Organometallics **1985**, *4*, 1025–1030

Binuclear Rhenium Complexes Bridged by Phosphine Bidentate Ligands, $Re_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)_2$, $Re_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}Me_2PCH_2PMe_2)$, and $Re_2(CO)_6(\mu\text{-}Me_2PCH_2PMe_2)_2$. Preparation and Reactions with Alkynes, Water, Methanol, and a Hydrogen Donor[1]

Kang-Wook Lee and Theodore L. Brown*

School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Received October 4, 1984

$Re_2(CO)_6(\mu\text{-dppm})_2$, **1a**, $Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-dmpm})$, **1b**, and $Re_2(CO)_6(\mu\text{-dmpm})_2$, **1c** (dppm = $Ph_2PCH_2PPh_2$; dmpm = $Me_2PCH_2PMe_2$), were synthesized by thermal or photochemical reactions of $Re_2(CO)_8(\mu\text{-}L\frown L)$ [$L\frown L$ = bis(diphenylphosphino)methane or bis(dimethylphosphino)methane] and $L\frown L$. The carbonyl ligands in **1** do not undergo a scrambling process up to 100 °C. The thermal reactions of **1a** and **1b** at high temperature (172 °C) with phenylacetylene yield $(\mu\text{-H})Re_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}CPh)$, **2a**, and $(\mu\text{-H})Re_2(CO)_4(\mu\text{-dppm})(\mu\text{-dmpm})(\mu\text{-C}{\equiv}CPh)$, **2b**, respectively. Reflux of $(\mu\text{-H})Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-C}{\equiv}CPh)$ and $(\mu\text{-H})Re_2(CO)_6(\mu\text{-dmpm})(\mu\text{-C}{\equiv}CPh)$ in *m*-xylene with excess dppm quantitatively yields **2a** and **2b**, respectively. Reflux of **1a** or **1b** in *m*-dichlorobenzene in the presence of water or methanol yields $(\mu\text{-H})Re_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-OR})$ (**3a**, R = H; **3b**, R = Me) or $(\mu\text{-H})Re_2(CO)_4(\mu\text{-dppm})(\mu\text{-dmpm})(\mu\text{-OR})$ (**3c**, R = H; **3d**, R = Me), respectively. Reflux of **1a** or **1b** in 1,2,4-trimethylbenzene results in the formation of $(\mu\text{-H})_2Re_2(CO)_4(\mu\text{-dppm})_2$, **4a**, or $(\mu\text{-H})_2Re_2(CO)_4(\mu\text{-dppm})(\mu\text{-dmpm})$, **4b**, respectively. No evidence was found for a bridging carbonyl complex, $Re_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2$. Reaction of **4a** with CO or phenylacetylene at 138 °C gives **1a** or **2a**, respectively. The alkynyl ligand in **2** undergoes a fluxional process. The ^1H and ^{13}C NMR spectral data of bridging dppm dirhenium carbonyl compounds are compared.

Introduction

Recent work has shown that the carbonyl ligands in $Mn_2(CO)_6(\mu\text{-dppm})_2$ [dppm = bis(diphenylphosphino)methane] undergo a scrambling process on the NMR time scale and the bridging carbonyl in $Mn_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2$ is involved in a wagging motion.[2] $Mn_2(CO)_6(\mu\text{-dppm})_2$ is converted into $Mn_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2$ by loss of CO on heating in *p*-xylene; the reverse reaction also occurs in the presence of CO.[2,3] $Mn_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2$ has been shown to react with various small ligands[4] and acids.[5] Further reactions of the subsequent products have been extensively investigated.[6] We became interested in preparing the analogous rhenium carbonyls $Re_2(CO)_6(\mu\text{-dppm})_2$, $Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-dmpm})$, and $Re_2(CO)_6(\mu\text{-dmpm})_2$ [dmpm = bis(dimethylphosphino)methane] as part of a continuing exploration of the reactions of bridging phosphorus ligand substituted dirhenium complexes with ROH (R = H, Me),[7] alkynes,[8] and alkenes.[9]

The compound $Re_2(CO)_8(\mu\text{-dppm})$ is considerably more reactive than $Re_2(CO)_6(\mu\text{-dppm})_2$. For example, $Re_2(CO)_8(\mu\text{-dppm})$ reacts with Me_3NO in acetonitrile to yield $Re_2(CO)_7(\mu\text{-dppm})(NCMe)$, but the corresponding reaction of $Re_2(CO)_6(\mu\text{-dppm})_2$ does not occur. Photochemical reaction of $Re_2(CO)_8(\mu\text{-dppm})$ with terminal alkyne gives $(\mu\text{-H})Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-C}{\equiv}CR)$; the equivalent reaction of $Re_2(CO)_6(\mu\text{-dppm})_2$ proceeds more slowly. In this research we have found that $Re_2(CO)_6(\mu\text{-dppm})_2$ undergoes decarbonylation at 168 °C; however, $Re_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2$ is not formed. Here we report the synthesis of $Re_2(CO)_6(\mu\text{-dppm})_2$, $Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-dmpm})$, and $Re_2(CO)_6(\mu\text{-dmpm})_2$, and their reactions with alkynes, water, methanol, and a hydrogen atom donor. We also report the thermal reactions of $(\mu\text{-H})Re_2(CO)_6(\mu\text{-}L\frown L)(\mu\text{-C}{\equiv}CR)$ ($L\frown L$ = dppm, dmpm; R = H, Ph) with dppm.

Results

Synthesis of $Re_2(CO)_6(\mu\text{-}L\frown L)_2$ Compounds. Photolysis of $Re_2(CO)_8(\mu\text{-dppm})$ in toluene in the presence of dppm or dmpm at ambient temperature for 12 h results in formation of $Re_2(CO)_6(\mu\text{-dppm})_2$, **1a**, or $Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-dmpm})$, **1b**, respectively. The corresponding reactions of $Re_2(CO)_8(\mu\text{-dmpm})$ with dppm or dmpm give **1b** or $Re_2(CO)_6(\mu\text{-dmpm})_2$, **1c**, respectively. Reflux of $Re_2(CO)_8(\mu\text{-dppm})$ or $Re_2(CO)_8(\mu\text{-dmpm})$ in *m*-xylene (bp 138 °C) in excess of dppm for 6 h also gives **1a** or **1b**, respectively. The yield in both the photochemical and thermal reactions is almost quantitative. Reflux of $Re_2(CO)_{10}$ in *m*-xylene in excess of dppm for 12 h leads to **1a** in 65% yield. All three compounds (**1a–c**) were characterized by IR, ^1H NMR, ^{13}C NMR, and mass spectra (Table I) and elemental analyses (Experimental Section).

The IR spectrum of **1a** in the carbonyl stretching region (1959 (m), 1927 (vs), 1871 (s) cm^{-1}) is very similar in pattern to that of $Mn_2(CO)_6(\mu\text{-dppm})_2$ or $Mn_2(CO)_6(\mu\text{-depm})_2$ (depm = $Et_2PCH_2PPh_2$) (1917 (s), 1900 (vs), 1855 (m) cm^{-1}).[10] The ^1H NMR spectra of **1a** and **1c** shows quintets for the methylene protons of the bridging ligands and a singlet for the methyl groups in **1c**, indicating that

---

[1] This research was supported by the National Science Foundation through Research Grant NSF CHE 83-12331.

[2] (a) Marsella, J. A.; Caulton, K. G. *Organometallics* **1982**, *1*, 274. (b) Caulton, K. G.; Adair, P. *J. Organomet. Chem.* **1976**, *114*, C11.

[3] (a) Commons, C. J.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1663. (b) Colton, R.; Commons, C. J. *Ibid.* **1975**, *28*, 1673.

[4] (a) Turney, T. W. *Inorg. Chim. Acta.* **1982**, *64*, L141. (b) Benner, L. S.; Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1977**, *159*, 289. (c) Benner, L. S.; Balch, A. L. *J. Organomet. Chem.* **1977**, *135*, 339.

[5] Aspinall, H. C.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 724.

[6] (a) Aspinall, H. C.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 838. (b) Aspinall, H. C.; Deeming, A. J.; Donovan-Mutz, S. *Ibid.* **1983**, 2669.

[7] Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *Organometallics* **1984**, *3*, 404.

[8] Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 631.

[9] Lee, K.-W.; Brown, T. L. *Organometallics*, in press.

[10] Wolff, T. E.; Klemann, L. P. *Organometallics* **1982**, *1*, 1667.

Table I. Spectroscopic Data for $Re_2(CO)_6(\mu\text{-}\widehat{L\ L})(\mu\text{-}\widehat{L'\ L'})$

	$\widehat{L\ L}$	$\widehat{L'\ L'}$	IR ν_{CO},[a] cm^{-1}	^{1}H NMR δ [b]	^{13}C NMR δ [b,c]	MS,[d] *m/e*
1a	dppm	dppm	1959 (m), 1927 (vs), 1871 (s)	7.29–7.38 (m, 40 H), 4.24 (quintet, 4 H, $J_{PH} + J_{P'H} = 8.2$ Hz)	210.5 (s, 4 C), 196.8 (s, 2 C)	1310
1b	dppm	dmpm	1952 (m), 1920 (vs), 1868 (s)	7.16–7.51 (m, 20 H), 4.17 (t, 2 H, $J_{PH} = 9.8$ Hz), 3.00 (t, 2 H, $J_{PH} = 10.1$ Hz), 1.80 (t, 12 H, $J_{PH} = 3.6$ Hz)	211.6 (s, 4 C), 197.0 (s, 2 C)	1062
1c	dmpm	dmpm	1943 (m), 1912 (vs), 1861 (s)	2.88 (quintet, 4 H, $J_{PH} + J_{P'H} = 8.6$ Hz), 1.72 (s, 24 H)	*e*	814

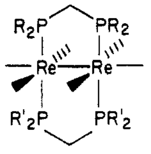
[a] Taken in toluene solution. [b] Taken in $CDCl_3$. [c] Carbonyl region. [d] Molecular ion peak based on ^{187}Re. [e] Not taken.

Table II. Spectroscopic Data for $(\mu\text{-H})Re_2(CO)_4(\mu\text{-}\widehat{L\ L})(\mu\text{-}\widehat{L'\ L'})(\mu\text{-}C{\equiv}CR)$

	R	$\widehat{L\ L}$	$\widehat{L'\ L'}$	IR ν_{CO},[a] cm^{-1}	^{1}H NMR δ [b]	^{13}C NMR δ [c]	MS,[d] *m/e*
2a	Ph	dppm	dppm	1936 (s), 1882 (s)	7.06–7.40 (m, 45 H), 3.71 (m, 2 H), 3.15 (m, 2 H), −11.65 (quintet, 1 H, $J_{PH} = 7.5$ Hz)	199.9 (s, 2 C), 196.8 (s, 2 C)	1356
2b	Ph	dppm	dmpm	1929 (s), 1878 (s)	7.07–7.46 (m, 25 H), 3.54 (q, 1 H, $J = 11.0$ Hz), 3.07 (q, 1 H, $J = 11.0$ Hz), 2.61 (q, 1 H, $J = 11.3$ Hz), 1.66 (q, 1 H, $J = 11.3$ Hz), 1.76 (t, 6 H, $J_{PH} = 2.6$ Hz), 1.57 (t, 6 H, $J_{PH} = 2.7$ Hz), −12.03 (quintet, 1 H, $J_{PH} = 7.5$ Hz)	201.0 (s, 2 C), 197.3 (s, 2 C)	1108
2d	H	dppm	dppm	1935 (s), 1881 (s)	7.20–7.42 (m, 40 H), 4.11 (s, 1 H), 3.98 (m, 2 H), 3.08 (m, 2 H), −11.89 (quintet, 1 H, $J_{PH} = 7.1$ Hz)	199.6 (s, 2 C), 196.5 (s, 2 C)	1280

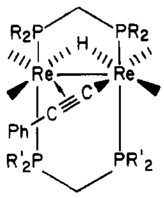
[a] Taken in toluene solution. [b] Taken in CD_2Cl_2. [c] Carbonyl region. [d] Molecular ion peak based on ^{187}Re.

the two bridging ligands are in symmetric positions. The ^{13}C NMR spectrum of **1a** in the carbonyl region at ambient temperature exhibits two singlets [δ 210.5 (s, 4 C), 196.8 (s, 2 C)]. A similar spectrum was observed with $Mn_2(CO)_6(\mu\text{-dppm})_2$.[2] The field desorption mass spectra (FDMS) of **1a**, **1b**, and **1c** show the molecular ion peaks at *m/e* 1310, 1062, and 814, respectively. On the basis of these spectroscopic data, we propose that **1** has the same structure as $Mn_2(CO)_6(\mu\text{-dppm})_2$. The peak at 210.5 ppm in ^{13}C NMR spectrum of **1a** corresponds to four equatorial carbonyls and that at 196.8 ppm to two axial carbonyls. The spectrum is unchanged at 100 °C.



1a, R = R' = Ph
b, R = Ph; R' = Me
c, R = R' = Me

Reactions of 1a and 1b with Phenylacetylene, Water, and Methanol. Reflux of **1a** or **1b** in *m*-dichlorobenzene solution (bp 172 °C) with an excess of phenylacetylene for 6–12 h yields $(\mu\text{-H})Re_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}CPh)$, **2a** (65%), or $(\mu\text{-H})Re_2(CO)_4(\mu\text{-dppm})(\mu\text{-dmpm})(\mu\text{-}C{\equiv}CPh)$, **2b** (60%), respectively, characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectra (Table II). The hydrido resonances in the ^{1}H NMR spectra of **2a** and **2b** are quintets, indicating that four phosphorus atoms are symmetrically located with respect to the bridging hydride. The methylene protons of the bridging phosphorus ligands of **2b** give rise to four quartets. This evidence of magnetic nonequivalence is consistent with observations in $(\mu\text{-H})Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-X})$ (X = OH, Cl, C≡CPh).[7-9] The ^{13}C NMR spectra of **2a** and **2b** exhibit two singlets of equal intensity, indicating that no carbonyl is located trans to the phosphorus atom. The FDMS of **2a** and **2b** show molecular ion peaks at *m/e* 1356 and 1108, respectively. On the basis of these spectroscopic data, the structure shown below for **2** is proposed. The equivalent reaction of **1c** does not yield a significant amount of **2c**.



2a, R = R' = Ph
b, R = Ph; R' = Me
c, R = R' = Me

Reflux of **1a** or **1b** in *m*-dichlorobenzene in the presence of ROH (R = H, Me) for 6 h gives $(\mu\text{-H})Re_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-OR})$ (**3a**, R = H; **3b**, R = Me) or $(\mu\text{-H})Re_2(CO)_4(\mu\text{-dppm})(\mu\text{-dmpm})(\mu\text{-OR})$ (**3c**, R = H; **3d**, R = Me), characterized by IR, ^{1}H NMR, and mass spectra (Table III). The IR spectra of **3a** and **3c** show the hydroxo stretching band at 3614 and 3610 cm^{-1}, respectively, and the ^{1}H NMR spectra of **3a** and **3c** in CD_2Cl_2 also show the hydroxo proton peaks at −0.97 and −1.45 ppm, respectively. The appearance of the bridging hydroxo proton in the upfield region (0 to −2 ppm) in the ^{1}H NMR spectrum is consistent with that in $(\mu\text{-H})Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-OH})$.[7]

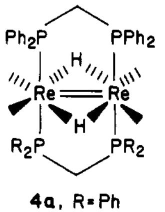
Table III. Spectroscopic Data for $(\mu\text{-H})\mathrm{Re_2(CO)_4}(\mu\text{-dppm})(\mu\text{-L}^\frown\text{L})(\mu\text{-OR})$

	$\mathrm{L}^\frown\mathrm{L}$	R	IR ν_{CO},[a] cm^{-1}	^1H NMR δ [b]	FDMS,[c] *m/e*
3a	dppm	H	1923 (s), 1852 (s)	7.06–7.43 (m, 40 H), 4.55 (m, 2 H), 3.34 (m, 2 H), −0.97 (quintet, 1 H, J_{PH} = 3.0 Hz), −8.34 (quintet, 1 H, J_{PH} = 7.2 Hz)	1272
3b	dppm	Me	1923 (s), 1851 (s)	7.07–7.48 (m, 40 H), 3.98 (s, 3 H), 3.53 (m, 2 H), 3.12 (m, 2 H), −8.93 (quintet, 1 H, J_{PH} = 9.0 Hz)	1286
3c	dmpm	H	1913 (s), 1842 (s)	6.96–7.48 (m, 20 H), 4.68 (q, 1 H, *J* = 10.6 Hz), 3.29 (q, 1 H, *J* = 10.3 Hz), 2.43 (q, 1 H, *J* = 10.6 Hz), 1.62 (q, 1 H, *J* = 12.1 Hz), 1.78 (m, 12 H), −1.45 (br, 1 H), −9.06 (quintet, 1 H, J_{PH} = 7.2 Hz)	1024
3d	dmpm	Me	1913 (s), 1842 (s)	6.96–7.44 (m, 20 H), 4.15 (q, 1 H, *J* = 11.1 Hz), 3.98 (s, 3 H), 3.09 (q, 1 H, *J* = 11.1 Hz), 1.76–2.02 (m, 14 H), −9.31 (quintet, 1 H, J_{PH} = 8.4 Hz)	1038

[a] Taken in CH_2Cl_2. [b] Taken in CD_2Cl_2. [c] Molecular ion peak based on ^{187}Re.

The IR (ν_{CO}) and ^1H NMR (bridging hydride and methylene protons of dppm and dmpm) spectra of 3 are very similar to those of 2, indicating that the two compounds possess analogous structures (refer to Scheme I for the structure of 3).

Reactions of 1a and 1b with Hydrogen Atom Donors or H_2. Reflux of **1a** or **1b** in 1,2,4-trimethylbenzene gives $(\mu\text{-H})_2\mathrm{Re_2(CO)_4}(\mu\text{-dppm})_2$, **4a** (50%), or $(\mu\text{-H})_2\mathrm{Re_2(CO)_4}(\mu\text{-dppm})(\mu\text{-dmpm})$, **4b** (40%). The same reaction in the presence of a good hydrogen atom donor such as 9,10-dihydroanthracene or decalin results in a higher yield (65%) of 4. The IR spectrum of the reaction mixture does not show a bridging carbonyl peak, indicating that $\mathrm{Re_2(CO)_4}(\mu\text{-CO})(\mu\text{-L}^\frown\text{L})_2$ either is not formed or is unstable. The hydrido peak in the ^1H NMR spectrum of **4a** is a quintet; the IR spectrum of **4a** (1929 (s), 1866 (s, br) cm^{-1}) is very similar to that of **2a** (1936 (s), 1882 (s) cm^{-1}), indicating that the two compounds have a similar orientation of CO groups. Accordingly, we propose the structure shown below for 4. The Re–Re bond is formulated as a double bond to attain an 18-electron count about each Re, as in $H_2Re_2(CO)_8$.[11]



4a, R = Ph
b, R = Me

Diffusion of H_2 through a refluxing solution of **1a** in *m*-dichlorobenzene (172 °C) also leads to **4a** (~60%).

When **4a** is refluxed in *m*-xylene in the presence of phenylacetylene or CO, it is quantitatively converted to **2a** or **1a**, respectively. However, under the same conditions, **4a** does not react with PPh_3 or $P(OMe)_3$.

Reaction of $(\mu\text{-H})\mathrm{Re_2(CO)_6}(\mu\text{-L}^\frown\text{L})(\mu\text{-C}{\equiv}\text{CR})$ ($\mathrm{L}^\frown\mathrm{L}$ = dppm, dmpm; R = H, Ph) with dppm. Reflux of $(\mu\text{-H})\mathrm{Re_2(CO)_6}(\mu\text{-dppm})(\mu\text{-C}{\equiv}\text{CPh})$ or $(\mu\text{-H})\mathrm{Re_2(CO)_6}(\mu\text{-dmpm})(\mu\text{-C}{\equiv}\text{CPh})$ in *m*-xylene with an excess of dppm for 6 h quantitatively yields **2a** or **2b**, respectively. The corresponding reaction of $(\mu\text{-H})\mathrm{Re_2(CO)_6}(\mu\text{-dppm})(\mu\text{-C}{\equiv}\text{CH})$ also yields $(\mu\text{-H})\mathrm{Re_2(CO)_4}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CH})$, **2d**. The hydrido peak in the ^1H NMR spectrum of **2d** is also a quintet. The ^{13}C NMR spectrum of **2d** at −80 °C show four singlets of equal intensity (δ 199.7 (s), 198.1 (s), 197.5 (s), 195.1 (s)).

Discussion

On the basis of variable-temperature ^{13}C NMR spectra, which show two singlets (2:1 ratio) at −74 °C and only one singlet above −20 °C, Caulton and Marsella[2] have proposed that the carbonyl ligands in $\mathrm{Mn_2(CO)_6}(\mu\text{-dppm})_2$ undergo a scrambling process. By contrast, the ^{13}C NMR spectrum of **1a** shows two singlets (2:1 ratio) at 17 °C and no significant change at 100 °C. The Re–Re bond distance in a particular dinuclear compound is invariably longer than the Mn–Mn distance in the corresponding structure. The higher activation energy toward CO exchange in **1a** is probably due to the larger metal–metal distance and to the generally higher energy of metal–terminal CO bond dissociation in rhenium carbonyls.

Reflux of $\mathrm{Mn_2(CO)_6}(\mu\text{-dppm})_2$ in *p*-xylene solution (bp 138 °C) is known to give $\mathrm{Mn_2(CO)_4}(\mu\text{-CO})(\mu\text{-dppm})_2$ by loss of one carbonyl ligand.[2,3] **1a** does not undergo decarbonylation under the same conditions. However, reflux of **1a** at higher temperature (168 °C) results in loss of CO to form **4a**, probably by abstraction of hydrogen from the solvent. On the other hand, $(\mu\text{-H})\mathrm{Re_2(CO)_4}(\mu\text{-dppm})_2(\mu\text{-C}{\equiv}\text{CPh})$ wherein the alkynyl ligand bridges two metal atoms is stable, even under the relatively harsh conditions of its formation.

The steps in formation of 2 from 1 are believed to be CO dissociation, alkyne substitution, C–H bond oxidative addition at Re, and alkynyl ligand substitution for CO.[8] The initial step in formation of 3 or 4 from 1 is also expected to be CO dissociation. The pathway for formation of 1 or 2 via reaction of 4 with CO or phenylacetylene is probably ligand substitution on the unsaturated compound, H-H reductive elimination, C-H oxidative addition in the case of phenylacetylene, and another ligand substitution (or π bond formation of the alkynyl ligand into the other metal center).[12] The decreasing order of reactivity, $\mathrm{Re_2(CO)_6}(\mu\text{-dppm})_2 > \mathrm{Re_2(CO)_6}(\mu\text{-dppm})(\mu\text{-dmpm}) > \mathrm{Re_2(CO)_6}(\mu\text{-dmpm})_2$, is consistent with obser-

---

[11] Bennett, M. J.; Graham, W. A. G.; Hoyano, J. K.; Hutcheon, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 6232.

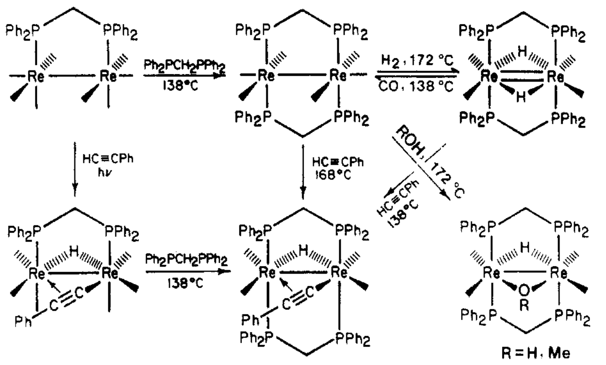
[12] (a) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1056; *J. Organomet. Chem.* **1975**, *85*, C29. (b) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313.

Table IV. Comparison of ^{1}H NMR and ^{13}C NMR Spectral Data for Bridging dppm Dirhenium Carbonyls (δ)[a]

	^{1}H[b]		^{13}C		
	P-CH$_2$-P	$\mathrm{Re}\overset{\mathrm{H}}{—}\mathrm{Re}$	CO trans to P	other COs	ref
dppm	2.86 (t, J_{PH} = 1.5 Hz)				d
$Re_2(CO)_8(\mu$-dppm)	4.35 (t, J_{PH} = 10.0 Hz)		193.9 (t, 2 C, $J_{PC} + J_{P'C}$ = 56.0 Hz)	200.7 (s, 4 C),[b] 189.8 (s, 2 C)	e
$Re_2(CO)_6(\mu$-dppm)$_2$	4.24 (quintet, $J_{PH} + J_{P'H}$ = 8.2 Hz)			210.5 (s, 4 C),[b] 196.8 (s, 2 C)	d
$(\mu$-H)$Re_2(CO)_8(\mu$-C≡CPh)		−13.07 (s)		184.6 (s, 2 C),[c] 182.1 (s, 2 C) 181.6 (s, 4 C)	f, g
$(\mu$-H)$Re_2(CO)_6(\mu$-dppm)-(μ-C≡CPh)	3.11 (q, 1 H, J = 11.4 Hz), 2.57 (q, 1 H, J = 11.8 Hz)	−11.85 (t, J_{PH} = 10.0 Hz)	187.4 (t, 2 C, $J_{PC} + J_{P'C}$ = 71.3 Hz)	192.7 (s, 2 C),[c] 189.8 (s, 2 C)	f
$(\mu$-H)$Re_2(CO)_4(\mu$-dppm)$_2$-(μ-C≡CPh)	3.70 (m), 3.06 (m)	−11.68 (quintet, J_{PH} = 7.5 Hz)		199.9 (s, 2 C),[c] 196.8 (s, 2 C)	d
$(\mu$-H)$_2Re_2(CO)_8$		−9.04 (s)			h
$(\mu$-H)$_2Re_2(CO)_6(\mu$-dppm)	3.13 (t, J_{PH} = 10.8 Hz)	−7.51 (t, J_{PH} = 10.4 Hz)[c]			i
$(\mu$-H)$_2Re_2(CO)_4(\mu$-dppm)$_2$	3.80 (quintet, $J_{PH} + J_{P'H}$ = 9.0 Hz	−6.80 (quintet, J_{PH} = 7.9 Hz)[c]			d

[a] dppm = bis(diphenylphosphino)methane. [b] Taken in CDCl$_3$. [c] Taken in CD$_3$Cl$_2$. [d] This work. [e] Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *Organometallics* **1984**, *3*, 404. [f] Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L., submitted for publication. [g] Nubel, P. O.; Brown, T. L. *Organometallics* **1984**, *3*, 29. [h] Bennett, M. J.; Graham, W. A. G.; Hoyano, J. K.; Hutcheon, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 6232. [i] Prest, D. W.; Mays, M. J.; Raithby, P. R.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1982**, 737.

Scheme I



vations on the manganese analogues.[10,13] The summarized reactions are shown in Scheme I.

Fluxional Behavior of the Bridging Alkynyl Ligand. It has been established that the alkynyl ligand of (μ-H)Re$_2$(CO)$_6$(μ-dppm)(μ-C≡CR)[8] undergoes a rapid fluxional process at room temperature in which the σ and π bonds of the bridging alkynyl group are rapidly interchanged between two metal atoms. Analogous fluxional behavior for the alkynyl ligand of (μ-H)Re$_2$(CO)$_8$(μ-C≡CPh)[14] and (μ-H)$_2$Os$_3$(CO)$_9$(μ_3-alkyne)[15] has also been reported. The variable-temperature ^{13}C NMR spectra of **2d** are shown in Figure 1. Four carbonyl peaks of equal intensity (δ 199.7 (s), 198.1 (s), 197.5 (s), 195.1 (s)) are observed at −80 °C. As the temperature is raised, the peaks coalesce at −48 °C and finally coalesce to two sharp carbonyl peaks above 5 °C (δ 199.4 (s), 196.5 (s)). These results indicate that the alkynyl ligand of **2d** undergoes the type of fluxional process described earlier. The $\Delta G^{\ddagger}_c$ value estimated from the coalescence temperature and resonance separation[16] is 10.3 kcal/mol, almost the same as the value of 10.5 kcal/mol observed for (μ-H)Re$_2$-

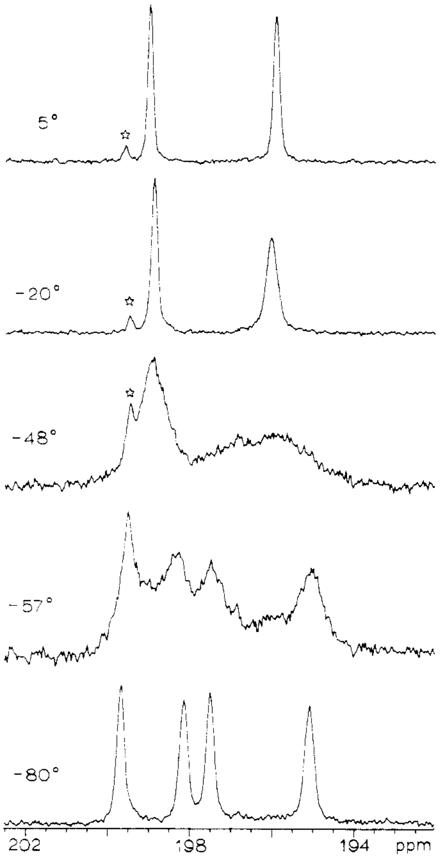


Figure 1. Variable-temperature ^{13}C NMR spectra of (μ-H)-Re$_2$(CO)$_4$(μ-dppm)$_2$(μ-C≡CH), **2d**, in the carbonyl region. The peak marked with an asterisk is due to an impurity.

---

(13) Mn$_2$(CO)$_6$(μ-dmpm)$_2$ does not undergo decarbonylation under conditions where Mn$_2$(CO)$_8$(μ-dppm)$_2$ undergoes such decarbonylation. King, R. B.; RaghuVeer, K. S. "Abstracts of Papers", 185th National Meeting of the American Chemical Society, Seattle, WA, Mar 1983; American Chemical Society: Washington, DC, 1983.

(14) Nubel, P. O.; Brown, T. L. *Organometallics* **1984**, *3*, 29.

(15) Deeming, A. J. *J. Organomet. Chem.* **1978**, *150*, 123.

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

$(CO)_6(\mu\text{-dppm})(\mu\text{-C}\equiv\text{CH})$.[8] The steric and electronic influence of dppm on the ligand exchange process is negligible.

Comparison of ^{1}H and ^{13}C NMR Spectra for Bridging dppm Dirhenium Carbonyls. The ^{1}H and ^{13}C NMR spectra of bridging dppm dirhenium complexes are shown in Table IV. Substitution of dppm for CO in μ-hydrido μ-alkynyl and bis(μ-hydrido) complexes causes a downfield shift of the ^{1}H NMR signals due to the hydrido proton and the methylene protons of dppm. The carbonyl peaks in the ^{13}C NMR spectra also shift downfield as expected, as more dppm replaces CO. The ^{31}P–Re–^{1}H coupling constant is known to depend on the P–Re–H angle.[9] The magnitude of the ^{31}P–Re–^{1}H coupling constant becomes smaller as more dppm is substituted, indicating that the P–Re–H angle becomes more acute, consistent with a shortened Re–Re bond distance. It is noteworthy that the bridging hydrido peaks in the ^{1}H NMR spectrum of bis(μ-hydrido)dirhenium complexes show an unusual downfield chemical shift (−6.80 to −9.04 ppm).[17]

Experimental Section

Experimental details are as described elsewhere.[8,9]

$Re_2(CO)_8(\mu\text{-dppm})$ and $Re_2(CO)_8(\mu\text{-dmpm})$ were prepared from $Re_2(CO)_{10}$ as previously described.[7]

Synthesis of $Re_2(CO)_6(\mu\text{-L}^\frown\text{L})_2$ Compounds. In a typical reaction, $Re_2(CO)_8(\mu\text{-dppm})$ (0.355 g, 0.362 mmol), dppm (0.417 g, 1.085 mmol), and toluene (15 mL) were added into a 50-mL Schlenk flask. The solution was freeze–pump–thaw–degassed and then irradiated at ambient temperature for 12 h. After the liquid portion was removed under reduced pressure, the pure product **1a** was separated as a yellow solid on silica gel coated preparative TLC plates using toluene, hexane, and ethyl acetate (3:3:1) and recrystallized from hexane and methylene chloride. The yield of **1a** was 90% (0.426 g, 0.326 mmol). Anal. Calcd for $C_{56}H_{44}P_4O_6Re_2$ (**1a**): C, 51.37; H, 3.39; P, 9.46. Found: C, 50.46; H, 3.35; P, 9.70.

The corresponding reactions of $Re_2(CO)_8(\mu\text{-dmpm})$ (0.263 g, 0.359 mmol) with dppm (0.420 g, 1.093 mmol) and dmpm (0.141 g, 1.036 mmol) were also carried out as in the previous procedure. **1b** (0.331 g, 87%) and **1c** (0.265 g, 91%) were isolated as yellow solids in the respective reaction. Anal. Calcd for $C_{36}H_{36}P_4O_6Re_2$ (**1b**): C, 40.75; H, 3.42; P, 11.68. Found: C, 40.80; H, 3.55; P, 11.70. The analytical data for **1c** were not satisfactory because a small amount of impurities could not be removed. However, the other spectroscopic data unambiguously support formulation of the major product **1c**. Spectroscopic data for **1a**, **1b**, and **1c** are listed in Table I.

Reflux of $Re_2(CO)_8(\mu\text{-dppm})$ and $Re_2(CO)_8(\mu\text{-dmpm})$ in *m*-xylene with an excess of dppm for 6 h also gave **1a** and **1b**, respectively, in similar yields as in the photochemical reactions. For example, $Re_2(CO)_8(\mu\text{-dppm})$ (0.215 g, 0.219 mmol), dppm (0.252 g, 0656 mmol), and 20 mL of *m*-xylene were added into a 100-mL two-necked flask equipped with a refluxing condenser. The solution was refluxed for 6 h. The pure product was isolated as in the previous procedure.

The one-step reaction of $Re_2(CO)_{10}$ with excess dppm also gave **1a** (65%). $Re_2(CO)_{10}$ (0.270 g, 0.414 mmol), dppm (0.636 g, 1.655 mmol), and *m*-xylene (25 mL) were added into a 100-mL two-necked flask equipped with a refluxing condenser. The solution was refluxed for 8 h. After the liquid was removed under reduced pressure, the pure product **1a** was isolated on a preparative TLC plate using toluene, hexane, and ethyl acetate (3:3:1). The yield of **1a** was 65% (0.352 g, 0.269 mmol). The minor products were not characterized.

Reaction of 1a and 1b with Phenylacetylene, Water, or Methanol. **1a** (0.215 g, 0.164 mmol), phenylacetylene (0.5 mL), and *m*-dichlorobenzene (20 mL) were added into a 100-mL two-necked flask equipped with a condenser. The solution was refluxed for 6 h. The liquid portion was removed under reduced pressure, and the remaining mixture was applied to a silica gel preparative TLC plate for separation. The solvent system of methylene chloride, hexane, and toluene (2:1:1) was used as the developing solvent. The pure product was isolated and recrystallized from hexane and methylene chloride as a yellow solid. The yield of **2a** was 65% (0.140 g, 0.103 mmol). Anal. Calcd for $C_{62}H_{50}P_4O_4Re_2$ (**2a**): C, 54.94; H, 3.72; P, 9.14. Found: C, 55.39; H, 3.91; P, 9.22.

The corresponding reaction of **1b** (0.198 g, 0.186 mmol) was also carried out for 12 h as in the previous procedure. **2b** (0.123 g, 0.111 mmol, 60%) was isolated. The spectroscopic data for **2a** and **2b** are listed in Table II.

The reactions of **1a** and **1b** with ROH (R = H, Me) in *m*-dichlorobenzene were carried out for 6 h as in the previous procedure. The yields for **3a**, **3b**, **3c**, and **3d** are 70, 45, 68, and 52%, respectively. The spectroscopic data are listed in Table III. Anal. Calcd for $C_{54}H_{46}P_4O_5Re_2$ (**3a**): C, 51.02; H, 3.65; P, 9.75. Found: C, 49.52; H, 3.63; P, 9.53. Anal. Calcd for $C_{35}H_{40}P_4O_5Re_2$ (**3d**): C, 40.54; H, 3.89; P, 11.95. Found: C, 40.81; H, 3.74; P, 11.71.

Reaction of 1a and 1b with Hydrogen Donors or Hydrogen. **1a** (0.215 g, 0.164 mmol) and 1,2,4-trimethylbenzene (20 mL) were added into a 100-mL two-necked flask equipped with a condenser. The solution was refluxed for 6 h. The solvent was removed under reduced pressure, and the remaining mixture was dissolved in methylene chloride. As hexane was added into the CH_2Cl_2 solution, a yellow solid precipitated. The product was recrystallized from hexane and methylene chloride. The yield was 50%. The corresponding reaction in the presence of a hydrogen donor such as decalin or 9,10-dihydroanthracene gives a higher yield of **4a** (~65%): IR (CH_2Cl_2) ν_{CO} 1929 (s), 1866 (s, br) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.80 (quintet, 4 H, $J_{PH} + J_{P'H}$ = 9.0 Hz),[18] −6.80 (quintet, 2 H, J_{PH} = 7.9 Hz); FDMS M$^+$ at *m/e* 1256. Anal. Calcd for $C_{54}H_{46}P_4O_4Re_2$ (**4a**): C, 51.67; H, 3.69; P, 9.87. Found: C, 52.37; H, 3.77; P, 10.21.

The corresponding reaction of **1b** (0.099 g, 0.093 mmol) was also carried out for 18 h as in the previous procedure. The yield of **4b** was 50%: IR (CH_2Cl_2) ν_{CO} 1920 (s), 1857 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.38 (m, 8 H), 7.16 (m, 12 H), 3.71 (t, 2 H, J_{PH} = 10.3 Hz), 2.29 (t, 2 H, J_{PH} = 10.3 Hz), 1.91 (t, 12 H, $J_{PH} + J_{P'H}$ = 6.6 Hz), −7.29 (quintet, 2 H, J_{PH} = 8.2 Hz); FDMS M$^+$ at *m/e* 1008. Anal. Calcd for $C_{34}H_{38}P_4O_4Re_2$ (**4b**): C, 40.56; H, 3.80; P, 12.30. Found: C, 39.89; H, 3.78; P, 12.34.

Diffusion of H_2 through a refluxing solution of **1a** or **1b** in *m*-dichlorobenzene for 5 h also gives **4a** (60%) or **4b** (55%).

Reaction of $(\mu\text{-H})Re_2(CO)_6(\mu\text{-L}^\frown\text{L})(\mu\text{-C}\equiv\text{CR})$ ($\text{L}^\frown\text{L}$ = dppm, dmpm; R = H, Ph) with dppm. In a typical reaction, $(\mu\text{-H})Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-C}\equiv\text{CPh})$ (0.125 g, 0.122 mmol) and dppm (0.187 g, 0.486 mmol) were added into a 100-mL two-necked flask containing *m*-xylene (25 mL) and equipped with a condenser. The solution was refluxed for 6 h. The liquid portion was removed under reduced pressure. The yellow solid **2a** was isolated by preparative TLC and recrystallization using methylene chloride, hexane, and toluene (2:1:1). The yield was 82%.

The corresponding reactions of $(\mu\text{-H})Re_2(CO)_6(\mu\text{-dmpm})(\mu\text{-C}\equiv\text{CPh})$ and $(\mu\text{-H})Re_2(CO)_6(\mu\text{-dppm})(\mu\text{-C}\equiv\text{CH})$ were also performed as in the previous procedure. **2b** (76%) and **2d** (70%) were isolated. The spectroscopic data for **2d** are listed in Table II.

Acknowledgment. High-field NMR facilities were provided by the National Science Foundation (NSF Grant CHE 79-16100). High-resolution mass spectrometer facilities were supported in part by a grant from the National Institute of General Medicine Sciences (GM 27029). The ZAB-HF mass spectrometer was purchased in part with grants from the Division of Research Resources, National Institutes of Health (RR 01575), and the National Science Foundation (PCM 8121494).

Registry No. **1a**, 95648-63-8; **1b**, 95648-64-9; **1c**, 90624-20-7; **2a**, 95648-65-0; **2b**, 95648-66-1; **2d**, 95648-67-2; **3a**, 95648-68-3; **3b**,

---

[17] The hydrido peak in the ^{1}H NMR spectrum of $(\mu\text{-H})_2Mn_2(CO)_4(\mu\text{-dppm})_2$ appears at δ − 15.40 (quintet, J_{PH} = 18.7 Hz); refer to ref 6a.

[18] The apparent H_{PH} is the average of J_{PH} and $J_{P'H}$; Balc, A. L. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. Ed.; Plenum Press: New York, 1983.

95648-69-4; **3c**, 95648-70-7; **3d**, 95648-71-8; **4a**, 95648-72-9; **4b**, 95648-73-0; (μ-H)$Re_2(CO)_8$(μ-C≡CPh), 82621-44-1; (μ-H)$Re_2(CO)_6$(μ-dppm)(μ-C≡CPh), 94111-25-8; $Re_2(CO)_8$(μ-dppm), 82292-83-9; $Re_2(CO)_8$(μ-dmpm), 88271-76-5; $Re_2(CO)_{10}$, 14285-68-8; (μ-H)$Re_2(CO)_6$(μ-dmpm)(μ-C≡CPh), 94111-26-9; (μ-H)$Re_2(CO)_6$(μ-dppm)(μ-C≡CH), 94090-60-5; $Re_2(CO)_4$(μ-CO)(μ-dppm)$_2$, 95674-03-6; $Re_2(CO)_4$(μ-CO)(μ-dppm)(μ-dmpm), 95674-04-7; dppm, 2071-20-7; dmpm, 64065-08-3; HC≡CPh, 536-74-3.

Photochemical Reactions of $Re_2(CO)_9L$, 1,2-$Re_2(CO)_8L_2$, and $Re_2(CO)_8(\mu\text{-}\overset{\frown}{L\;L})$ with Alkenes[1]

Kang-Wook Lee and Theodore L. Brown*

School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Received August 27, 1984

The photochemical reactions of $Re_2(CO)_9L$ (L = PMe_3, PPh_3) with ethylene give (μ-H)$Re_2(CO)_8$(μ-CH=CH_2), (μ-H)$Re_2(CO)_7$(μ-CH=CH_2)L (**1**, L = PMe_3; **2**, L = PPh_3) and (μ-H)$Re_2(CO)_6$(μ-CH=CH_2)L_2 (**3a**, L = PMe_3; **3b**, L = PPh_3). There are four isomers each of **1** and **2** relating to the locations of the phosphine ligand. Photolysis of 1,2-$Re_2(CO)_8L_2$ (L = PMe_3, PPh_3) in the presence of ethylene yields mainly **3a** or **3b**. The equivalent reaction of a 3:2 mixture of $Re_2(CO)_{10}$ and 1,2-$Re_2(CO)_8(PMe_3)_2$ yields (μ-H)-$Re_2(CO)_8$(μ-CH=CH_2) and **1**; that of the 1:1 mixture of 1,2-$Re_2(CO)_8(PMe_3)_2$ and 1,2-$Re_2(CO)_8(PPh_3)_2$ gives (μ-H)$Re_2(CO)_6$(μ-CH=CH_2)(PMe_3)(PPh_3) as one of several products. The results are consistent with metal–metal bond cleavage as the important primary photoprocess. The photochemical reactions of $Re_2(CO)_8$(μ-dmpm), -(μ-dppe), and -(μ-dmpe) with H_2C=CHR (R = H, Me) proceed very slowly to give (μ-H)$Re_2(CO)_6$(μ-dmpm)(μ-CH=CHR), **4**, (μ-H)$Re_2(CO)_6$(μ-CH=CHR)(dppe), **5**, and (μ-H)$Re_2(CO)_6$(μ-CH=CHR)(dmpe), **6**. These reactions appear to proceed mainly by photodissociation of CO. Coordination of dmpe and dppe has undergone rearrangement to a chelate configuration. The μ-alkenyl ligand of **4** undergoes a rapid fluxional process at ambient temperature in which the σ- and π-bonds of the alkenyl group are interchanged between the bridged rhenium atoms.

Introduction

The mechanism of photolytic substitution reactions of $M_2(CO)_{10}$ (M = Mn, Re) with various ligands has been extensively studied. Reversible homolytic metal–metal bond cleavage, thermal substitution of photogenerated $\cdot M(CO)_5$ radicals, and recombination of substituted radicals have been proposed as the major reaction pathways (eq 1–3).[2] Crossover experiments with $^{185}Re_2(CO)_{10}$ and

$$M_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} 2\cdot M(CO)_5 \tag{1}$$

$$\cdot M(CO)_5 \xrightarrow{L} \cdot M(CO)_4L + CO \tag{2}$$

$$2\cdot M(CO)_4L \rightarrow 1,2\text{-}M_2(CO)_8L_2 \tag{3}$$

$^{187}Re_2(CO)_{10}$ have also provided evidence for a reversible metal–metal bond homolysis as a primary photoprocess.[3] On the other hand, recent studies of $Mn_2(CO)_{10}$,[4] $Mn_2(CO)_8(PR_3)_2$,[5] and $Re_2(CO)_8L_2$ (L = PR_3, AsR_3)[6] show that photochemical CO dissociative loss does compete with metal–metal bond homolysis when UV radiation of wavelength >310 nm is employed. The photochemical reaction of $Re_2(CO)_{10}$ with alkenes has been recently reported to yield (μ-H)$Re_2(CO)_8$(μ-CH=CHR) (R = H, CH_3, *n*-C_4H_9).[7,8] The proposed pathway for formation of these compounds involves metal–metal bond homolysis as a major process. However, there is no direct evidence either for the metal–metal bond cleavage or for CO dissociation in those reactions. Here we report the photochemical reactions of $Re_2(CO)_9L$, 1,2-$Re_2(CO)_8L_2$ (L = PMe_3, PPh_3),[9] a mixture of $Re_2(CO)_{10}$ and 1,2-$Re_2(CO)_8L_2$, and a mixture of $Re_2(CO)_8L_2$ and $Re_2(CO)_8L'_2$ with ethylene, which provide evidence for metal–metal bond cleavage. We also report the photochemical reaction of $Re_2(CO)_8(\mu\text{-}\overset{\frown}{L\;L})$ ($\overset{\frown}{L\;L}$ = bis(dimethylphosphino)methane (dmpm), bis(diphenylphosphino)ethane (dppe), and bis(dimethylphosphino)ethane (dmpe)), with alkenes as an extension of a previous study of the reactions of bridging phosphine ligand substituted dirhenium octacarbonyls with water, methanol, and alkynes.[10,11]

Results and Discussion

Photochemical Reactions of $Re_2(CO)_9L$ (L = PMe_3, PPh_3) with Ethylene. Photolysis of *eq*-$Re_2(CO)_9(PMe_3)$[9] in toluene in the presence of ethylene at ambient temperature for 2 h results in formation of (μ-H)$Re_2(CO)_8$(μ-CH=CH_2)[7] (25%), (μ-H)$Re_2(CO)_7$(μ-CH=CH_2)(PMe_3), **1** (60%), and (μ-H)$Re_2(CO)_6$(μ-CH=CH_2)$(PMe_3)_2$, **3a** (3%). The corresponding reaction of *ax*-$Re_2(CO)_9(PPh_3)$ gives (μ-H)$Re_2(CO)_8$(μ-CH=CH_2) (20%), (μ-H)$Re_2(CO)_7$(μ-CH=CH_2)(PPh_3), **2** (44%), and (μ-H)$Re_2(CO)_6$(μ-CH=CH_2)$(PPh_3)_2$, **3b** (24%). All compounds are characterized

---

[1] This research was sponsored by the National Science Foundation through Research Grant NSF CHE 81-19525 and 83-12331.

[2] (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (b) Morse, D. L.; Wrighton, M. S. *Ibid.* **1976**, *98*, 3931. (c) Byers, B. H.; Brown, T. L. *Ibid.* **1975**, *97*, 947. (d) Kidd, D. R.; Brown, T. L. *Ibid.* **1978**, *100*, 4095. (e) Brown, T. L. *Ann. N. Y. Acad. Sci.* **1980**, *333*, 80.

[3] Stolzenberg, A. M.; Muetterties, E. *J. Am. Chem. Soc.* **1983**, *105*, 822.

[4] (a) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934. (b) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249. (c) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536. (d) Pöe, A.; Fox, A. *J. Am. Chem. Soc.* **1980**, *102*, 2497. (e) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.

[5] Herrick, R. S.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 4550.

[6] Hanckel, J. M.; Brown, T. L., unpublished results.

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

[8] Franzreb, K.-H.; Kreiter, C. G. *J. Organomet. Chem.* **1983**, *246*, 189.

[9] The numerical prefixes in compound names denote the metal centers. The stereochemistry of ligand placement, where known, is denoted by the terms ax (for axial) and eq (for equatorial).

[10] Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *Organometallics* **1984**, *3*, 404.

[11] Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 631.

0276-7333/85/2304-1030$01.50/0