

Bridging Phosphorus Ligand Substituted Dirhenium Octacarbonyl Compounds. Preparation and Reactions with Water and Methanol¹

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The bridging ligand substituted dirhenium octacarbonyl compounds, 1,2-*eq,eq*-Re₂(CO)₈(L-L), L-L = bis(dimethylphosphino)methane (dmpm), bis(diphenylphosphino)methane (dppm), bis(dimethylphosphino)ethane (dmpe), and bis(diphenylphosphino)ethane (dppe), have been synthesized in high yield from L-L and (μ-H)(μ-CH=CHC₄H₉)Re₂(CO)₈. Re₂(CO)₈(dppe) and Re₂(CO)₈(dmpe) undergo rapid intramolecular exchange involving a twist about the Re-Re axis. The relative photochemical reaction rates of Re₂(CO)₈(L-L) with water or methanol are in the order dppe > dmpe > dppm > dmpm. The major products are (μ-H)(μ-OR)Re₂(CO)₈(L-L) and (μ-OR)₂Re₂(CO)₈(L-L) (R = H or CH₃). However, these products could be isolated from the reaction mixtures only for the dmpm and dppm compounds. The structure of (μ-H)(μ-OH)Re₂(CO)₈(dppm) was determined by conventional crystallographic techniques by using Mo Kα X-rays. The crystals belong to the triclinic space group *P* $\bar{1}$ with *a* = 10.904 (2) Å, *b* = 11.099 (2) Å, *c* = 14.646 (2) Å, α = 84.69 (1)°, β = 83.18 (1)°, γ = 60.69 (1)°, and *Z* = 2. *R*_F = 0.031 for 5547 reflections having 2θ < 70° and *I* > 6σ(*I*). The molecular structure consists of two Re(CO)₃ units bridged by hydrido, hydroxo, and dppm ligands. The Re-Re distance is 3.030 (1) Å, the Re-H distances of the H-bridge are 1.84 (8) and 2.00 (8) Å, and the Re-O distances are 2.177 (5) and 2.160 (5) Å. Formation of (μ-H)(μ-OR)Re₂(CO)₈(L-L) and other products in the reactions is thought to proceed via two pathways, one involving metal-metal bond rupture and the other involving CO dissociation. The stability of (μ-H)(μ-OH)Re₂(CO)₈(dppm) or (μ-H)(μ-OH)Re₂(CO)₈(dmpm) is ascribable to the presence of the relatively rigid bridging phosphine ligand that maintains the metal atoms in close proximity. Reactions of (μ-H)(μ-OR)Re₂(CO)₈(L-L) and (μ-OR)₂Re₂(CO)₈(L-L) with dry HCl leads to formation of (μ-H)(μ-Cl)Re₂(CO)₈(L-L) and (μ-Cl)₂Re₂(CO)₈(L-L), respectively.

Introduction

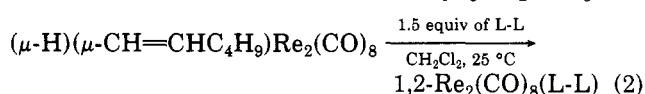
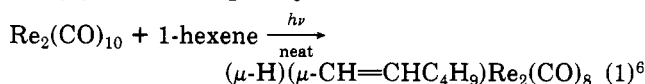
Binuclear transition-metal complexes bridged by phosphine ligands such as bis(dimethylphosphino)methane (dmpm), bis(diphenylphosphino)methane (dppm), bis(dimethylphosphino)ethane (dmpe), and bis(diphenylphosphino)ethane (dppe), and 2-(diphenylphosphino)pyridine (Ph₂PPy) have been extensively studied.³ We become interested in preparing dirhenium carbonyl complexes containing such ligands, as part of a continuing exploration of the reactions of dirhenium complexes with water,⁴ pyridine,⁵ alkenes,⁶ and alkynes.⁷ There are only a few examples of reaction of water with metal carbonyls to form μ-hydrido μ-hydroxo complexes.^{4,8,9} The photochemical reaction of Re₂(CO)₁₀ with water is believed to involve an unstable intermediate, Re₂(CO)₈(H₂O)₂, which is proposed to lose H₂O, followed by oxidative addition of an O-H bond of the remaining water, to form (μ-hydrido)(μ-hydroxo)dirhenium octacarbonyl. This hypothesized product in turn is thought to decompose to the

observed products HRe(CO)₅ and Re₄(CO)₁₂(OH)₄.⁴ The compound (μ-H)(μ-OH)Re₂(CO)₈ is apparently too unstable to detect in these reactions; by contrast, (μ-H)(μ-OH)Os₂(CO)₁₀ is very stable.⁸ This difference in stabilities is consistent with the proposed pathway for decomposition of the dirhenium compound.⁴ The bridging Os(CO)₄ group maintains the intact trinuclear framework; (μ-H)(μ-OH)Re₂(CO)₈ lacks the third metal center to hold the two metal centers in proximity. As a test of the notion that stability is related to this bridging function and as part of a general effort to explore the effects of phosphine ligands on the properties of (μ-hydrido)dirhenium compounds, we have prepared dirhenium carbonyl compounds containing bridging bidentate phosphorus ligands.

Here we report the preparation of Re₂(CO)₈(L-L) and their photochemical reactions with water and methanol. We also report on the thermal reaction of those products with HCl and the X-ray crystal structure of (μ-H)(μ-OH)Re₂(CO)₈(dppm).

Results

Synthesis of Re₂(CO)₈(L-L) (L-L = dppm (I), dmpm (II), dppe (III), dmpe (IV)). Recently it has been demonstrated that (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl, prepared by the photolytic reaction of Re₂(CO)₁₀ with 1-alkene, is an excellent precursor for 1,2 diequatorially substituted dirhenium octacarbonyls.⁶ The reaction of (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl with a bis(phosphine) ligand, L-L, in CH₂Cl₂ solution quantitatively yields 1,2-Re₂(CO)₈(L-L).



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(2) (a) University of Illinois, Urbana-Champaign. (b) University of Arkansas.

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Table I. Physical Properties of $\text{Re}_2(\text{CO})_8(\text{L-L})$

L-L	IR ν_{CO} , ^a cm^{-1}	UV, ^b nm	¹ H NMR, δ	¹³ C NMR, ^d δ	M ⁺ , ^e m/e
dppm (I)	2073 (m), 2020 (m) 1980 (s), 1956 (w) 1940 (w), 1915 (m)	313 (ϵ 12 700) 330 (11 300)	7.30-7.50 (m, 20 H) ^c 4.40 (t, 2 H, $J_{\text{PH}} = 10.0$ Hz)	200.7 (s, 4 C) 193.9 (t, 2 C, $J_{\text{PC}} + J_{\text{P}'\text{C}} =$ 56.0 Hz) 189.8 (s, 2 C) 201.8 (s, 4 C)	982
dmpm (II)	2067 (m), 2012 (s) 1980 (sh), 1971 (vs) 1947 (m), 1934 (sh)	289 (8800) 331 (13 800)	3.11 (t, 2 H, $J_{\text{PH}} = 10.2$ Hz) ^d 1.80 (t, 12 H, $J_{\text{PH}} = 3.5$ Hz)	193.7 (t, 2 C, $J_{\text{PC}} + J_{\text{P}'\text{C}} =$ 57.0 Hz) 189.5 (s, 2 C) 200.9 (br, 4 C)	734
dppe (III)	1914 (s) 2070 (m), 2017 (m) 1983 (s), 1944 (m) 1943 (m), 1915 (s)	273 (9800) 336 (15 300)	7.30-7.60 (m, 20 H) ^c 2.17 (d, 4 H, $J_{\text{PH}} = 14.5$ Hz)	193.2 (d, 2 C, $J_{\text{PC}} = 49.9$ Hz) 189.9 (d, 2 C, $J_{\text{PC}} = 7.4$ Hz) 201.8 (br, 4 C)	996
dmpe (IV)	2066 (w), 2010 (m) 1973 (s), 1938 (m) 1911 (s)	278 (8900) 334 (15 000)	1.76 (d, 12 H, $J_{\text{PH}} = 7.7$ Hz) ^d 1.63 (d, 4 H, $J_{\text{PH}} = 13.9$ Hz)	193.7 (d, 2 C, $J_{\text{PC}} = 52.9$ Hz) 189.5 (s, 2 C)	748

^a Taken in toluene solution. ^b Taken in CH_2Cl_2 solution. ^c Taken in CD_2Cl_2 . ^d Taken in CDCl_3 . ^e 70-eV electron impact; Re = 187.

The alkene replacement with dmpm and dmpe is complete within a few hours. However, it goes more slowly (~ 3 days) with dppm and dppe. It is noteworthy that this synthesis route provides an exceptionally clean access to the $\text{Re}_2(\text{CO})_8(\text{L-L})$ compounds, which are otherwise very difficult to obtain.

The physical properties of the 1,2- $\text{Re}_2(\text{CO})_8(\text{L-L})$ products are shown in Table I. All of these compounds are air-stable, pale yellow solids. The $\sigma-\sigma^*$ transitions in the UV are shifted 20-26 nm to longer wavelength as compared with that of $\text{Re}_2(\text{CO})_{10}$, as is typical of 1,2 diequatorially substituted dirhenium carbonyls.⁵ The absorption patterns in the CO stretching region of the IR spectra are similar to those of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{L})_2$ (L = CH_3CN^4 or py^5).

The ¹³C NMR spectra of I-IV in the carbonyl region in CDCl_3 solvent, displayed in Figure 1 for the case of I, show only three peaks in the intensity ratios 2:1:1 (201/194/190 ppm). The peaks at 194 ppm are triplets for I and II, $J_{\text{PC}} + J_{\text{P}'\text{C}} = 56.0$ and 57.0 Hz, respectively, and doublets for III and IV, $J_{\text{PC}} = 49.9$ and 52.9 Hz, respectively. The triplet pattern is presumably an example of a "deceptively simple" ABX spectrum, actually AA'X because the chemical shifts of A (P) and B (P') are nearly the same.^{10,11} The peaks at 201 and 190 ppm are singlets for I and II and broad singlets or doublets with small coupling constant (7.4 Hz) for III and IV, at room temperature. The relatively large ³¹P-¹³C coupling constants reflected in the multiplets at 194 ppm indicate that these carbonyls are located trans to phosphorus.¹² The small or zero ³¹P-¹³C coupling

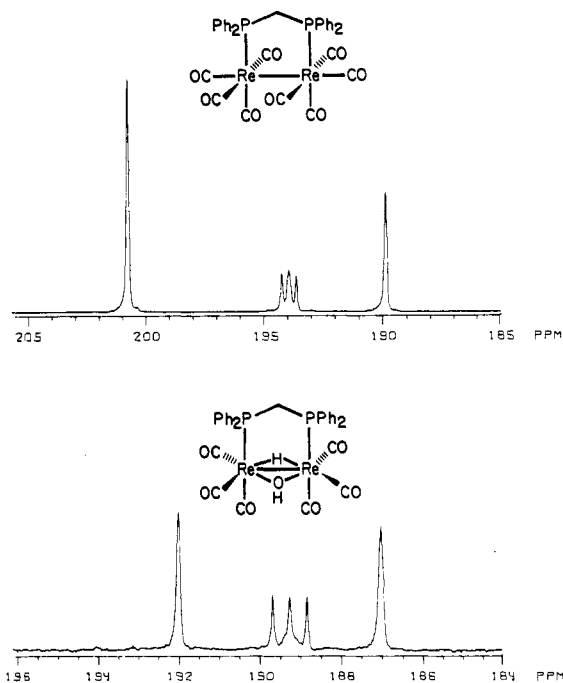


Figure 1. The carbonyl region of ¹³C NMR spectrum of $\text{Re}_2(\text{CO})_8(\text{dppm})$ (top) and $(\mu\text{-H})\text{Re}_2(\text{CO})_8(\text{dppm})$, Va (bottom).

constant evident for the peaks at 201 and 190 ppm indicates that these carbonyls are located cis to phosphorus: the peak at 190 ppm is assigned to the axial carbonyls and that at 201 ppm to the equatorial carbonyls.

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(11) The ¹³C NMR spectra of the carbon bonded to P in the phenyl group of $\text{Re}_2(\text{CO})_8(\text{dppm})$ and the carbon in the methyl group of $\text{Re}_2(\text{CO})_8(\text{dmpm})$ are also the triplets: $J_{\text{PC}} + J_{\text{P}'\text{C}} = 49.2$ and 36.0 Hz, respectively, which we believe are the examples of the deceptively simple spectra.

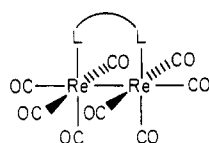
(12) For derivatives of Ru, Os, Rh, Ir, Pd, Pt, and Re, it is generally found that ²J(A-M-B) (A, B = ¹³C, ³¹P, ¹H) is large when A and B are mutually trans and is small when A and B are mutually cis; and for derivatives $\text{M}(\text{CO})_6$ (M = Cr, Mo, W) and $\text{Fe}(\text{CO})_5$ it is generally small for both cis and trans coupling; Mann, B. E. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1974; Vol. XII.

Table II. Spectroscopic Data of Compound $(\mu\text{-X})(\mu\text{-Y})\text{Re}_2(\text{CO})_6(\text{L-L})$

L-L	X	Y	IR, cm^{-1}	$^1\text{H NMR}, \delta$	$\text{M}^+, \text{m/e}$
dppm	Va	H	2037 (s), 2012 (s) 1940 (m), 1917 (sh) 1908 (s) 3566 (w, br)	7.10–7.60 (m, 20 H) ^b 3.39 (q, 1 H, $J = 10.4$ Hz) 2.49 (q, 1 H, $J = 10.0$ Hz) 0.02 (t, 1 H, $J_{\text{POH}} = 5.0$ Hz) –9.18 (t, 1 H, $J_{\text{PH}} = 11.0$ Hz)	944
	VIa	OH	2029 (s), 2011 (m) 1924 (m), 1908 (sh) 1890 (s) 3586 (w, br)	7.20–7.50 (m, 20 H) ^b 3.25 (t, 2 H, $J_{\text{PH}} = 11.6$ Hz) –0.35 (t, 2 H, $J_{\text{POH}} = 4.0$ Hz)	960
	Vc	H	2038 (s), 2013 (s) 1943 (m), 1923 (sh) 1912 (w)	7.11–7.46 (m, 20 H), 4.52 (s, 3 H) ^b 3.48 (q, 1 H, $J = 11.3$ Hz) 2.58 (q, 1 H, $J = 11.3$ Hz) –9.11 (t, 1 H, $J_{\text{PH}} = 10.5$ Hz)	958
	VIc	OCH ₃	2027 (s), 2010 (m) 1924 (m), 1893 (w) 1885 (sh)	7.17–7.66 (m, 20 H) ^b 4.33 (s, 6 H) 3.71 (t, 2 H, $J_{\text{PH}} = 11.0$ Hz)	e
dmpm	Vb	H	2035 (m), 2010 (m) 1936 (m), 1918 (m) 1902 (s) 3560 (w, br)	–0.66 (t, 1 H, $J_{\text{POH}} = 5.0$ Hz) ^c –9.98 (t, 1 H, $J_{\text{PH}} = 11.0$ Hz)	896
	VIb	OH	2027 (m), 2010 (m) 1917 (m), 1903 (sh) 1883 (s) 3575 (w, br)	–0.95 (t, $J_{\text{POH}} = 4.9$ Hz) ^c	912

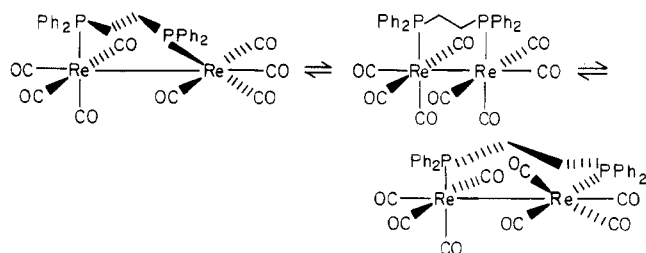
^a Taken in toluene solution. ^b Taken in CD_2Cl_2 . ^c Taken in CDCl_3 and the methyl and methylene protons could not be resolved. ^d FD, $\text{Re} = 187$. ^e FD shows $(\text{M} + \text{H}_2\text{O})^+$.

All spectroscopic evidences taken together lead us to conclude that the L-L ligand bridges the two rhenium atoms with each phosphorus atom occupying an equatorial site:



- I, L-L = dppm
 II, L-L = dmpm
 III, L-L = dppe
 IV, L-L = dmpe

The ^{13}C NMR spectrum of III in the carbonyl region in CD_2Cl_2 solvent at high temperature (≥ 33 °C) displays three peaks in the intensity ratios 2:1:1 (201/193/190 ppm) as those in I and II. As the temperature is lowered from 33 to –50 °C, two peaks at 193 and 190 ppm remain essentially unchanged. However, the peak at 201 ppm assigned to the equatorial carbonyl cis to phosphorus coalesces at 5 °C and finally splits into two sharp peaks at 204 and 199 ppm at –50 °C showing four carbonyl peaks of equal intensity (Figure 2). These ^{13}C NMR results indicate that at high temperature III undergoes a rapid fluxional process in which the Re–Re axis is rapidly twisting back and forth:



When the bridging ligand is changed from dppe to dmpe, the coalescence temperature decreases to –60 °C. This result suggests, not surprisingly, that the steric requirements of the groups bound to phosphorus in the bridging phosphine ligand play a role in determining the barrier to

the rearrangement. No comparable changes were noted in the ^{13}C NMR spectra of I or II upon cooling to –80 °C. It is unlikely that there is sufficient extension in the ligand backbone to allow for a significant twist about the Re–Re bond, as seen for the two-carbon system. In any case, if more than one potential minimum exists, the barrier to interconversion is quite low.

Photochemical Reaction of $\text{Re}_2(\text{CO})_8(\text{L-L})$ with Water. The sunlamp source, in conjunction with the Pyrex flask as a filter, is known to provide a distribution of light consisting of wavelengths ≥ 297 nm.^{13a} The low-pressure mercury lamp source provides UV light consisting primarily of 254-nm wavelength.^{13b}

Sunlamp photolysis of 1.0×10^{-2} M $\text{Re}_2(\text{CO})_8(\text{dppm})$ in wet toluene or benzene in the Pyrex flask for 3 days leads to a 35% yield of $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_6(\text{dppm})$, Va, and a 35% yield of $(\mu\text{-OH})_2\text{Re}_2(\text{CO})_6(\text{dppm})$, VIa, characterized by IR, ^1H NMR, ^{13}C NMR, and mass spectra. The corresponding reaction in the quartz cell with a mercury lamp source yields about 60% Va and 15% VIa. The reaction in the Pyrex flask with the same mercury lamp source shows the same product distribution and almost the same reaction rate as that in the Pyrex flask with sunlamp irradiation. The corresponding reaction of $\text{Re}_2(\text{CO})_8(\text{dmpm})$ yields $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_6(\text{dmpm})$, Vb, and $(\mu\text{-OH})_2\text{Re}_2(\text{CO})_6(\text{dmpm})$, VIb. The product distribution and reactivity follow the same pattern for the reaction of $\text{Re}_2(\text{CO})_8(\text{dppm})$, depending on the light source. However, the reaction is relatively slower. Spectroscopic data for V and VI are shown in Table II. The IR spectrum of each product shows the hydroxo stretching band (3560–3586 cm^{-1}). Electron-impact mass spectrum (70 eV) of Va shows M^+ and $(\text{M} - \text{H}_2\text{O})^+$ peaks; the fast atom bombardment mass spectrum shows M^+ and $(\text{M} - \text{OH})^+$ peaks. The ^1H NMR spectrum of Va in the upfield region shows two significant peaks, i.e., δ 0.02 (t, $J_{\text{POH}} = 5.0$ Hz) and –9.18 (t, $J_{\text{PH}} = 11.0$ Hz). The former (δ 0.02) is assigned to the hydroxo proton since it shifts downfield in wet NMR

(13) (a) Gard, D. R. Ph.D. Thesis, University of Illinois, Urbana-Champaign, IL, 1981. (b) Referred from *Catalogue of Oriol Corporation of America*.

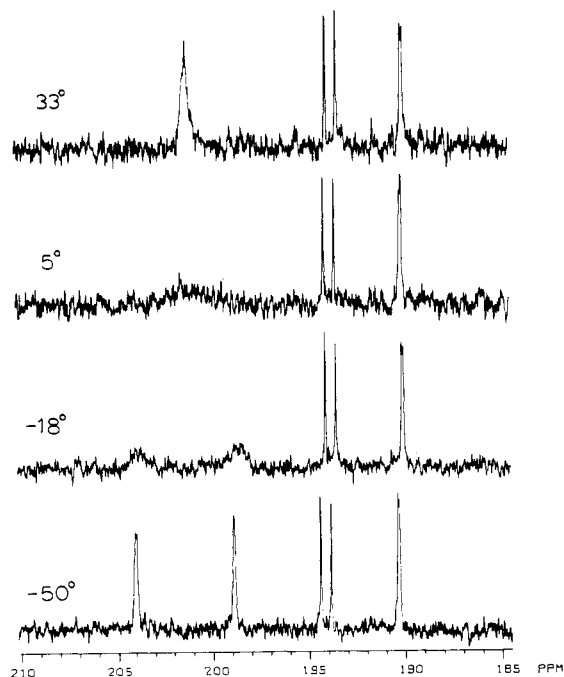
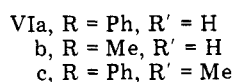
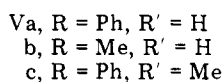
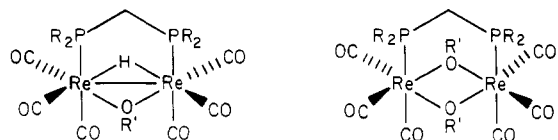


Figure 2. Variable-temperature ^{13}C NMR spectra of $\text{Re}_2(\text{CO})_8(\text{dppe})$, III, in the carbonyl region.

solvent and disappears upon adding a drop of D_2O . The latter ($\delta -9.18$) is assigned to the proton bridging between two rhenium atoms, coupled to two equivalent phosphorus nuclei. The ^{13}C NMR spectrum (Figure 1) of Va in the carbonyl region displays three peaks of equal intensity; δ 192.0 (s), 189.2 (t, $J_{\text{PC}} + J_{\text{PC}} = 76.0$ Hz), and 187.0 (s). The triplet at 189.2 ppm can also be interpreted as a deceptively simple "ABX spectrum"; the observed splitting is the average of J_{PC} and J_{PC} .¹⁰ On the basis of these spectroscopic data V is assigned to the following structure



To confirm the structure of Va, an X-ray crystal structure determination was carried out. An ORTEP illustration is provided in Figure 3. The atomic positional parameters and the important bond lengths and angles are displayed in Tables III and IV, respectively.

In the ^1H NMR spectrum of VIa, the triplet at -0.35 ppm is assigned as the hydroxo protons since it disappears upon adding a drop of D_2O and the integration is the same as that of the methylene protons of the bridging dppe ligand. Because of the similarity of the IR spectra of Va and VIa, we propose that VIa has a structure analogous to Va, as shown.

In the photolysis of $\text{Re}_2(\text{CO})_8(\text{dppe})$ in wet toluene, there is another product in addition to Va and VIa that could not be isolated. The ^1H NMR spectrum of the reaction mixture shows two unidentified peaks, δ 0.08 (d, $J = 3.2$ Hz) and 3.72 (t, $J = 10.7$ Hz). The integrated intensities of the two peaks are almost equal. However, the IR spectrum of this reaction mixture does not show any significant bands other than those attributable to Va and VIa, which indicates that the unidentified product may have a structure similar to V or VI, but we have not fully characterized it. The triplet resonance structure at δ 3.72

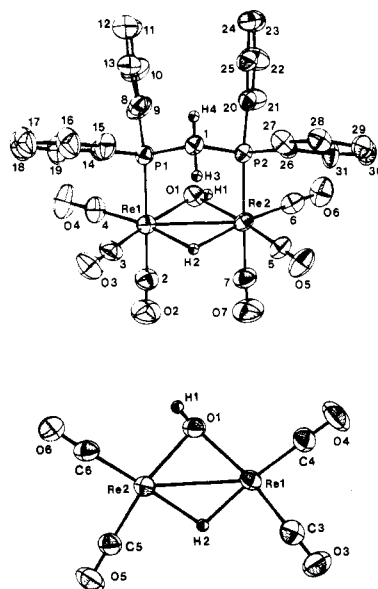
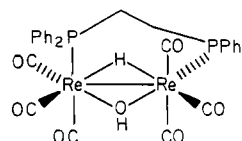


Figure 3. ORTEP drawings of $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_8(\text{dppe})$, Va (top), and $\text{Re}_2(\text{CO})_4(\text{H})(\text{OH})$ unit (bottom).

in the ^1H NMR could be due to the methylene protons of the bridging dppe ligand. The peak at δ 0.08, which disappears upon adding D_2O , could be associated with an OH group.

When the bridging ligand is dppe or dmpe, which contain a two-carbon chain backbone structure, the reaction goes faster and the final products are different than when the bridging ligand has a one-carbon backbone. The photochemical reaction of 1.0×10^{-2} M $\text{Re}_2(\text{CO})_8(\text{dppe})$ in wet toluene is complete within 18 h. However, the only isolated product from the reaction of $\text{Re}_2(\text{CO})_8(\text{dppe})$ or $\text{Re}_2(\text{CO})_8(\text{dmpe})$ is $\text{HRe}(\text{CO})_3(\text{dppe})$ or $\text{HRe}(\text{CO})_3(\text{dmpe})$, respectively. No evidence for bridging hydride was found in the ^1H NMR spectrum of the reaction mixture of $\text{Re}_2(\text{CO})_8(\text{dmpe})$. The $\text{Re}_2(\text{CO})_8(\text{dppe})$ reaction mixture shows peaks at $\delta -14.15$ (dd, $J = 20.5, 13.6$ Hz), 0.09 (t, $J = 3.0$ Hz), and -0.88 (t, $J = 3.4$ Hz). The former two peaks (-14.15 and 0.09 ppm) are suggestive of bridging hydrido and hydroxo by virtue of their upfield chemical shifts. The peak at -0.88 ppm is similar to the hydroxo proton of VIa. These similarities to the ^1H NMR spectra of Va and VIa suggest that $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_8(\text{dppe})$, VIIa, and $(\mu\text{-OH})_2\text{Re}_2(\text{CO})_8(\text{dppe})$, VIIIa, may be products. Supporting evidence for these assignments is provided by conversion to analogous compounds in which chloro is substituted for hydroxo, as discussed later.

Observation of a doublet of doublets for the bridging hydrido resonance in VIIa suggests that the two phosphorus atoms are not symmetrically located with respect to hydrido. The $^{31}\text{P}\text{-M-H}$ coupling constant in organometallic complexes is generally in the range of 10–25 Hz for a cis configuration and 80–120 Hz for a trans configuration.¹⁴ Thus, the coupling constants of the bridging hydrido ($J_{\text{PH}} = 20.5, 13.6$ Hz) correspond to a cis $^{31}\text{P}\text{-Re-H}$ configuration. A possible structure is as follows



(14) (a) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* 1966, 1407. (b) Kruse, W.; Atalla, R. *Chem. Commun.* 1968, 921. (c) Kruck, V. T. *Angew. Chem.* 1967, 79, 27.

Table III. Atomic Positional Parameters for $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_8(\text{dppm})^{a,b}$

atom	x	y	z	B, Å ²
Re(1)	0.23602 (2)	0.22885 (2)	0.15398 (2)	2.694 (5)
Re(2)	0.01935 (2)	0.52887 (2)	0.18393 (2)	2.626 (5)
P(1)	0.0959 (2)	0.1549 (2)	0.2644 (1)	2.62 (3)
P(2)	-0.1201 (2)	0.4557 (2)	0.2968 (1)	2.49 (3)
O(1)	0.0412 (4)	0.3752 (4)	0.0934 (3)	3.3 (1)
O(2)	0.4255 (6)	0.3128 (6)	0.0205 (5)	6.0 (2)
O(3)	0.4899 (5)	0.0574 (6)	0.2648 (4)	5.2 (2)
O(4)	0.3358 (7)	-0.0256 (6)	0.0404 (4)	6.3 (2)
O(5)	0.0346 (6)	0.6987 (5)	0.3303 (4)	5.0 (1)
O(6)	-0.2524 (6)	0.7759 (5)	0.1189 (4)	5.0 (2)
O(7)	0.1993 (6)	0.6318 (6)	0.0585 (5)	6.7 (2)
C(1)	-0.0131 (6)	0.2853 (6)	0.3502 (4)	2.7 (1)
C(2)	0.3534 (7)	0.2836 (7)	0.0689 (5)	3.8 (2)
C(3)	0.3947 (7)	0.1217 (7)	0.2226 (5)	3.6 (2)
C(4)	0.2953 (8)	0.0712 (7)	0.0823 (5)	3.9 (2)
C(5)	0.0276 (7)	0.6375 (6)	0.2742 (5)	3.4 (2)
C(6)	-0.1496 (7)	0.6842 (6)	0.1442 (5)	3.5 (1)
C(7)	0.1353 (8)	0.5893 (7)	0.1024 (6)	4.3 (2)
C(8)	-0.0245 (6)	0.1096 (5)	0.2202 (5)	2.7 (1)
C(9)	-0.0500 (8)	0.1331 (7)	0.1292 (5)	4.4 (2)
C(10)	-0.1452 (8)	0.1027 (8)	0.0963 (6)	5.1 (2)
C(11)	-0.2138 (7)	0.0459 (7)	0.1542 (6)	4.5 (2)
C(12)	-0.1821 (8)	0.0159 (8)	0.2450 (7)	4.8 (2)
C(13)	-0.0884 (7)	0.0471 (7)	0.2780 (5)	3.8 (2)
C(14)	0.2000 (6)	0.0007 (6)	0.3353 (5)	3.3 (1)
C(15)	0.2039 (8)	-0.0026 (7)	0.4276 (5)	3.9 (2)
C(16)	0.2870 (9)	-0.1244 (9)	0.4749 (6)	5.4 (3)
C(17)	0.3646 (9)	-0.2432 (8)	0.4294 (7)	5.6 (2)
C(18)	0.359 (1)	-0.2401 (8)	0.3364 (7)	5.9 (3)
C(19)	0.2805 (9)	-0.1214 (7)	0.2888 (6)	4.7 (2)
C(20)	-0.2706 (6)	0.4445 (6)	0.2641 (5)	2.8 (1)
C(21)	-0.3121 (7)	0.4773 (8)	0.1764 (5)	4.2 (2)
C(22)	-0.4253 (8)	0.4655 (9)	0.1538 (6)	5.4 (2)
C(23)	-0.4965 (8)	0.4202 (8)	0.2179 (7)	4.9 (2)
C(24)	-0.4570 (7)	0.3894 (7)	0.3060 (6)	4.4 (2)
C(25)	-0.3448 (7)	0.4012 (7)	0.3296 (6)	3.7 (2)
C(26)	-0.2005 (6)	0.5693 (6)	0.3934 (4)	2.8 (1)
C(27)	-0.1776 (7)	0.5266 (7)	0.4845 (5)	3.5 (2)
C(28)	-0.2390 (8)	0.6207 (7)	0.5535 (5)	3.8 (2)
C(29)	-0.3239 (7)	0.7589 (7)	0.5319 (5)	4.0 (2)
C(30)	-0.3487 (8)	0.8026 (7)	0.4431 (6)	4.4 (2)
C(31)	-0.2867 (8)	0.7110 (6)	0.3726 (5)	3.7 (2)
H(1)	-0.06 (1)	0.44 (1)	0.06 (1)	19 (6)
H(2)	0.208 (7)	0.377 (7)	0.218 (5)	5 (2)
H(3)	0.076 (7)	0.305 (6)	0.394 (5)	4 (2)
H(4)	-0.076 (8)	0.255 (7)	0.388 (6)	6 (2)

^a Numbers in parentheses are the estimated standard deviation in the last significant digit. ^b Isotropic thermal parameters for those atoms refined anisotropically were calculated according to: Hamilton, W. C. *Acta Crystallogr.* 1959, 12, 609.

The two P–Re–H angles are different. The larger coupling constant (20.5 Hz) may correspond to the larger P–Re–H angle and the smaller one (13.6 Hz) to the smaller P–Re–H angle.

Photochemical Reaction of $\text{Re}_2(\text{CO})_8(\text{L-L})$ with Methanol. All four compounds, I–IV, photochemically react with methanol in toluene. The reactions are relatively faster than that with water. A $(\mu\text{-hydrido})(\mu\text{-methoxy})\text{dirhenium}$ compound was expected as major product, by analogy with the reaction with water. However, the ¹H NMR spectrum of the product mixture from reaction of either III or IV does not exhibit resonances ascribable to bridging hydrido. Instead, $\text{HRe}(\text{CO})_3(\text{dppe})$ and $\text{HRe}(\text{CO})_3(\text{dmpe})$ are the separated products.¹⁵

Reaction of I or II with methanol reveals the same reaction pattern as that with water. For example, sunlamp photolysis of 1.0×10^{-2} M $\text{Re}_2(\text{CO})_8(\text{dppm})$ in 10% methanol/90% toluene solution is complete within 36 h, with production of about 50% $(\mu\text{-H})(\mu\text{-OCH}_3)\text{Re}_2(\text{CO})_8$

(dppm), Vc, and about 20% $(\mu\text{-OCH}_3)_2\text{Re}_2(\text{CO})_8(\text{dppm})$, VIc. $\text{HRe}(\text{CO})_3(\text{dppm})$ is not seen among the products. The corresponding reaction of I using a mercury lamp in a quartz cell proceeds at least twice as rapidly, yielding predominantly Vc. The spectroscopic data are set out in Table II. The ¹H NMR and IR spectra of Vc and VIc are very similar as those of Va and VIa, respectively, indicating similar structures. The corresponding reaction of I with methanol-*d*₁ yields products containing from one to five deuterium atoms.

Reaction of II with methanol shows the same pattern as for I. Although the major products could not be isolated, the ¹H NMR spectrum of the reaction mixture in CDCl₃ shows the bridging metal hydride peak at δ -9.88 (t, *J*_{PH} = 10.7 Hz) and the methyl proton peaks due to the methoxy group at 4.22 (s) and 4.16 ppm (s). The former two peaks (-9.88 and 4.22 ppm) may correspond to $(\mu\text{-H})(\mu\text{-OCH}_3)\text{Re}_2(\text{CO})_8(\text{dmpm})$; the latter may correspond to $(\mu\text{-OCH}_3)_2\text{Re}_2(\text{CO})_8(\text{dmpm})$. The IR of the reaction mixture displays a spectrum very similar to the analogous reaction mixture of I. One difference in the two reactions is that $(\mu\text{-H})_2\text{Re}_2(\text{CO})_8(\text{dmpm})$ was isolated from the re-

(15) Flitcroft, N.; Leach, J. M. *J. Inorg. Nucl. Chem.* 1970, 32, 137.

Table IV. Selected Bond Distances and Bond Angles for $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_6(\text{dppm})^a$

(a) Bond Distances (Å)			
Re ₁ -Re ₂	3.030 (1)	P ₁ -C ₈	1.818 (7)
Re ₁ -P ₁	2.453 (2)	P ₁ -C ₁₄	1.829 (7)
Re ₁ -O ₁	2.177 (5)	P ₂ -C ₁	1.825 (9)
Re ₁ -C ₂	1.950 (7)	P ₂ -C ₂₀	1.826 (7)
Re ₁ -C ₃	1.896 (8)	P ₂ -C ₂₆	1.820 (7)
Re ₁ -C ₄	1.911 (8)	O ₁ -H ₁	1.14 (16)
Re ₁ -H ₂	1.84 (8)	O ₂ -C ₂	1.140 (9)
Re ₂ -P ₂	2.464 (2)	O ₃ -C ₃	1.146 (9)
Re ₂ -O ₁	2.160 (5)	O ₄ -C ₄	1.148 (9)
Re ₂ -C ₅	1.908 (8)	O ₅ -C ₅	1.145 (9)
Re ₂ -C ₆	1.914 (8)	O ₆ -C ₆	1.157 (9)
Re ₂ -C ₇	1.949 (9)	O ₇ -C ₇	1.132 (10)
Re ₂ -H ₂	2.00 (7)	C ₁ -H ₄	0.99 (10)
P ₁ -C ₁	1.840 (7)	C ₁ -H ₃	1.27 (8)

(b) Bond Angles (deg)			
Re ₂ -Re ₁ -P ₁	90.19 (4)	Re ₁ -P ₁ -C ₁	112.4 (2)
Re ₂ -Re ₁ -O ₁	45.4 (1)	Re ₁ -P ₁ -C ₈	118.3 (2)
Re ₂ -Re ₁ -C ₂	91.0 (2)	Re ₁ -P ₁ -C ₁₄	114.6 (2)
Re ₂ -Re ₁ -C ₃	125.6 (2)	C ₁ -P ₁ -C ₈	105.0 (3)
Re ₂ -Re ₁ -C ₄	146.0 (3)	C ₁ -P ₁ -C ₁₄	103.0 (4)
Re ₂ -Re ₁ -H ₂	40 (3)	C ₈ -P ₁ -C ₁₄	101.7 (3)
P ₁ -Re ₁ -O ₁	88.1 (2)	Re ₂ -P ₂ -C ₁	112.7 (3)
P ₁ -Re ₁ -C ₂	177.9 (2)	Re ₂ -P ₂ -C ₂₀	121.2 (2)
P ₁ -Re ₁ -C ₃	89.4 (2)	Re ₂ -P ₂ -C ₂₆	112.5 (2)
P ₁ -Re ₁ -C ₄	90.8 (3)	C ₁ -P ₂ -C ₂₀	103.0 (4)
P ₁ -Re ₁ -H ₂	97 (3)	C ₁ -P ₂ -C ₂₆	104.1 (3)
O ₁ -Re ₁ -C ₂	94.0 (3)	C ₂₀ -P ₂ -C ₂₆	101.3 (3)
O ₁ -Re ₁ -C ₃	170.6 (3)	Re ₁ -O ₁ -Re ₂	88.6 (2)
O ₁ -Re ₁ -C ₄	100.6 (3)	Re ₁ -O ₁ -H ₁	176 (8)
O ₁ -Re ₁ -H ₂	85 (3)	Re ₂ -O ₁ -H ₁	95 (9)
C ₂ -Re ₁ -C ₃	88 (3)	P ₁ -C ₁ -P ₂	112.1 (4)
C ₂ -Re ₁ -C ₄	89.1 (3)	P ₁ -C ₁ -H ₄	109 (5)
C ₂ -Re ₁ -H ₂	83 (3)	P ₁ -C ₁ -H ₃	106 (3)
C ₃ -Re ₁ -C ₄	88.4 (3)	P ₂ -C ₁ -H ₄	77.9 (7)
C ₃ -Re ₁ -H ₂	86 (3)	P ₂ -C ₁ -H ₃	103 (3)
C ₄ -Re ₁ -H ₂	171 (3)	H ₄ -C ₁ -H ₃	118 (6)
Re ₁ -Re ₂ -P ₂	90.05 (4)	P ₂ -Re ₂ -O ₁	88.6 (2)
Re ₁ -Re ₂ -O ₁	45.9 (1)	P ₂ -Re ₂ -C ₅	90.0 (2)
Re ₁ -Re ₂ -C ₅	123.9 (2)	P ₂ -Re ₂ -C ₆	90.3 (3)
Re ₁ -Re ₂ -C ₆	145.8 (2)	P ₂ -Re ₂ -C ₇	175.7 (3)
Re ₁ -Re ₂ -C ₇	90.7 (3)	O ₁ -Re ₂ -C ₅	169.7 (3)
Re ₁ -Re ₂ -H ₂	36 (2)	O ₁ -Re ₂ -C ₆	99.9 (3)
O ₁ -Re ₂ -C ₇	95.0 (3)	Re ₁ -C ₂ -O ₂	177.9 (7)
C ₅ -Re ₂ -C ₆	90.3 (3)	Re ₁ -C ₃ -O ₃	179.4 (7)
C ₅ -Re ₂ -C ₇	86.1 (3)	Re ₁ -C ₄ -O ₄	177.4 (3)
C ₆ -Re ₂ -C ₇	91.1 (3)	Re ₂ -C ₅ -O ₅	177.7 (7)
		Re ₂ -C ₆ -O ₆	178.3 (7)
		Re ₂ -C ₇ -O ₇	175.5 (9)

^a Numbers in parentheses are the estimated standard deviation in the last significant digit.

action involving II. The ¹H NMR spectrum of this compound in CDCl₃ shows the triplet at δ -8.18 (*J*_{PH} = 10.7 Hz); field desorption mass spectrum, FDMS, also gives the molecular ion peak, *m/e* 680 (*R* = 187). The same reaction with CH₃OD yields (μ-D)(μ-OCH₃)Re₂(CO)₆(dmpm), (μ-OCH₃)₂Re₂(CO)₆(dmpm), and (μ-D)₂Re₂(CO)₆(dmpm) as products characterized by FDMS and ¹H NMR.

Photochemical Reaction of (μ-H)(μ-OH)Re₂(CO)₆(dppm) and (μ-H)(μ-OCH₃)Re₂(CO)₆(dppm) with ROH (R = H and CH₃). To investigate whether the products (μ-OH)₂Re₂(CO)₆(L-L) arise from (μ-H)(μ-OR)Re₂(CO)₆(L-L), compounds Va and Vc were irradiated in wet toluene or 10% methanol/90% toluene solvent. The reaction proceeded over about 5 days to yield the corresponding (μ-OR)₂Re₂(CO)₆(dppm). In a separate experiment, after the reaction of I with water was complete in a 3-day period, the reaction mixture was irradiated for 3 more days. The ratio of Va/VIa remains unchanged, indicating that although a small portion of VI may be produced via V, the

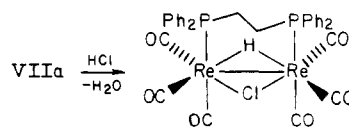
major pathway includes a certain intermediate that is discussed later.

The photochemical reaction of either Va or Vc with CH₃OD yields only VIc without any deuterium incorporation. Photolysis of Vc in the presence of carbon-13 labeled carbon monoxide gives mixtures of Vc containing from zero to six ¹³CO molecules.

Thermal Reaction of (μ-H)(μ-OH)Re₂(CO)₆(L-L) and (μ-OR)₂Re₂(CO)₆(L-L) (R = H and CH₃) with HCl.¹⁶ The μ-hydrido μ-alkoxo and bis(μ-alkoxo) complexes all react with HCl to yield the μ-hydrido μ-chloro and bis(μ-chloro) complexes, respectively. For example, bubbling hydrogen chloride gas through a solution of Va in toluene quantitatively gives (μ-H)(μ-Cl)Re₂(CO)₆(dppm) within minutes at room temperature. The IR spectrum in the carbonyl region of this product is similar to that of Va except that the bands are shifted 5–15 cm⁻¹ to higher frequency. The ¹H NMR spectrum in CDCl₃ exhibits a signal due to bridging hydride at δ -10.87 (*t*, *J*_{PH} = 10.5 Hz) and the two separate methylene protons at 3.51 (*q*, *J* = 11.5 Hz) and 2.66 ppm (*q*, *J* = 11.5 Hz), consistent with the structure of Va (Table I). The mass spectrum shows the molecular ion peaks, M⁺ 958 (25), 960 (100), 962 (92), and 964 (22). The relative intensities are consistent with the presence of two rhenium atoms and one chlorine atom.

Using field desorption techniques, it was not possible to observe the molecular ion peak of VIc, which is believed (on the basis of IR and ¹H NMR spectra) to be one of the products from the photochemical reaction of I with methanol. Since the reaction of VIa or Vc with HCl yields (μ-Cl)₂Re₂(CO)₆(dppm) or (μ-H)(μ-Cl)Re₂(CO)₆(dppm), respectively, it can be presumed that the reaction of the proposed product VIc with HCl should yield (μ-Cl)₂Re₂(CO)₆(dppm), as is apparently the case. The spectroscopic data (IR, ¹H NMR, MS) of the products from these reactions are displayed in the Experimental Section.

We have noted that the photochemical reaction of Re₂(CO)₆(dppe) in wet toluene yields VIIa and VIIb, as evidenced in the ¹H NMR results. In the hope that the proposed compounds might be more fully identified through formation of stable derivatives, the reaction mixture of III with water was treated with HCl, to replace the hydroxo group by chloro. Although the expected products, (μ-H)(μ-Cl)Re₂(CO)₆(dppe) and (μ-Cl)₂Re₂(CO)₆(dppe), could not be separated by preparative TLC,¹⁷ FDMS shows the molecular ion peaks of both (μ-H)(μ-Cl)Re₂(CO)₆(dppe) and (μ-Cl)₂Re₂(CO)₆(dppe). An ¹H NMR spectrum of the product mixture in CDCl₃ exhibits a triplet at δ -10.53 (*J* = 11.5 Hz). That is, the bridging hydrido that appears in VIIa as a doublet of doublets is seen as a triplet. Whereas the proton is coupled to two nonequivalent phosphorus nuclei in VIIa, a rearrangement has occurred in the course of the replacement reaction, to produce equivalent phosphorus sites.

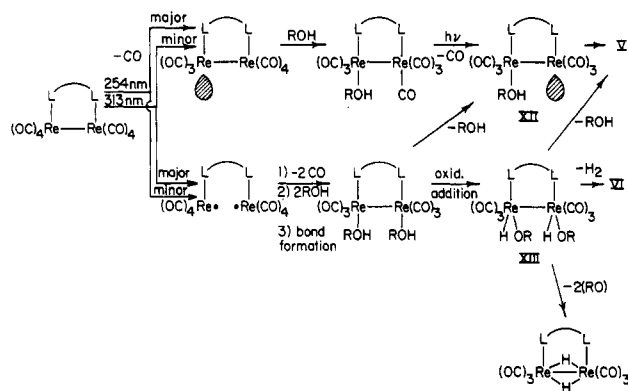


Although the bridging hydroxo group (but not the hydrido) is susceptible to electrophilic attack, as evidenced by the reaction with HCl, compounds V and VI are not

(16) Photochemical reaction of I or III with HCl does not yield the μ-hydrido μ-chloro compound.

(17) Since the corresponding dppm compounds could not be separated, this separation was not expected.

Scheme I



would give a doublet of doublets for the bridging hydrido in the ^1H NMR spectrum, as observed.

Neither $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_6(\text{dmpe})$ nor $(\mu\text{-OH})_2\text{Re}_2(\text{CO})_6(\text{dmpe})$, expected as products from the photochemical reaction of $\text{Re}_2(\text{CO})_8(\text{dmpe})$ with water, were detected in the ^1H NMR. The major product $\text{HRe}(\text{CO})_3(\text{dmpe})$ may arise via $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_6(\text{dmpe})$ by a pathway analogous to that previously proposed.⁴ However, it is noteworthy that $[\text{Re}(\text{CO})_3(\text{OH})]_4$ was not observed as a product, as might have been expected from the proposed mechanism.

Mechanism. A general pathway involving metal-metal bond homolysis has been suggested for formation of dinuclear compounds containing a bridging hydrido ligand upon photochemical reaction of $\text{Re}_2(\text{CO})_{10}$.^{5,6} Isolation of V in this work provides supporting evidence for existence of the proposed intermediate XI and for the suggested mechanism of photochemical reaction of $\text{Re}_2(\text{CO})_{10}$ with water.⁴

Because the bridging ligand in $\text{Re}_2(\text{CO})_8(\text{L-L})$ retains the two metal centers in proximity, the radicals produced by photolysis rapidly reform the metal-metal bond. This reformation competes with ligand substitution for CO. Further, the steric and electronic properties of phosphine ligands have been shown to reduce the labilities of carbonyl radicals toward substitution. At the same time, prolonged irradiation makes other pathways, notably CO dissociation, more likely. Photolysis of I with water using 254-nm radiation yields mainly Va, while photolysis using 313-nm radiation produces almost equal amounts of Va and VIa. These results indicate that the photochemical reaction of $\text{Re}_2(\text{CO})_8(\text{L-L})$ with ROH may occur via either CO dissociation or homolytic metal-metal bond cleavage, depending on the irradiation wavelengths. The former pathway is favored by use of 254-nm radiation and the latter by use of 313-nm radiation. Dissociation of CO (Scheme I) would leave the coordinatively unsaturated species $\text{Re}_2(\text{CO})_7(\text{L-L})$ which could pick up ROH. Dissociation of CO from the other metal center would yield V via an O-H oxidative addition process. On the other hand, homolytic metal-metal bond cleavage leads to three products V, VI, and $(\mu\text{-H})_2\text{Re}_2(\text{CO})_6(\text{L-L})$. The bis(μ -hydrido) compound is found only in the reaction of II with methanol. As shown in Scheme I, V would arise from 313-nm radiation through substitution of a CO on each metal center by ROH, reformation of the metal-metal bond, and then loss of one ROH ligand, followed by O-H oxidative addition. The presence of intermediate XIII is suggested by the observation of V, VI, and $(\mu\text{-H})_2\text{Re}_2(\text{CO})_6(\text{L-L})$ as products. If the rhenium metal centers were highly electrophilic, the order of reductive elimination from XIII should be $\text{H-H} > \text{H-OR} > \text{RO-OR}$. However, the presence of electron-donating groups on the phosphine ligand and OR could

change that order. In the reaction of II with methanol RO-OR reductive elimination occurs to yield $(\mu\text{-H})_2\text{Re}_2(\text{CO})_6(\text{dmpm})$. In this case, with electron-donating CH_3 groups on phosphorus and alkoxy, RO-OR reductive elimination is apparently competitive with H-H reductive elimination.

The photochemical reaction of I with CH_3OD mainly yields $(\mu\text{-D})(\mu\text{-OCH}_3)\text{Re}_2(\text{CO})_6(\text{dppm})$, with deuterium incorporation into the dppm ligand; II mainly yields $(\mu\text{-D})(\mu\text{-OCH}_3)\text{Re}_2(\text{CO})_6(\text{dmpm})$ without deuterium incorporation into the dmpm ligand. At this stage the mechanism for deuterium exchange is not clear. However, oxidative addition of the ortho C-H bonds in the phenyl rings²² in an unsaturated intermediate probably occurs at some stage to effect hydrogen-deuterium exchange, with subsequent C-D reductive elimination that involves a deuterium already bound to the metal.

Photochemical Reaction of V with ROH (R = H and CH_3). Photochemical reaction of Va or Vc with CH_3OH proceeds very slowly ($t_{1/2} \approx 5$ days) to yield VIc but does not proceed in the presence of CO. These results indicate that the initial dissociation of CO leads to an unsaturated species, which competitively reacts with either CH_3OH or dissolved CO. The final product VIc may be formed via H-H reductive elimination in the ROH-substituted compound, followed by CO substitution. The ^{13}C NMR spectrum of the carbon-13 labeled CO-substituted Va shows an equal distribution of CO to the three different sites.

In summary, we have reported here the synthesis in high yield of dinuclear rhenium compounds containing bridging phosphine ligands and their photochemical reactions with water and methanol. The reactions with water that involve $\text{Re}_2(\text{CO})_8(\text{L-L})$ compounds where L-L is either dppm or dmpm lead to stable compounds with either $(\mu\text{-H})(\mu\text{-OH})$ or $(\mu\text{-OH})_2$ groups bridging between the metal atoms. The X-ray structure of $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_6(\text{dppm})$, Va, reveals a slightly asymmetric arrangement of bridging ligands, but one that is quite similar to that observed for the analogous compound $(\mu\text{-H})(\mu\text{-OH})\text{Os}_2(\text{CO})_{10}$. The fact that Va is quite stable, whereas the analogous $(\mu\text{-H})(\mu\text{-OH})\text{Re}_2(\text{CO})_8$ is unstable, illustrates the important role of the bridging group, which may be a metal carbonyl fragment such as $\text{Os}(\text{CO})_4$ or a bidentate bridging phosphine ligand, in maintaining the structure.

Experimental Section

General Data. All reactions were carried out under an argon atmosphere. Photochemical reactions were performed by irradiation with a General Electric 275-W sunlamp using Pyrex Schlenk vessels or with an Oriel 17 mA mercury-argon lamp using a quartz vessel. Benzene and toluene were distilled from CaH_2 under nitrogen and degassed prior to use. Dirhenium decacarbonyl, bis(diphenylphosphino)methane (dppm) and -ethane (dppe) (Pressure Chemical Co.), and bis(dimethylphosphino)methane (dmpm) and -ethane (dmpe) (Strem Chemicals) were all used without further purification. 1-Hexene was distilled from CaH_2 under nitrogen. Hydrogen chloride purchased from Air Product and Chemicals, Inc., was used without further purification. Reagent grade solvents (hexane, toluene, CH_2Cl_2 , ethyl acetate) were also used without purification for chromatography and recrystallization. Silica gel (70-230 mesh, EM Reagents) was employed for column chromatography. Preparative TLC plates (20 \times 20 cm, 2.0 mm silica with UV₂₅₄ fluorescent indicator) were

(22) (a) Bennett, M. A.; Milner, D. L. *Chem. Commun.* 1967, 581. (b) McKinney, R. J.; Hoxmeier, R.; Kaesz, H. D. *J. Am. Chem. Soc.* 1975, 97, 3059. (c) Jones, C. E.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Dalton Trans.* 1974, 992 and references therein. (d) Barder, T. J.; Petrick, S. M.; Walton, R. A.; Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* 1983, 105, 4090.

obtained from Brinkmann Instruments, Inc.

Infrared spectra were obtained on a Beckmann IR-4240 spectrophotometer. Electronic spectra were recorded on a Hitachi 100-80A spectrophotometer using matched 1.0-cm quartz cells. Electron-impact (70 eV), fast atom bombardment, and field desorption mass spectra were obtained with Finnigan-MAT CH-5 and 731 mass spectrometers. ^1H NMR and ^{13}C NMR were obtained by using a Nicolet NT-360 instrument at 360 and 90 MHz, respectively, or a Varian XL-200 instrument. ^{13}C NMR spectra were obtained by using natural abundance compounds. Spectra were recorded at ambient temperature except where indicated. Data are referred to tetramethylsilane at δ 0. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

Preparation of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{L-L})$. $\text{Re}_2(\text{CO})_{10}$ (1.000 g, 1.53 mmol) and 1-hexene (150 mL) were added into a 250-mL, flame-dried, argon-flushed Pyrex Schlenk flask. After being degassed, the solution was irradiated with a GE 275-W sunlamp to form (μ -hydrido)(μ -hexenyl)dirhenium octacarbonyl. 1-Hexene was removed under reduced pressure. Methylene chloride (100 mL) and bis(diphenylphosphino)methane (0.884 g, 2.30 mmol) were added into the crude (μ -hydrido)(μ -hexenyl)dirhenium octacarbonyl. The mixture was allowed to stir for 3 days. The corresponding reactions of bis(dimethylphosphino)methane and -ethane were carried out in a nitrogen glovebox and completed within a few hours.

The final product was separated from silica gel column chromatography using toluene, hexane, and ethyl acetate (7:7:2) and recrystallized from methylene chloride and hexane. In the case of $\text{Re}_2(\text{CO})_8(\text{dppe})$, $\text{Re}_2(\text{CO})_8(\text{dmpe})$, or $\text{Re}_2(\text{CO})_8(\text{dmpm})$, methylene chloride and hexane (1:1) were used for column chromatography. Yields are in the range of 90%, based on $\text{Re}_2(\text{CO})_{10}$ used. The physical properties were shown in Table I. Anal. Calcd for $\text{C}_{33}\text{H}_{22}\text{O}_8\text{P}_2\text{Re}_2$ (I): C, 40.41; H, 2.26. Found: C, 40.24; H, 2.07.

Photochemical Reactions of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{L-L})$ with Water. $\text{Re}_2(\text{CO})_8(\text{dppm})$ (0.100 g, 0.102 mmol) was added into a 50-mL, flame-dried, argon-flushed Schlenk flask containing degassed wet toluene (20 mL) and capped with a rubber septum. After irradiation of the solution with a GE 275-W sunlamp for 3 days, solvent was removed under reduced pressure. The pure products were separated on silica gel coated preparative thin layer chromatography (TLC) plates using methylene chloride and hexane and recrystallized from the same solvent system. Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{O}_7\text{P}_2\text{Re}_2$ (Va): C, 39.49; H, 2.57. Found: C, 40.16; H, 2.51.

The equivalent reaction of $\text{Re}_2(\text{CO})_8(\text{dmpm})$ (0.075 g, 0.102 mmol) was carried out for 3 days. The pure products were separated by using silica gel column chromatography at -20°C . The desired product from the reaction of $\text{Re}_2(\text{CO})_8(\text{dppe})$ was so unstable that it could not be isolated. The physical properties of isolated products are listed in Table II.

Photochemical Reactions of 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{dppm})$ and 1,2-*eq,eq*- $\text{Re}_2(\text{CO})_8(\text{dmpm})$ with Methanol. $\text{Re}_2(\text{CO})_8(\text{dppm})$ (0.100 g, 0.102 mmol) was added to a 50-mL Schlenk flask containing degassed toluene (18 mL) and methanol (2 mL). The vessel was capped with a rubber septum and flushed with argon. After irradiation of solution with a GE 275-W sunlamp for 36 h, all liquid was removed under reduced pressure. The pure products were separated on silica gel coated preparative TLC plates using methylene chloride and hexane and recrystallized from the same solvent system. Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{O}_7\text{P}_2\text{Re}_2$ (Vc): C, 40.85; H, 2.79. Found: C, 41.04; H, 2.65. The physical properties are listed in Table II.

Repetition of this procedure with methyl alcohol- d_1 was performed to determine whether there is H/D exchange in the product.

Photochemical Reaction of (μ -H)(μ -OR) $\text{Re}_2(\text{CO})_8(\text{dppm})$ with ROH (R = H and CH_3). (μ -H)(μ -OH) $\text{Re}_2(\text{CO})_8(\text{dppm})$ (0.015 g, 0.016 mmol) or (μ -H)(μ -OCH $_3$) $\text{Re}_2(\text{CO})_8(\text{dppm})$ (0.012 g, 0.016 mmol) was added to a 50-mL Schlenk flask containing degassed wet toluene (10 mL) or a mixture of methanol (1 mL) and toluene (9 mL). The solution was irradiated with a GE 275-W sunlamp for 3–5 days. The bis(μ -hydroxo) or bis(μ -methoxo) complexes were slowly formed and characterized by ^1H NMR and IR (Table II).

Reaction of (μ -H)(μ -OR) $\text{Re}_2(\text{CO})_8(\text{L-L})$ or (μ -OR) $_2\text{Re}_2(\text{CO})_8(\text{L-L})$ (R = H and CH_3) with HCl. In a typical reaction, (μ -H)(μ -OH) $\text{Re}_2(\text{CO})_8(\text{dppm})$ (0.010 g, 0.011 mmol) was added into a 50-mL three-necked flask containing 20 mL of toluene. Dry hydrogen chloride was bubbled through the solution with rigorous stirring for 5 min. The solvent was removed under reduced pressure. The pure product was obtained in 90% yield after the mixture was filtered through a silica gel column. The same product was obtained from the reaction of HCl with (μ -H)(μ -OCH $_3$) $\text{Re}_2(\text{CO})_8(\text{dppm})$.

(μ -H)(μ -Cl) $\text{Re}_2(\text{CO})_8(\text{dppm})$: IR (toluene) ν_{CO} 2051 (s), 2026 (m), 1920 (m), 1940 (m), 1922 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ -10.87 (t, 1 H, $J_{\text{PH}} = 10.5$ Hz), 7.20–7.45 (m, 20 H) 3.51 (q, 1 H, $J = 11.5$ Hz), 2.66 (q, 1 H, $J = 11.5$ Hz); MS (70 eV), molecular ions at m/e (relative intensity) 958 (25), 960 (100), 962 (92), 964 (22).

An analogous product was obtained from the reaction of HCl with (μ -OR) $_2\text{Re}_2(\text{CO})_8(\text{L-L})$. (μ -Cl) $_2\text{Re}_2(\text{CO})_8(\text{dppm})$: IR (toluene) ν_{CO} 2050 (s), 2037 (m), 1960 (m), 1945 (m), 1918 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 7.20–7.45 (m, 20 H), 4.04 (t, 2 H, $J_{\text{PH}} = 11.3$ Hz); MS (70 eV), molecular ions at m/e (relative intensity) 992 (20), 994 (80), 996 (100), 998 (50), 1000 (7).

From reaction of HCl with (μ -H)(μ -OH) $\text{Re}_2(\text{CO})_8(\text{dmpm})$, (μ -H)(μ -Cl) $\text{Re}_2(\text{CO})_8(\text{dmpm})$: IR (toluene) ν_{CO} 2049 (m), 2023 (m), 1957 (m), 1938 (m), 1917 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ -11.49 (t, 1 H, $J_{\text{PH}} = 10.7$ Hz), 2.02 (m, 2 H) 1.76 (t, 6 H, $J = 3.6$ Hz), 1.69 (t, 6 H, $J = 3.7$ Hz); MS (70 eV), molecular ions at m/e (relative intensity) 710 (22), 712 (93), 714 (100), 716 (32).

From reaction of HCl with (μ -OH) $_2\text{Re}_2(\text{CO})_8(\text{dmpm})$, (μ -Cl) $_2\text{Re}_2(\text{CO})_8(\text{dmpm})$: IR (toluene) ν_{CO} 2051 (s), 2036 (m), 1955 (m), 1940 (m), 1914 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 2.71 (t, 2 H, $J_{\text{PH}} = 12.2$ Hz), 1.90 (d, 12 H, $J_{\text{PH}} = 7.7$ Hz); MS (70 eV), molecular ions at m/e (relative intensity) 744 (19), 746 (81), 748 (100), 750 (51), 752 (8).

X-ray Structure Determination. A colorless single crystal of (μ -H)(μ -OH) $\text{Re}_2(\text{CO})_8(\text{dppm})$ was mounted with epoxy on a glass fiber for data collection made with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo K α X-rays ($\lambda = 0.71073$ Å) at ambient temperature. Unit cell parameters (determined from 25 reflections with $28^\circ < 2\theta < 34^\circ$) are $a = 10.904$ (2) Å, $b = 11.099$ (2) Å, $c = 14.646$ (2) Å, $\alpha = 84.69$ (1) $^\circ$, $\beta = 83.18$ (1) $^\circ$, $\gamma = 60.69$ (1) $^\circ$, $V = 1533.6$ (6) Å 3 , and $D_{\text{calcd}} = 2.042$ g cm^{-3} . There are two molecules in the unit cell which belongs to the triclinic space group $P\bar{1}$. A total of 10555 independent reflections were measured at speeds of 2–20 $^\circ$ min $^{-1}$ using θ - 2θ scans over a range of $(1.0 \times 0.35 \tan \theta)^\circ$ for $2^\circ < 2\theta < 70^\circ$. The analytical absorption correction ($\mu = 81.43$ cm^{-1}) varied from 0.41 to 1.0 (average 0.78) for the approximately parallelepiped crystal bounded by 10 faces at face-center distances of 0.01–0.02 mm. Three standard reflections measured periodically during data collection varied less than 0.8% and thus indicated good crystal stability.

The rhenium atoms were located by analysis of a Patterson map, and the remaining atoms were located by difference Fourier techniques. The final full-matrix least-squares refinement included positional and anisotropic thermal parameters for all non-hydrogen atoms as well as positional and isotropic thermal parameters for four hydrogen atoms (those of the methylene group, the H bridge, and the OH group). Hydrogen atoms of the phenyl groups were included in the structure factor calculation at idealized positions (C–H = 0.95 Å) with isotropic B values of 1.2 times the B values of the carbon atoms to which they are bonded. The refinement included 396 parameters and 5547 observed reflections ($I > 6\sigma(I)$) for a reflection/parameter ratio of 14.0/1 and produced $R = 0.031$, $R_w = 0.041$, and GOF = 1.01. Least-squares weighting was based on σ_F values derived from counting statistics ($p = 0.06$). The four largest peaks on a final difference map (1.5 – 1.7 e Å $^{-3}$) were all within 0.9 Å of a Re atom. Atomic scattering factors and anomalous dispersion corrections were taken from ref 23. The final atomic positional parameters are given in Table III, and Table IV gives selected intramolecular distances and angles.

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88271-88-9; Re₂(CO)₁₀, 14285-68-8; Re, 7440-15-5; (μ -H)(μ -CH=C₄H₉)Re₂(CO)₈, 88294-19-3; 1-hexene, 592-41-6.

Supplementary Material Available: Thermal parameters (Table V), calculated hydrogen atom positions (Table VI), distances and angles associated with the phenyl groups (Table VII), crystal shape data (Table VIII), and observed and calculated structure factor amplitudes (Table IX) (61 pages). Ordering information is given on any current masthead page.

Paramagnetic Organometallic Molecules. 17.¹ Redox Chemistry of Homo- and Heteronuclear Carbon-, Germanium-, or Phosphorus-Capped Trimetal Clusters

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The redox chemistry of a series of capped tetrahedral clusters has been investigated by electrochemical and spectral techniques. Both homonuclear RECo₃ (R = Me, Ph, E = Ge, P) and heteronuclear RECo₂M (R = Me, Ph, E = C, Ge, M = Cr, Mo, W; R = Me, Ph, E = P, M = Fe) and RPCoMM' (R = Me, Ph, M = Fe, M' = Mo, Ni) clusters are represented. The diamagnetic homonuclear cobalt clusters all undergo an electrochemically and chemically reversible one-electron reduction to the respective radical anions, and these were characterized by an analysis of their isotropic and anisotropic ESR spectra. Incorporation of another metal induces kinetic instability, and the redox behavior is a function of the capping group and the number of disparate metal atoms. Radical anions of the RECoMM' clusters give paramagnetic fragmentation products under all conditions. The electrochemical behavior displayed by RCo₂M clusters is unusual in that an electrochemically and chemically irreversible process is followed by a chemically reversible step; possible interpretations of these data are given. Oxidation of the paramagnetic cluster RPCo₃(CO)₉ is chemically reversible, but attempts to isolate the cation were unsuccessful. Electrochemical and spectral parameters (IR, electronic, ESR) for this series of clusters and other capped trimetal clusters are compared and correlated with steric and electronic requirements of the metal and capping atoms.

Earlier papers in this series have dealt with the redox chemistry of the capped clusters CCo₃,^{2,3} SCo₃,⁴ SCo₂Fe,⁴ and C₂Co₂.⁵ Clusters of this type, in common with all neutral transition-metal carbonyl clusters of three or four nuclearity, characteristically undergo a one-electron reduction to a radical anion where the additional electron occupies an antibonding orbital centered on the metallic fragment.^{2,4,6} These radical anions are activated to nucleophilic substitution, and electron-induced reactions offer a rapid and efficient synthesis of cluster derivatives.⁷ However, the radical anions have varying degrees of

thermodynamic and kinetic stability. The rate of decay is a function of metal-metal "bond strength", carbonyl configuration around the cluster, ion-pair formation or cation-anion association, and temperature.^{8,9} A detailed ESR study of SCo₂Fe(CO)₉ indicated⁴ that in a heteronuclear cluster the unpaired electron density is unequally distributed over the metallic unit although the radical anion has a reasonably long half-life.

The recent systematic synthesis of a variety of trinuclear clusters ECo₃(CO)₉ (I, E = RSi, RGe),¹⁰ ECo₂M'(CO)₈(Cp) (II, E = RC, RGe, M' = Cr, Mo, W),¹¹ RPCo₂Fe(CO)₉,¹² and EFeCoMo(CO)₈(Cp) (III,¹³ E = RP, S), presented an opportunity to ascertain whether the generalizations formulated above were applicable to clusters with capping groups other than carbon or sulfur and to heteronuclear

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