m, sh), 1923 (ms) cm^{-1}. The rate of this reaction was studied as discussed above for I (26 °C, toluene). The pseudo-first-order rate constant is 4.9×10^{-4} s^{-1} and is independent of initial pyridine concentration in the range 0.107–0.537 M.

Reactions of I with Phosphines. Treatment of a CH_2Cl_2 or hexane solution of I with excess triphenylphosphine results in essentially quantitative production of the disubstituted complex (μ-H)(μ-C≡CPh)$Re_2(CO)_6(PPh_3)_2$, V, in 2 h. IR, ^1H NMR, and mass spectral data for V are contained in Table I; the $^{13}C\{^1H\}$ NMR in C_6D_6 solution exhibits resonances in the carbonyl region at 194.1 (s), 189.3 (s), and 187.3 ppm (d, $J_{^{31}P-^{13}C}$ = 70 Hz) of relative intensity 1:1:1. V slowly decomposes in solution but is stable in solid form.

^1H NMR monitoring of the reaction (in CD_2Cl_2) revealed an intermediate hydride resonance at δ −12.02 (d, $J_{^{31}P-(\mu\text{-}H)}$ = 8.5 Hz), assigned to a monosubstituted complex, (μ-H)(μ-C≡CPh)$Re_2(CO)_7(PPh_3)$. This species is the major initial product of the reaction but undergoes rapid substitution to give the disubstituted end product. In the IR spectrum, product bands at 2106, 2035, and 1971 cm^{-1} (hexane) are observed during early stages of the reaction. By comparison with the IR spectrum of (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(py) (Table I), these are ascribed to the monosubstituted PPh_3 species.

(1) This research was sponsored by the National Science Foundation through research Grant NSF CHE 81-19525.
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(3) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* in press.

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Table I. Spectroscopic Data for I and Substitution Products III-V

compd	^{1}H NMR,[a] δ	ν_{CO},[b] cm^{-1}	FDMS
I	−13.01 (s, 1 H, μ-H), 7.57 (m, 2 H, Ph_α), 7.44 (m, 3 H, Ph_β + Ph_γ)	2119 (vw), 2094 (w), 2023 (s), 2002 (m), 1982 (ms)	M^+ 698
III	−10.42 (s, 1 H, μ-H), 8.49 (d, 2 H, py_α), 7.75 (m, 3 H, py_γ + Ph_α), 7.50 (t, 2 H, Ph_β), 7.42 (t, 1 H, Ph_γ), 7.27 (t, 2 H, py_β), $J_{\alpha\beta,\beta\gamma}$(py, Ph) = 5-7 Hz[c]	2103 (w), 2031 (s), 2005 (s), 1988 (s), 1961 (s), 1935 (m, sh), 1924 (ms)	M^+ 749
IV	−7.40 (s, 1 H, μ-H), 8.61 (dd, 4 H, py_α), 7.71 (m, 4 H, $2py_\gamma$ + $2Ph_\alpha$), 7.48 (t, 2 H, Ph_β), 7.40 (t, 1 H, Ph_γ), 7.22 (m, 4 H, py_β); $J_{\alpha\beta,\beta\gamma}$(py) = 6-7, $J_{\alpha\gamma}$(py) ≃ 1, $J_{\alpha\beta,\beta\gamma}$(Ph) = 7-8 Hz	2033 (w), 2011 (vs), ~1928 (sh), 1919 (vs)	M^+ 800
V	−11.28 (t, 1 H, μ-H), 7.1-7.6 (m, $2PPh_3$ + C≡CPh), $J^{31}_{P-(\mu-H)}$ = 7.9 Hz	2033 (w), 2018 (vs), 1938 (m, sh), 1926 (vs)	$[M - CO]^+$ 1138

[a] CD_2Cl_2 solution. [b] Heptane solution for I; toluene solution for III-V. [c] Assignments aided by decoupling experiments.

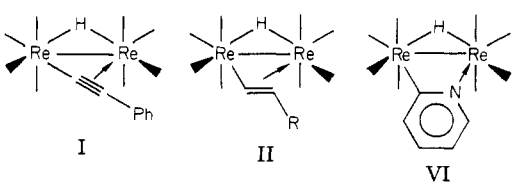
Reaction of I with excess triisobutylphosphine (hexane solution), as monitored by IR, proceeds as with PPh_3. The disubstituted product (μ-H)(μ-C≡CPh)$Re_2(CO)_6$[P(*i*-Bu)$_3$]$_2$ is soluble in hexane and exhibits absorptions in the IR at 2032 (w), 2012 (s), ~1935 (sh), and 1927 (vs) cm^{-1}. Complete reaction requires 3–4 h.

Treatment of a hexane solution of I with excess trimethylphosphine results in immediate formation of an air-stable, white precipitate. Complete conversion of I to this product occurs within 1 min. C, H, and P analysis and FDMS (M^+ 776) of the precipitate are consistent with formulation as (μ-H)(μ-C≡CPh)$Re_2(CO)_8(PMe_3)$, i.e., formal addition of PMe_3 to I. The product is stable in benzene or toluene solution at 25 °C in the presence of excess PMe_3 over a period of at least 1–2 h, but slowly decomposes to I in the absence of PMe_3. The IR spectrum of the compound in toluene solution exhibits bands in the carbonyl region at 2091 (vw), 2067 (w), 1993 (s), 1986 (sh), 1974 (m), 1940 (mw), and 1920 (w) cm^{-1}. This pattern is similar to the IR spectrum of I, but shifted to lower frequencies. ^{1}H NMR (CD_2Cl_2, 0 °C) is also consistent with (μ-H)(μ-C≡CPh)$Re_2(CO)_8(PMe_3)$: δ −15.39 (d, 1 H, μ-H), 1.35 (d, 9 H, Me of PMe_3), 7.25 (t, 2 H, Ph_β), 7.03 (t, 1 H, Ph_γ), 6.79 (d, 2 H, Ph_α), $J_{\alpha\beta,\beta\gamma}$(Ph) = 7.5 Hz, $J^{31}_{P-H(Me)}$ = 12.0 Hz, $J^{31}_{P-(\mu-H)}$ = 4.6 Hz. A weak hydride resonance was observed at δ −12.3 (d, J = 1 Hz) of 5–10% intensity relative to the δ −15.39 resonance.

Other Substrates. I does not react with ethylene (1 atm, hexane solution) over a period of 1 day at 25 °C, nor after 8 h at 50 °C. Little or no reaction is observed (by IR) when I is treated with excess phenylacetylene (50 equiv, hexane solution) for 15 h at 50 °C.

Discussion

Structure of (μ-H)(μ-C≡CPh)$Re_2(CO)_8$, I. The structure of I is analogous to the μ-hydrido μ-alkenyl compounds II and the μ-hydrido μ-pyridyl octacarbonyl complex VI[4] as judged by the similarity of the IR spectra in the carbonyl region (particularly above 2010 cm^{-1}).[5,6]

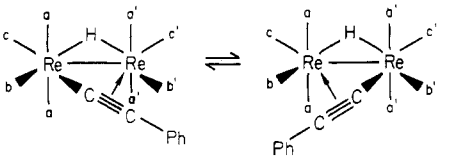


I II VI

The bridging character of the hydride is indicated by its high-field NMR chemical shift. The σ,π-bridging mode of coordination of the acetylide ligand has precedent in numerous polynuclear transition-metal complexes.[7] A triosmium analogue of I, (μ-H)(μ-C≡CPh)$Os_3(CO)_{10}$, was obtained by Deeming et al. in 10% yield from the reaction of $H_2Os_3(CO)_{10}$ with phenylacetylene.[8]

The formation of I in the reaction of II with phenylacetylene is a consequence of facile elimination of olefin from II, which occurs upon treatment with numerous other substrates as well.[2,3] This allows coordination of phenylacetylene at one Re center and subsequent intramolecular oxidative addition of acetylenic C–H at the other Re to yield I. An analogous reaction sequence is proposed for the reactions of olefins with II.[2,3]

Fluxional Behavior of the Bridging Acetylide Ligand. The ^{13}C NMR spectrum of I is consistent with a rapid fluxional process (eq 1) at 20 °C in which the σ and π bonds of the μ-acetylide ligand are rapidly interchanged between the bridged rhenium atoms. On the ^{13}C NMR



(1)

time scale, the fluxional molecule possesses an effective plane of symmetry perpendicular to the Re–Re bond. Thus, carbonyls a and a′ are equivalent (singlet at 181.6 ppm), as are b and b′ (184.6 ppm) and c and c′ (182.1 ppm). The b carbonyls, which are approximately trans to the bridging hydride, are assigned to the 184.6 ppm resonance due to the observation of ^{13}C–(μ-^{1}H) coupling (3.5 Hz).

Analogous fluxional behavior has been well established for the alkenyl ligand of several (μ-H)(μ-CH=CHR)$Os_3(CO)_{10}$ complexes[9] and, more recently, for (μ-H)(μ-alke-

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(5) IIa, R = CH_3: IR (hexane) ν_{CO} 2114 (vw), 2083 (w), 2017 (s), 1994 (m), 1979 (ms), 1975 (sh), 1967 (m) cm^{-1}.

(6) VI: IR (hexane) ν_{CO} 2112 (vw), 2086 (w), 2015 (s), 2006 (m), 1994 (m), 1979 (w), 1960 (ms), 1958 (sh) cm^{-1}.

(7) (a) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *21*, 957. (b) Abu Salah, O. M.; Bruce, M. I.; Churchill, M. R.; Bezman, S. A. *J. Chem. Soc., Chem. Commun.* **1972**, 858. (c) Bruce, M. I.; Clark, R.; Howard, J.; Woodward, P. *J. Organomet. Chem.* **1972**, *42*, C107. (d) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

(8) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

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

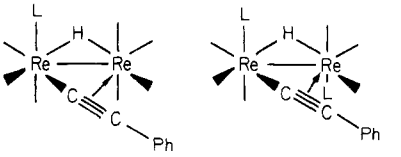
nyl)$Re_2(CO)_8$, II.[3] The triosmium analogue of I, $(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)Os_3(CO)_{10}$,[8] apparently has not been investigated with respect to fluxional character.

Reactivity of I. I undergoes remarkably facile thermal CO substitution by pyridine or PPh_3. This reactivity contrasts with that observed for both II and VI; II (R = H, Me, Et, *n*-Bu, Ph) undergoes elimination of olefin to yield 1,2-$Re_2(CO)_8L_2$, L = py or PPh_3,[2,3] while VI is inert at room temperature. (Slow CO substitution of VI occurs at 80 °C.[4a]) $Re_2(CO)_{10}$ is also essentially inert toward substitution at room temperature; the first-order rate constant for substitution by PPh_3 at 30 °C is estimated to be less than 10^{-13} s^{-1}.[10]

The kinetics results for the reaction of I with pyridine are consistent with a CO dissociative mechanism; the first-order rate constant is 4.9×10^{-4} s^{-1} at 26 °C. This exceptional CO lability, as compared with $Re_2(CO)_{10}$, II, and VI, is not readily understandable in terms of ground-state electronic effects. It is possible that lability results from stabilization of the transition state of the dissociative process. Brown and co-workers[10,11] have determined that ligands which are good electron donors, particularly π donors such as Cl^-, Br^-, and NCO^-, labilize the cis carbonyls of octahedral complexes through stabilization of the coordinatively unsaturated transition-state species. The lability of I may be due to an analogous effect of the acetylide ligand, which possesses two pairs of p_π electrons. One pair is involved in coordination; the other is available for π donation in the unsaturated transition state. (The hydrido alkenyl complex, II, possesses only one pair, which is involved in coordination to the second metal atom.) No previous studies of the labilizing ability of acetylide ligands (bridging or terminal) have been performed, presumably due to the scarcity of metal carbonyl acetylide complexes. Carty and co-workers[7d,12] found that facile CO substitution (in addition to nucleophilic attack at the acetylide ligand, vide infra) occurs in reactions of isocyanides with $M_2(CO)_6(\mu\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$, M = Fe and Ru. Interestingly, we find that substitution of a methoxy group in the para position of the phenyl ring of I has no detectable effect upon the rate of reaction with pyridine, i.e., CO lability.

Although II eliminates olefin at room temperature in the presence of pyridine, PPh_3, or excess olefin,[2,3] elimination of phenylacetylene from I does not occur. This indicates that the μ-acetylide ligand is more strongly coordinated to the $(\mu\text{-}H)Re_2(CO)_8$ unit than the μ-alkenyl ligand, perhaps due to stronger M→acetylide π-back-bonding in I. Evidence for this is seen in the IR spectra (heptane solution); the three highest frequency carbonyl bands of I (2119, 2094, 2023 cm^{-1}) are significantly higher in energy than the corresponding bands of II, R = Ph (2113, 2083, 2017 cm^{-1}). Steric effects may also be important, as steric interactions of carbonyl ligands with the μ-alkenyl ligand are likely greater than with the μ-acetylide moiety.

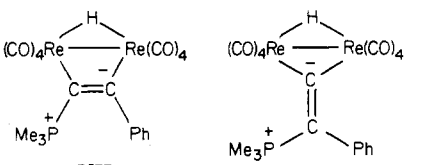
The IR spectra in the carbonyl region of the mono- and disubstituted derivatives of I are very similar to those of the corresponding substituted derivatives of VI, i.e., $(\mu\text{-}H)(\mu\text{-}NC_5H_4)Re_2(CO)_7L$ and $(\mu\text{-}H)(\mu\text{-}NC_5H_4)Re_2(CO)_6L_2$, L = py or PPh_3.[4a] The structures of the substitution products of VI were deduced by a combination of IR and X-ray crystallographic methods. On the basis of the IR similarity, we propose analogous structures, A and B, for



A B

the mono- and disubstituted (L = py, PPh_3) derivatives, respectively, of I. In both A and B, L is trans to a carbonyl and cis to the μ-acetylide ligand. One L is coordinated to each rhenium in the disubstituted complex B. The ^{13}C NMR spectrum of V, $(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)Re_2(CO)_6(PPh_3)_2$ (B, L = PPh_3), indicates rapid fluxional motion of the μ-acetylide ligand at room temperature, as proposed for I (eq 1); only three carbonyl resonances are observed, all of equal intensity, with the 187.3 ppm resonance assignable to the two carbonyls (equivalent on the NMR time scale) trans to PPh_3 due to the observation of strong ^{13}C–^{31}P coupling (70 Hz).[13] The μ-acetylide ligand of IV, $(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)Re_2(CO)_6(py)_2$ (B, L = py), is also fluxional, as indicated by the equivalence of the pyridines in the ^1H NMR spectrum at room temperature. It is likely that fluxional motion of the μ-acetylide ligand is also characteristic of the monosubstituted species A. Interestingly, we observe that disubstitution (A → B) is much faster for L = PPh_3 than for L = pyridine (<2 h vs. ~10 days at 25 °C).

Treatment of I with PMe_3 does not result in CO substitution. Instead, rapid nucleophilic attack occurs at the μ-acetylide ligand to generate a dipolar addition product, VII or VIII. VII is the result of α-attack at the acetylide



VII VIII

ligand, while VIII is the product of β-attack. We cannot exclude either possibility from the spectroscopic data at hand, but ^1H NMR indicates only one major product. Both structures are consistent with the observed IR spectrum (similar to I but shifted to lower frequencies) and molecular weight. Nucleophilic attack at bridging acetylide ligands in di- and polynuclear metal carbonyl complexes has extensive precedent in work done by Carty and co-workers involving P, N, and C nucleophiles.[7d,14] Treatment of $(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)Os_3(CO)_{10}$ with PMe_2Ph is also known to yield a dipolar addition product analogous to VII or VIII.[15]

The difference in the reactivity of PMe_3 and PPh_3 toward I is likely the result of steric effects. Treatment of I with P(*i*-Bu)$_3$, a more basic but larger nucleophile than PMe_3, results in CO substitution; no dipolar addition product is detected. Nucleophilic attack at the acetylide ligand is precluded (or the resulting dipolar addition product is unstable) due to the steric requirements of P(*i*-Bu)$_3$. For the same reasons, a dipolar addition product is not observed in reactions with PPh_3, which has a similar cone angle (145°) to P(*i*-Bu)$_3$ (143°).[16]

(10) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.
(11) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.
(12) Carty, A. J.; Mott, G. N.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *212*, C54.
(13) The ^{13}C NMR spectrum of 1,2-*ax*,*ax*-$Re_2(CO)_8(PPh_3)_2$ in the carbonyl region shows only a singlet at 200.3 ppm ($CDCl_3$). Thus, ^{31}P–^{13}CO coupling is essentially absent in this complex, in which all carbonyls are cis to ^{31}P. We also note that trans ^{31}P–^{13}CO coupling is generally larger than cis ^{31}P–^{13}CO coupling: Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.
(14) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163–93.
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Experimental Section

General Data. Dirhenium decacarbonyl was purchased from Pressure Chemical Co. and used without further purification. Hexane, pentane, toluene, and methylene chloride were distilled prior to use. Phenylacetylene was purchased from Aldrich and degassed before use; (*p*-methoxyphenyl)acetylene was distilled under reduced pressure. Pyridine was predried over KOH, distilled under argon, and stored over 3A molecular sieves (Linde). Triphenylphosphine was recrystallized twice from ethanol; trimethylphosphine and triisobutylphosphine were used as obtained (Strem Chemicals, Inc.) and handled in an inert-atmosphere box. CP grade ethylene and propylene were obtained from Linde and used directly.

Infrared spectra were obtained by using a Beckman IR-4240 spectrophotometer. Field desorption mass spectra (FDMS) were obtained with a Varian MAT 731 spectrometer equipped with a field desorption source; m/e values are reported relative to Re_2, m/e 372. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. ^1H NMR spectra were obtained by using a Nicolet NT-360 instrument at 360.06 MHz. Spectra were recorded at ambient temperature except where indicated. ^{13}C NMR spectra were obtained by using the same instrument at 90.55 MHz; broad-band ^1H decoupling (±5 ppm of center frequency) was employed where indicated.

Preparation of (μ-H)(μ-*trans*-CH=CHCH$_3$)Re$_2$(CO)$_8$, IIa. $Re_2(CO)_{10}$ (0.40 g, 0.61 mmol) was dissolved in 10 mL of toluene under argon in a 50-mL Pyrex Schlenk flask. The solution was saturated with propylene (1 atm) and then photolyzed[17] for 20 h at room temperature. IR analysis after photolysis indicated near complete (~90%) conversion of $Re_2(CO)_{10}$ to (μ-H)(μ-CH=CHCH$_3$)Re$_2$(CO)$_8$. Reaction of the remaining $Re_2(CO)_{10}$ was effected by vacuum degassing the reaction solution to remove evolved CO, resaturating with 1 atm of propylene, and photolyzing 2–3 more hours. Vacuum removal of solvent after photolysis left a yellow, oily residue. IIa, a pale yellow oil, was isolated in pure form by column chromatography (4:1 hexane/CH_2Cl_2; silica gel, 70–230 mesh, EM Reagents) and subsequent sublimation (50 °C, 0.1 mm) of the chromatographed product: yield 0.3 g (75–80%); IR (hexane) ν_{CO} see ref 5. Anal. Calcd for $C_{11}H_6O_8Re_2$: C, 20.69; H, 0.95. Found: C, 21.05; H, 0.98.

Preparation of I. IIa (0.30 g, 0.47 mmol) was dissolved in 20 mL of hexane under argon. After addition of phenylacetylene (0.50 mL, 4.5 mmol), the solution was stirred at room temperature for 10 h. Subsequent vacuum removal of solvent left a yellow-brown oil. The oil was subjected to dynamic vacuum (0.1 mm) for 1 day to remove excess phenylacetylene. Dissolution of the oil in hexane, filtration to remove insoluble material, and slow evaporation of solvent (via water aspirator) from the filtrate afforded orange-brown crystals of I (0.23 g, 70%). Anal. Calcd for $C_{16}H_6O_8Re_2$: C, 27.51; H, 0.86. Found: C, 27.70; H, 0.70.

Preparation of (μ-H)(μ-*p*-C≡CC$_6$H$_4$OCH$_3$)Re$_2$(CO)$_8$. IIa (0.22 g, 0.34 mmol) was dissolved in 4 mL of CH_2Cl_2 under argon. After addition of (*p*-methoxyphenyl)acetylene (0.1 mL, 0.7 mmol), the solution was stirred at room temperature for 20 h. Vacuum removal of solvent left a brown oil that was subjected to dynamic vacuum for 1–2 days to remove excess (*p*-methoxyphenyl)-acetylene. Dissolution of the oil in pentane, filtration, and slow evaporation of solvent from the filtrate afforded (μ-H)(μ-*p*-C≡CC$_6$H$_4$OCH$_3$)Re$_2$(CO)$_8$ as orange-brown crystals: IR (hexane) ν_{CO} 2119 (vw), 2093 (w), 2021 (s), 2001 (m), 1979 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ −13.00 (s, 1 H, μ-H), 7.51 (d, 2 H, Ph$_{\alpha or \beta}$), 6.96 (d, 2 H, Ph$_{\beta or \alpha}$), 3.86 (s, 3 H, OCH$_3$), $J_{\alpha\beta}$(Ph) = 8.6 Hz. Anal. Calcd for $C_{17}H_8O_9Re_2$: C, 28.02; H, 1.11. Found: C, 28.70; H, 1.05.

Reactions of I. Except where indicated, reactions were performed at room temperature (25 °C) under inert atmosphere (argon) using a (0.5–1.0) × 10^{-2} M initial concentration of I. Exclusion of room light had no effect upon any of the reactions studied.

(A) Pyridine. I (0.015 g, 0.021 mmol) was dissolved in 3.0 mL of hexane or CH_2Cl_2 under argon. Pyridine (0.087 mL, 1.1 mmol) was added via syringe, and the solution was magnetically stirred at room temperature for 1.5 h. Vacuum removal of solvent and excess pyridine afforded a yellow oil. Dissolution of the oil in 4:1 hexane/CH_2Cl_2 and subsequent evaporation of solvent yielded III, (μ-H)(μ-C≡CPh)Re$_2$(CO)$_7$(py), as a yellow solid. Recrystallization (slow evaporation, hexane/CH_2Cl_2) afforded pale yellow crystals of III. Anal. Calcd for $C_{20}H_{11}NO_7Re_2$: C, 32.04; H, 1.48; N, 1.87. Found: C, 32.28; H, 1.48; N, 2.07.

IV, (μ-H)(μ-C≡CPh)Re$_2$(CO)$_6$(py)$_2$, was obtained in crystalline form by allowing a hexane solution of I (0.015 g) and pyridine (0.087 mL) to stand undisturbed at room temperature for several days. After about 1 day, IV begins to precipitate out of solution in the form of thin, whitish needles. After a 5-day reaction period, the crystalline precipitate was collected by filtration and washed with hexane. Recrystallization from hexane/CH_2Cl_2 (slow evaporation) afforded pale yellow needles of IV. Anal. Calcd for $C_{24}H_{16}N_2O_6Re_2$: C, 36.00; H, 2.01; N, 3.50. Found: C, 36.05; H, 2.07; N, 3.36.

Kinetics experiments involving reactions of I and (μ-H)(μ-*p*-C≡CC$_6$H$_4$OCH$_3$)Re$_2$(CO)$_8$ with pyridine were performed using an initial dirhenium reactant concentration of 5.37 × 10^{-3} M. 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 box[18] (maintained at 26 °C by a stream of dry thermostated air). After the reactants were mixed, solutions were injected into the thermostated IR cell.

(B) Triphenylphosphine. I (0.015 g, 0.021 mmol) and PPh$_3$ (0.11 g, 0.42 mmol) were loaded into a Schlenk reaction vessel and dissolved in 3.0 mL of hexane or CH_2Cl_2 under argon. With hexane as solvent, V, (μ-H)(μ-C≡CPh)Re$_2$(CO)$_6$(PPh$_3$)$_2$, was obtained in crystalline form by allowing the solution to stand undisturbed at room temperature for 2 h. Pale yellow crystals of V precipitate from solution during this period, which were isolated by filtration and washed with hexane. Anal. Calcd for $C_{50}H_{36}O_6P_2Re_2$: C, 51.45; H, 3.11; P, 5.31. Found: C, 51.83; H, 3.04; P, 5.37.

(C) Triisobutylphosphine. I (0.005 g, 0.007 mmol) was dissolved in 1.5 mL of hexane under argon. P(*i*-Bu)$_3$ (0.03 g, 0.15 mmol) was added via syringe, and the solution was stirred at room temperature. Samples were periodically withdrawn via gas-tight syringe for IR analysis. Products were not isolated.

(D) Trimethylphosphine. I (0.03 g, 0.04 mmol) was dissolved in 3 mL of hexane under argon, and PMe$_3$ (0.05 g, 0.7 mmol) was added via syringe to the stirred solution. (μ-H)(μ-C≡CPh)-Re$_2$(CO)$_8$(PMe$_3$) immediately precipitated from the solution in the form of a whitish crystalline solid; after a 5-min reaction period, the precipitate was isolated by filtration and washed with hexane. Anal. Calcd for $C_{19}H_{15}O_8PRe_2$: C, 29.46; H, 1.95; P, 4.00. Found: C, 29.62; H, 1.92; P, 4.32.

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Registry No. I, 82621-44-1; IIa, 82638-69-5; III, 87567-01-9; IV, 87556-63-6; V, 87556-64-7; (μ-H)(μ-*p*-C≡CC$_6$H$_4$OCH$_3$)Re$_2$(CO)$_8$, 87556-65-8; Re$_2$(CO)$_{10}$, 14285-68-8; py, 110-86-1; PPh$_3$, 603-35-0; P(*i*-Bu)$_3$, 4125-25-1; PMe$_3$, 594-09-2; Re, 7440-15-5; propylene, 115-07-1; phenylacetylene, 536-74-3; (*p*-methoxyphenyl)acetylene, 768-60-5.

(16) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(17) The irradiation source was a General Electric 275-W sunlamp,[2-4] placed ~5 cm from the reaction vessel. The solution was maintained at room temperature (25 °C) during photolysis by forced-air cooling of the reaction vessel.

(18) Absi-Halabi, M.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2982.