Organometallics **1985**, *4*, 1030–1036

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$\equiv$CPh), 82621-44-1; (μ-H)Re$_2$(CO)$_6$(μ-dppm)(μ-C$\equiv$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$\equiv$CPh), 94111-26-9; (μ-H)Re$_2$(CO)$_6$(μ-dppm)(μ-C$\equiv$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$\equiv$CPh, 536-74-3.

Photochemical Reactions of Re$_2$(CO)$_9$L, 1,2-Re$_2$(CO)$_8$L$_2$, and Re$_2$(CO)$_8$(μ-$\overset{\frown}{\mathrm{L\ L}}$) with Alkenes[1]

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The photochemical reactions of Re$_2$(CO)$_9$L (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)$_8$L$_2$ (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$_2$C=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 ·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

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

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

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

^{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)$_8$L$_2$ (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$_4$H$_9$).[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)$_9$L, 1,2-Re$_2$(CO)$_8$L$_2$ (L = PMe$_3$, PPh$_3$),[9] a mixture of Re$_2$(CO)$_{10}$ and 1,2-Re$_2$(CO)$_8$L$_2$, and a mixture of Re$_2$(CO)$_8$L$_2$ and Re$_2$(CO)$_8$L$'_2$ with ethylene, which provide evidence for metal–metal bond cleavage. We also report the photochemical reaction of Re$_2$(CO)$_8$(μ-$\overset{\frown}{\mathrm{L\ L}}$) ($\overset{\frown}{\mathrm{L\ L}}$ = 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)$_9$L (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

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[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

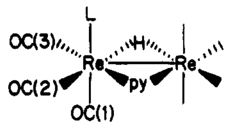
Table I. ^{1}H NMR Spectra of (μ-H)$Re_2(CO)_7$(μ-CH=CH_2)(PMe_3), 1 (δ)[a]

compd	bridging hydride	vinyl protons
1a	−14.75 (d, J_{PH} = 18.8 Hz)	6.58 (dd, J_{HH} = 15.6 and 11.2 Hz) 5.77 (dd, J_{HH} = 11.2 and 2.2 Hz) 4.12 (dd, J_{HH} = 15.6 and 2.2 Hz)
1b	−14.54 (d, J_{PH} = 13.6 Hz)	7.41 (dd, J_{HH} = 16.7 and 10.7 Hz) 5.80 (dd, J_{HH} = 10.7 and 3.3 Hz) 3.93 (dd, J_{HH} = 16.7 and 3.3 Hz)
1c	−14.54 (d, J_{PH} = 13.6 Hz)	7.41 (dd, J_{HH} = 16.7 and 10.7 Hz) 5.80 (dd, J_{HH} = 10.7 and 3.3 Hz) 3.88 (dd, J_{HH} = 16.7 and 3.3 Hz)
1d	−14.08 (d, J_{PH} = 8.6 Hz)	6.60 (dd, J_{HH} = 17.2 and 11.2 Hz) 6.23 (dd, J_{HH} = 11.2 and 3.1 Hz) 4.61 (dd, J_{HH} = 17.2 and 3.1 Hz)

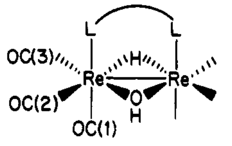
[a] Taken in $CDCl_3$.

by IR, ^{1}H NMR, and field desorption mass spectra (FDMS). 1 has four major isomers, depending on the location of the phosphine ligand. Although each compound could not be separated, decoupling techniques and measurement of integrated intensities in the ^{1}H NMR spectra have made it possible to identify four independent sets of the vinyl and bridging hydrido protons, as shown in Table I.

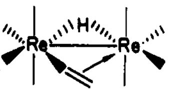
Since the mutual orientation of coordination spheres about the Re–Re bond is eclipsed in (μ-H)$_2$$Re_2(CO)_8$,[12] ($\mu$-H)$Re_2(CO)_7$($\mu$-$NC_5H_4$)L (L = CO, $ONMe_3$),[13] I, and (μ-H)$Re_2(CO)_6$(μ-dppm)(μ-OH),[10] II, a similar orientation is to be expected in 1 and 2. The magnitude of the ^{1}H–M–^{31}P coupling constant generally depends on the H–M–P angle. The larger the angle, the larger the coupling constant.[14] The H–Re–L angles in I and II decrease in the order H–Re–C(2) (164–172°) > H–Re–L (86–100°) ≳ H–Re–C(1) (80–88°) > H–Re–C(3) (71–85°). The phosphine ligand in 1 and 2 can be located at four sites analogous to sites L, C(1), C(2), and C(3) in I or II, giving rise to the four isomers alluded to above and identified in the ^{1}H NMR spectra. Assuming an analogous relationship between the magnitude of the ^{1}H–Re–^{31}P coupling constant and H–Re–P angle, the structures of the four isomers can be partially assigned. As shown in Table I, the ^{1}H–Re–^{31}P coupling constants decrease in the order **1a** (18.8 Hz) > **1b** ≈ **1c** (13.6 Hz) > **1d** (8.6 Hz), so we can assign the location of the phsophine ligand as shown below. The alkenyl ligand in dirhenium complexes is known to undergo a rapid fluxional process,[7] so the location of the phosphine ligand on either rhenium center at the corresponding site gives the same compound. The yields of the four isomers, estimated by ^{1}H NMR integration using a standard sample are 15, 18, 18, and 13% for **1a**, **1b**, **1c**, and **1d**, respectively. The hydrido protons in **1b** and **1c** exhibit exactly the same chemical shift and coupling constant, but the vinyl protons show different chemical shifts, indicating that the two "axial" phosphine ligand locations are distinguishable in terms of the vinyl ligands as would be expected from the presumed structure.[7a,15]



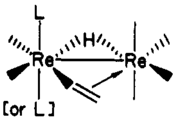
I, L = CO; $ONMe_3$



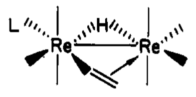
II, $\overset{\frown}{L\ L}$ = dppm



1a



1b (or 1c), L = PMe_3



1d

We cannot identify all the vinyl protons in **2** because of the huge phenyl proton peaks. However, it is reasonable to assume that **2** exhibits the same isomerism as **1**, on the basis of three major hydrido peaks in the ^{1}H NMR spectrum ($CDCl_3$) [δ −13.61 (d, J_{PH} = 8.4 Hz), −13.92 (d, J_{PH} = 16.7 Hz), −14.01 (d, J_{PH} = 11.1 Hz); the relative ratios are 11:3:2]. Similar spectroscopic data were obtained for **2** prepared via a different route.[15] Clearly, the geometry of products in both cases does not depend on the orientation of phosphines in the reactants.

Photochemical Reactions of 1,2-$Re_2(CO)_8L_2$ (L = PMe_3, PPh_3) with Ethylene. The photochemical reaction of 1,2-*dieq*-$Re_2CO)_8(PMe_3)_2$ with ethylene in toluene at ambient temperature for 18 h results in formation of **3a** (66%) and **1** (17%). The corresponding reaction of 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$ for 3 h yields **3b** (65%) and **2** (15%). Carbonyl stretching modes of **3a** are observed at 2085 (w), 1999 (s), 1943 (s), 1920 (s), and 1892 (s) cm^{-1} in toluene. The ^{1}H NMR spectrum of **3a** in $CDCl_3$ shows the vinyl proton peaks [δ 6.21 (ddd, 1 H, J_{HH} = 15.8 and 9.6 Hz, J_{PH} = 11.0 Hz), 5.80 (dd, 1 H, J_{HH} = 9.6 and 3.2 Hz), 4.04 (dd, 1 H, J_{HH} = 15.8 and 3.2 Hz)] and the bridging hydrido peak [δ − 14.01 (dd, 1 H, J_{PH} = 19.0 and 11.1 Hz)]. In the case of **3b**, the vinyl proton peaks cannot be resolved due to the huge phenyl peaks; however, a doublet of doublets at −11.99 ppm (J_{PH} = 21.8 and 11.2 Hz) was also observed. The ^{13}C NMR spectrum of **3b** in the carbonyl region displays six peaks of equal intensity at δ 194.2 (t, J_{PC} = 6.1 Hz), 193.9 (d, J_{PC} = 9.0 Hz), 192.2 (d, J_{PC} = 57.0 Hz), 185.1 (s), 183.9 (d, J_{PC} = 5.9 Hz), and 183.4 (d, J_{PC} = 7.3 Hz). The only peak with a large coupling constant (57.0 Hz) corresponds to the carbonyl trans to the phosphorus atom. The IR spectrum of **3b** (2096 (w), 2014 (s), 1995 (w), 1963 (m), 1925 (m), 1903 (m) cm^{-1}) is similar to that of **3a**. The ^{1}H NMR spectra of **3a** and **3b** exhibit two more minor hydrido peaks (a doublet of doublets and a triplet). However, the major peaks have more than 80% of the total integrated intensities of hydrido peaks, indicating that **3** is the predominant isomeric product. The

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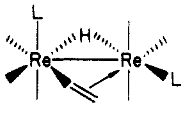
[12] Bennett, M. J.; Graham, W. A. G.; Hoyano, J. K.; Hutchenon, W. L. *J. Am Chem. Soc.* **1972**, *94*, 6232.

[13] Nubel, P. O.; Wilson, S. R.; Brown, T. L. *Organometallics* **1983**, *2*, 515.

[14] It is generally found that ^2J(A–M–B)(A, B = ^{13}C, ^{31}P, ^{1}H) is large when A and B are mutually trans and is small when A and B are mutually cis: (a) Mann, B. E. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1974; Vol. XII. (b) Pregosin, P. S.; Kunz, P. W. In "NMR Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1979; Vol. XVI.

[15] Nubel, P. O. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1983.

field desorption mass spectra of **3a** and **3b** show the molecular ion peaks at *m/e* 722 and 1094, respectively. The doublet of doublets and the relatively large coupling constants for the bridging hydride suggest that the two phosphorus atoms are not symmetrically located with respect to the hydrido proton and that the H–Re–P angles are relatively large. On the basis of these spectroscopic data, we propose that the predominant isomeric product in **3** has the structure shown below.



3a, L = PMe$_3$
b, L = PPh$_3$

The absence of $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$ among the products indicates that alkene substitution for CO is favored over that for the phosphine. The relative reaction rate based on consumption of reactants is much slower with 1,2-$Re_2(CO)_8(PMe_3)_2$ ($t_{1/2}$ = 6 h) than with 1,2-$Re_2(CO)_8(PPh_3)_2$ ($t_{1/2}$ = 1 h), indicating that the $\cdot Re(CO)_4(PMe_3)$ radical may be less labile toward alkene substitution than $\cdot Re(CO)_4(PPh_3)$.[16]

The reaction of 1,2-$Re_2(CO)_8L_2$ with 1-hexene does not yield a bridging hydrido–alkenyl compound. This suggests steric hindrance of recombination of $\cdot Re(CO)_3L(\text{alkene})$ radicals, or toward oxidative addition, occurring at a later stage.[7] **3b** decomposes under prolonged irradiation (~12 h). 1-Butene and *trans*-2-butene are the byproducts. For ethylene dimerization, the catalytic efficiency of 1,2-$Re_2(CO)_8L_2$ as a starting material is relatively low as compared with $Re_2(CO)_{10}$. We have not investigated the ethylene dimerization mechanism but expect that it would be analogous to that proposed for $Re_2(CO)_{10}$.[17]

Photochemical Reactions of Mixtures of Dinuclear Compounds with Ethylene. Both metal–metal bond homolysis and CO dissociative loss in the photochemical reactions of $Re_2(CO)_8L_2$ (L = CO, PMe$_3$, PPh$_3$) with ethylene are expected to be the major photoprocesses, as in flash photolysis of $M_2(CO)_{10}$ or $Me_2(CO)_8L_2$ (M = Mn, Re; L = PR$_3$).[4-6] However, the reactions of $Re_2(CO)_{10}$, $Re_2(CO)_9L$, and $Re_2(CO)_8L_2$ (L = PMeo, PPh$_3$) do not provide direct evidence either for metal–metal bond homolysis or for CO dissociation. In at least one instance involving bridging ligands it has been shown that the primary photoprocess, metal–metal bond homolysis, is not the major pathway leading to substitution, because of rapid reformation of the metal–metal bond.[11] In the present work we have designed various reactions to provide evidence for metal–metal bond homolysis. The photochemical reaction of $Re_2(CO)_{10}$ with ethylene yields $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$,[7] and the corresponding reaction of 1,2-$Re_2(CO)_8L_2$ mainly gives **3**, as discussed. If these reactions occur mainly via initial homolytic metal–metal bond cleavage as proposed,[7] reactions of solution mixtures of $Re_2(CO)_{10}$/1,2-$Re_2(CO)_8L_2$ or 1,2-$Re(CO)_8(PMe_3)_2$/1,2-$Re_2(CO)_8(PPh_3)_2$ should yield the disproportionated products $(\mu\text{-H})Re_2(CO)_7(\mu\text{-CH=CH}_2)L$ and $(\mu\text{-H})Re_2(CO)_6(\mu\text{-CH=CH}_2)(PMe_3)(PPh_3)$, respectively.

The photochemical reaction of a solution of $Re_2(CO)_{10}$ and 1,2-$Re_2(CO)_8(PMe_3)_2$ in 3:2 ratio with ethylene for 3 h gives 41% yield of $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$ and 46% yield of **1** and an insignificant amount of **3a**. Reaction of $Re_2(CO)_{10}$ and 1,2-$Re_2(CO)_8(PMe_3)_2$ in 1:1 ratio yields $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$ (16%), **1** (57%), and **3a** (8%). The corresponding reaction of $Re_2(CO)_{10}$ and 1,2-$Re_2(CO)_8(PMe_3)_2$ in 2:3 ratio yields $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$ (12%), **1** (63%), and **3a** (13%). As the ratio of $Re_2(CO)_{10}$/1,2-$Re_2(CO)_8(PMe_3)_2$ decreases, the yield of $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$ decreases, and the yields of **1** and **3a** increase, as expected.

The corresponding reaction of $Re_2(CO)_{10}$ and 1,2-$Re_2(CO)_8(PPh_3)_2$ in 1:1 ratio yields $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$ (16%), **2** (55%), and **3b** (17%). The equivalent reaction of the mixture of 1,2-$Re_2(CO)_8(PMe_3)_2$ and 1,2-$Re_2(CO)_8(PPh_3)_2$ in 1:1 ratio for 4 h yields **1** (6.7%), **2** (8.4%), **3a** (17%), **3b** (24%), and $(\mu\text{-H})Re_2(CO)_6(\mu\text{-CH=CH}_2)(PMe_3)(PPh_3)$, **3c** (19%).

The phosphine ligand disproportionated products **1**, **2**, and **3c** in the reactions described above and the absence of **3a** from the reaction of the 3:2 ratio of $Re_2(CO)_{10}$ and 1,2-$Re_2(CO)_8(PMe_3)_2$ suggest that the reaction proceeds mainly via metal–metal bond cleavage. If CO dissociation were the dominant mode of reaction, there would be little or no monophosphine product, whereas it is observed to be the major product.

The fact that the reaction of 1,2-$Re_2(CO)_8(PPh_3)_2$ with ethylene proceeds much faster than that of 1,2-$Re_2(CO)_8(PMe_3)_2$ indicates that steric hindrance to recombination of the ethylene-substituted radicals is less important than some other factors, probably thermal substitution into the radicals.[16] As indicated above, alkene substitution for CO in $\cdot Re(CO)_4(PMe_3)$ is likely slower than that in $\cdot Re(CO)_4(PPh_3)$, which is also slower than that in $\cdot Re(CO)_5$.[16] The fact that both $Re_2(CO)_9L$ and the $Re_2(CO)_{10}$ and 1,2-$Re_2(CO)_8L_2$ mixtures react photochemically with ethylene to give high yields of $(\mu\text{-H})Re_2(CO)_7(\mu\text{-CH=CH}_2)L$ is consistent with a recombination of $\cdot Re(CO)_4(CH_2\text{=}CH_2)$ and $\cdot Re(CO)_4L$ radicals. On the basis of these observations, we propose the mechanism shown in eq 4–9 as the major reaction pathways. The metal–

$$Re_2(CO)_{10} \underset{\text{fast}}{\overset{h\nu}{\rightleftharpoons}} 2\cdot Re(CO)_5 \tag{4a}$$

$$1,2\text{-}Re_2(CO)_8L_2 \underset{\text{fast}}{\overset{h\nu}{\rightleftharpoons}} 2\cdot Re(CO)_4L \tag{4b}$$

$$Re_2(CO)_9L \underset{\text{fast}}{\overset{h\nu}{\rightleftharpoons}} \cdot Re(CO)_5 + \cdot Re(CO)_4L \tag{4c}$$

$$\cdot Re(CO)_5 \xrightarrow{CH_2=CH_2} \cdot Re(CO)_4(CH_2=CH_2) + CO \tag{5a}$$

$$\cdot Re(CO)_4L \xrightarrow{CH_2=CH_2} \cdot Re(CO)_3L(CH_2=CH_2) + CO \tag{5b}$$

$$\cdot Re(CO)_4L \xrightarrow[\text{slow}]{CH_2=CH_2} \cdot Re(CO)_4(CH_2=CH_2) + L \tag{5c}$$

$$2\cdot Re(CO)_4(CH_2=CH_2) \rightarrow Re_2(CO)_8(CH_2=CH_2)_2 \tag{6a}$$

$$2\cdot Re(CO)_3L(CH_2=CH_2) \rightarrow Re_2(CO)_6L_2(CH_2=CH_2)_2 \tag{6b}$$

$$\cdot Re(CO)_4(CH_2=CH_2) + \cdot Re(CO)_3L(CH_2=CH_2) \rightarrow Re_2(CO)_7L(CH_2=CH_2)_2 \tag{6c}$$

$$\cdot Re(CO)_4(CH_2=CH_2) + \cdot Re(CO)_4L \rightarrow Re_2(CO)_8L(CH_2=CH_2) \tag{7}$$

$$\underset{n\,=\,0-2}{Re_2(CO)_{8-n}L_n(CH_2=CH_2)_2} \xrightarrow{-(CH_2=CH_2)} \xrightarrow[\text{addn}]{\text{oxid}} (\mu\text{-H})Re_2(CO)_{8-n}(\mu\text{-CH=CH}_2)L_n \tag{8}$$

$$Re_2(CO)_8L(CH_2=CH_2) \xrightarrow{-CO} \xrightarrow[\text{addn}]{\text{oxid}} (\mu\text{-H})Re_2(CO)_7(\mu\text{-CH=CH}_2)L \tag{9}$$

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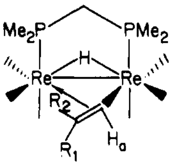
[16] The order of radical labilities has been proposed to be $\cdot M(CO)_5 > \cdot M(CO)_4L > \cdot M(CO)_3L_2$; more strongly σ-donating and weaker π-acid phosphines lead to a decreased lability of the metal center. (a) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* 1982, *104*, 4007 and references therein. (b) Pöe, A. *Trans. Met. Chem.* (*Weinheim, Ger.*) 1982, *7*, 65.

[17] Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* 1984, *106*, 3474.

metal bond homolyses in eq 4a–c correspond to eq 1, ethylene substitution in eq 5a–c to eq 2, and recombination of radicals in eq 6a–c to eq 3. The proposed reaction sequence is somewhat formal in that we have no evidence regarding whether C–H oxidative addition of olefin precedes or follows creation of the coordination vacancy at the second rhenium (eq 8 or 9). Further, given the limited information at hand regarding relative rates of appearance of products in the course of the reaction, the comparative importance of processes 8 and 9 is difficult to assess.

Photochemical Reactions of $Re_2(CO)_8(\mu\text{-}\overset{\frown}{L\ L})$ ($\overset{\frown}{L\ L}$ = dmpm, dppe, dmpe) with Alkenes. Sunlamp photolysis of $Re_2(CO)_8(\mu$-dmpm) in toluene in the presence of $H_2C{=}CHR$ (R = H, CH_3) at ambient temperature for 48 h gives 30–40% yield of (μ-H)$Re_2(CO)_6(\mu$-dmpm)(μ-CH=CHR) (**4a**, R = H; **4b** and **4c**, R = CH_3), characterized by IR, ^1H NMR, ^{13}C NMR, and mass spectra. The spectroscopic data for 4 are listed in Table II. The corresponding reactions of $Re_2(CO)_8(\mu$-dppe) and -(μ-dmpe) for 9–24 h yield 30–50% of (μ-H)$Re_2(CO)_6(\mu$-CH=CHR)(dppe), **5**, and (μ-H)$Re_2(CO)_6(\mu$-CH=CHR)(dmpe), **6**, respectively, wherein the bidentate phosphine ligand has been rearranged into a chelating ligand on a single Re center. All compounds have been characterized by IR, ^1H NMR, ^{13}C NMR, and mass spectra (Table III). The corresponding reaction of $Re_2(CO)_8(\mu$-dppm) does not yield an alkenyl-substituted complex, probably due to steric hindrance from the bulky phenyl groups.

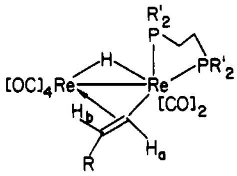
The triplet for the bridging hydrido resonance of 4 in ^1H NMR suggests that the two phosphorus atoms are symmetrically located with respect to the hydrido proton. The ^{13}C NMR spectrum of **4a** in the carbonyl region at −90 °C displays six doublets of equal intensity at δ 194.9 (J_{PC} = 1.0 Hz), 192.9 (J_{PC} = 61.8 Hz), 191.6 (J_{PC} = 6.9 Hz), 190.8 (J_{PC} = 7.5 Hz), 187.7 (J_{PC} = 7.0 Hz), and 187.5 (J_{PC} = 54.5 Hz). The four peaks with the small coupling constants (1.0–7.5 Hz) correspond to the carbonyls cis to the phosphorus atoms and the two peaks with large coupling constants to those trans to the phosphorus atoms. The IR spectrum of 4 in the carbonyl stretching region is very similar to that of (μ-H)$Re_2(CO)_6(\mu$-dppm)(μ-OH), the molecular structure of which has been recently reported.[10] On the basis of these spectroscopic data, we proposed that 4 has a structure analogous to that of (μ-H)$Re_2(CO)_6(\mu$-dppm)(μ-OH).



4a, $R_1 = R_2 = H$
b, R_1 = Me; R_2 = H
c, R_1 = H; R_2 = Me

In addition to the proton peaks corresponding to **4b** (Table II) in the ^1H NMR spectrum of the reaction mixture of $Re_2(CO)_8(\mu$-dmpm) with propylene, there are four other significant peaks at δ 7.12 (dq, 1 H, J_{HH} = 11.6 and 6.1 Hz), 5.23 (dt, 1 H, J_{HH} = 11.6 Hz, J_{PH} = 14.9 Hz), 2.34 (d, 3 H, J_{HH} = 6.1 Hz), and −13.53 (t, 1 H, J_{PH} = 10.4 Hz). These peaks are consistent with the *cis*-CH=CHMe isomer **4c** which could not be isolated by using preparative thin-layer chromatography, probably because it isomerizes to the trans isomer **4b**. The cis isomer **4c** is distinguished from the trans isomer **4b** by smaller coupling between the vinyl protons in the NMR spectrum (11.6 vs. 15.1 Hz). The integral intensities of the peaks corresponding to **4b** and **4c** are almost equal, indicating that the photochemical reaction of $Re_2(CO)_8(\mu$-dmpm) with propylene gives **4b** and **4c** in 1:1 ratio. Formation of similar isometric products from the reactions of $Re_2(CO)_{10}$ with propylene, 1-butene, and styrene has also been reported.[7a,8] Unlike the rapid isomerization ($t_{1/2}$ = 10–150 min at 25 °C) of (μ-H)$Re_2(CO)_8(\mu$-*cis*-CH=CHR) (R = Me, Et, Ph) to the trans isomer,[7a,17] the cis-CH=CHMe isomer **4c** does not convert into the corresponding trans isomer **4b** at ambient temperature for 3 days. The mechanism of the isomerization has been proposed to begin with intramolecular C–H reductive elimination.[17] In the case of **4c**, electron donation from the dmpm ligand to the Re center probably increases the activation energy of C–H reductive elimination.

The IR and ^{13}C NMR spectra of **5** and **6** are very different from those of 4, indicating that 5 and 6 may have a different structure. The ^{13}C NMR spectra of **5a** and **6a** (Table III), which show one doublet of doublets, one triplet, and four singlets suggest that the bidentate phosphine ligand is chelated on a single rhenium center. A similar pattern of ^{13}C NMR was observed in $Re_2(CO)_5$(dppm)(μ-η^1,η^2-CH=CH$_2$)(μ-η^1,η^2-C≡CPh)[11] wherein the dppm ligand acts as a chelate. The alkenyl protons have been identified in the ^1H NMR spectra; the field desorption mass spectra (FDMS) show the molecular ions. On the basis of these spectroscopic data we propose the structure shown below. No *cis*-CH=CHCH$_3$ isomer of 6 was observed in the ^1H NMR spectrum of the corresponding reaction mixture. The H_b proton in 5 and 6 shows coupling to phosphorus; in 4 it is the H_a proton that shows coupling to the phosphorus atom(s). In both cases the coupling probably occurs through the σ-bonds.[18] It is noteworthy that reactions of the bridging phosphorus ligand compounds with alkenes are much slower than for nonbridged systems. Dissociation of CO appears to be the major reaction pathway in the photochemical reactions of $Re_2(CO)_8(\mu$-dppm) and $Re_2(CO)_8(\mu$-dmpm) with alkynes.[11] It is likely that the reaction with alkenes also occurs via initial CO dissociation.



5a, R = H; R' = Ph
b, R = CH_3; R' = Ph
6a, R = H, R' = CH_3
b, R = CH_3, R' = CH_3

Fluxional Behavior of the μ-Alkenyl Ligand. It has been established that the alkenyl ligand of (μ-H)$Os_3(CO)_{10}(\mu$-C(R)=CHR′)[19] or (μ-H)$Re_2(CO)_8(\mu$-CH=CHR)[7] undergoes a rapid fluxional process at room temperature in whcih the σ- and π-bonds of the μ-alkenyl group are rapidly interchanged between two bridged metal atoms. Figure 1 shows the variable-temperature ^{13}C NMR spectra of (μ-H)$Re_2(CO)_6(\mu$-dmpm)(μ-CH=CH$_2$), **4a**.

Only three carbonyl peaks of equal intensity are observed above 17 °C. As the temperature is lowered, the peaks coalesce at −55 °C and finally split into six carbonyl peaks. These results indicate that the alkenyl ligand of **4a** undergoes a fluxional process.

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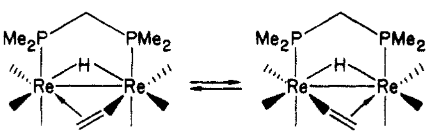
[18] We are not aware of any example of ^{31}P–^1H coupling through π-bonding in organometallic compounds.

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



The $\Delta G_c^‡$ value estimated from the coalescence temperature and the peak separation is 9.8 kcal/mol, quite similar to the values ranging from 10 to 12.7 kcal/mol in related systems.[7,19]

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. Solutions were maintained at ambient temperature (~25 °C) during photolysis by forced-air cooling of the reaction vessels. Hexane and toluene were distilled from CaH_2 under nitrogen and degassed prior to use. Dirhenium decacarbonyl, bis(diphenylphosphino)ethane (dppe) (Pressure Chemical Co.), bis(dimethylphosphino)methane (dmpm), bis(dimethylphosphino)ethane (dmpe), trimethylphosphine (Strem Chemicals), and triphenylphosphine (Aldrich) were all used without further purification. Ethylene, propylene (Union Carbide), and ^{13}CO (99%, Monsanto) were also used without further purification. Reagent grade solvents (hexane, CH_2Cl_2) 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 × 20 cm, 2.0 mm silica with UV_{254} fluorescent indicator) were obtained from Brinkmann Instruments, Inc.

Infrared spectra were obtained on a Beckmann IR-4240 spectrophotometer. Electronic spectra were recorded on an IBM-9430 spectrophotometer using 1.0-cm quartz cells. (Extinction coefficients are reported in units of M^{-1} cm^{-1}.) Fast atom bombardment (FAB) and field desorption mass spectra (FDMS) were obtained with Finnigan-MAT 731 and ZAB-HF mass spectrometers in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. ^1H NMR and ^{13}C NMR were obtained by using a Nicolet NIC-360 instrument at 360 and 90 MHz, respectively. The ^{13}C NMR spectra of carbonyl groups were obtained by using ^{13}CO-enriched compounds. The enrichment was carried out on the starting materials [$Re_2(CO)_8(\mu$-dppe), -(μ-dmpe), and -(μ-dmpm)] by photolysis under ^{13}CO-enriched (99%) atmosphere for 12 h. Spectra were recorded at ambient temperature except where indicated. Data were referred to tetramethylsilane at δ 0. Elemental Analyses were performed by the Unviersity of Illinois Microanalytical Laboratory.

***eq*-$Re_2(CO)_9(PMe_3)$, *ax*-$Re_2(CO)_9(PPh_3)$, and 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$** were prepared from $Re_2(CO)_{10}$ by literature procedures.[7,20] *eq*-$Re_2(CO)_9(PMe_3)$: IR (hexane) ν_{CO} 2103 (w), 2037 (m), 2016 (w), 1977 (s), 1994 (s, sh), 1978 (w), 1967 (w), 1951 (vw), 1935 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (d, J_{PH} = 8.7 Hz); UV (CH_2Cl_2) λ_{max} 277 (ϵ 11 900), 332 nm (13 100). *ax*-$Re_2(CO)_9(PPh_3)$: IR (toluene) ν_{CO} 2105 (w), 2033 (w), 1997 (vs), 1963 (w), 1935 (m) cm^{-1} [lit.[20] (hexane) 2105 (3.3), 2034 (2.4), 2000 (10), 1971 (6.5), 1944 (6.6) cm^{-1}]; UV (CH_2Cl_2) λ_{max} 289 (ϵ 26 800), 320 nm (18 900, sh) [lit.[21] (DMF) λ_{max} 320 nm]. 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$: IR (toluene) ν_{CO} 2012 (w), 1985 (w, sh), 1960 (vs) cm^{-1}; lit.[21] UV (DMF) λ_{max} 300 nm (ϵ 40 000).

1,2-*dieq*-$Re_2(CO)_8(PMe_3)_2$ was prepared from $Re_2(CO)_{10}$ as previously described:[7] IR (hexane) ν_{CO} 2068 (w), 2009 (m), 1975 (w, sh), 1965 (vs), 1930 (m), 1919 (s) cm^{-1} [lit.[7] (toluene) 2063 (w), 2005 (m), 1959 (s), 1925 (w), 1910 (m) cm^{-1}]; UV (CH_2Cl_2) λ_{max} 306 (ϵ 5200), 345 nm (5500).

$Re_2(CO)_8(\mu$-dmpm), -(μ-dppe), and -(μ-dmpe) were prepared as previously described.[10] Refer to ref 10 for UV data.

Photochemical Reactions of $Re_2(CO)_9(PMe_3)$ and -(PPh_3) with Ethylene. $Re_2(CO)_9(PMe_3)$ (0.103 g, 0.147 mmol) and toluene (10 mL) were added into a 50-mL Schlenk flask. The solution was freeze–pump–thaw–degassed and saturated with ethylene (1 atm). Photolysis at ambient temperature for 2 h resulted in near complete (>96%) reaction of $Re_2(CO)_9(PMe_3)$, as determined by IR spectroscopy. After the solvent was removed under reduced pressure, the products were separated as yellow solids on silica gel coated preparative TLC plates using hexane and methylene chloride (3:1) and recrystallized from the same solvent system. (μ-H)$Re_2(CO)_8(\mu$-CH=CH$_2$),[7] **1**, and **3a** were isolated. The yields determined by ^1H NMR of the reaction mixture for three products using (μ-H)$Re_2(CO)_7(\mu$-NC_5H_4)py as internal standard were 24, 60, and 3%, respectively. Anal. Calcd for $C_{12}H_{13}O_7PRe_2$ (**1**): C, 21.43; H, 1.95. Found: C, 21.52; H, 1.87. IR (hexane): ν_{CO} 2115 (vw), 2084 (w), 2034 (m), 2019 (s), 1996 (s), 1987 (s), 1977 (s), 1965 (s, br), 1940 (m) cm^{-1}. FDMS: M^+ at m/e 674 based on ^{187}Re. ^1H NMR spectral data are listed in Table I.

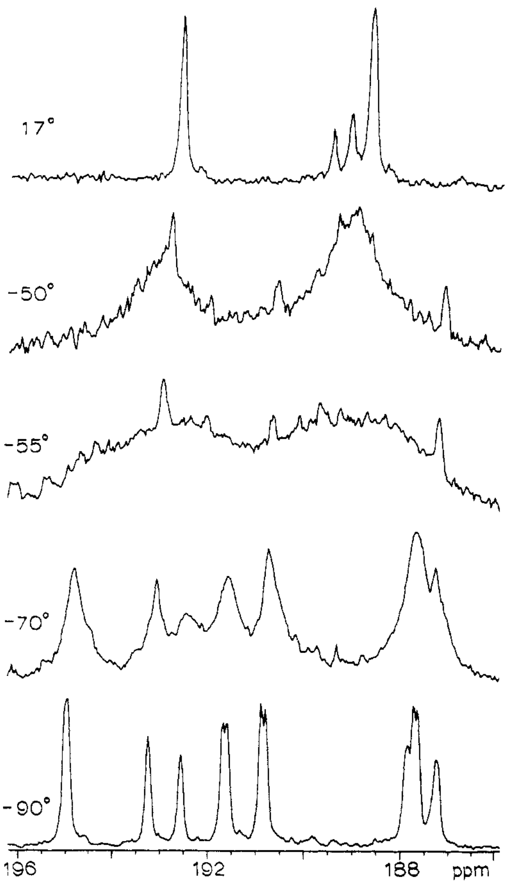


Figure 1. Variable-temperature ^{13}C NMR spectra of (μ-H)$Re_2(CO)_6(\mu$-dmpm)(μ-CH=CH$_2$), **4a**, in the carbonyl region.

The corresponding reaction of $Re_2(CO)_9(PPh_3)$ (0.125 g, 0.141 mmol) was also carried out as in the previous procedure. The yields for (μ-H)$Re_2(CO)_8(\mu$-CH=CH$_2$),[7] **2**,[15] and **3b** were 20, 44, and 24%, respectively. There are minor products (<10%) which could not be isolated and which were therefore not further investigated. **2**: IR (toluene) ν_{CO} 2105 (w), 2087 (w), 2033 (s), 2015 (s), 1998 (w, sh), 1985 (m, sh), 1973 (s), 1947 (s, br), 1922 (s, sh), 1918 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.51 (m), 6.16 (m), 5.74 (dd, J_{HH} = 10.0 and 2.5 Hz), 4.51 (dd, J_{HH} = 15.4 and 4.5 Hz), 3.59 (m), –13.61 (d, J_{PH} = 8.4 Hz), –13.92 (d, J_{PH} = 16.7 Hz), –14.01 (d, J_{PH} = 11.1 Hz); FDMS, M^+ at m/e 860 based on ^{187}Re. The spectra show evidence of minor impurities that persist through the workup, and elemental analyses were not entirely satisfactory [Anal. Calcd for $C_{27}H_{19}O_7PRe_2$ (**2**): C, 37.76; H, 2.23; P, 3.61. Found: C, 40.24; H, 3.04; P, 3.49].

Photochemical Reactions of 1,2-$Re_2(CO)_8(PPh_3)_2$ and -($PMe_3)_2$ with Ethylene. 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$ (0.135 g, 0.120 mmol) and toluene (10 mL) were added into a 50-mL Schlenk flask. The solution was degassed and saturated with ethylene (1 atm). Sunlamp irradiation at ambient temperature for 3 h resulted in near complete (>96%) reaction of 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$, as determined by IR spectroscopy. After re-

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(20) Koelle, V. *J. Organomet. Chem.* **1978**, *155*, 53.

(21) Lemoine, P.; Gross, M. *J. Organomet. Chem.* **1977**, *133*, 193.

Table II. Spectroscopic Data of $(\mu\text{-H})Re_2(CO)_6(\mu\text{-}\overset{\frown}{L\,L})(\mu\text{-CH=CHR})$, 4

$\overset{\frown}{L\,L}$	R	IR ν_{CO},[a] cm^{-1}	^1H NMR δ[b]	$^{13}C\{^1H\}$ NMR δ[c,d]	MS,[m/e]
dmpm	H	2042 (m)	6.02 (dd, 1 H, J_{HH} = 11.0 and 3.3 Hz)	193.2 (s, 2 C)	706
		2003 (s)	5.67 (m, 1 H)	189.7 (t, 2 C, $J_{PC} + J_{P'C}$ = 67.0 Hz)	
		1957 (m)	4.63 (dd, 1 H, J_{HH} = 14.5 and 3.3 Hz)	189.2 (s, 2 C)	
		1920 (vs)	1.78 (m, 1 H)		
		1903 (m, sh)	1.71 (t, 6 H, J_{HH} = 3.6 Hz)		
			1.64 (t, 6 H, J_{HH} = 3.0 Hz)		
			1.20 (m, 1 H)		
			−14.17 (t, 1 H, J_{PH} = 10.3 Hz)		
	CH_3	2037 (m)	5.50 (dq, 1 H, J_{HH} = 15.1 and 4.5 Hz)	*f*	720
		2001 (s)	5.07 (dt, 1 H, J_{HH} = 15.1 Hz, J_{PH} = 10.6 Hz)		
		1952 (m)	2.02 (d, 3 H, J_{HH} = 4.5 Hz)		
		1919 (s)	1.80 (m, 1 H)		
		1902 (m)	1.71 (t, 6 H, J_{PH} = 3.6 Hz)		
			1.64 (t, 6 H, J_{PH} = 3.3 Hz)		
			1.20 (m, 1 H)		
			−13.76 (t, 1 H, J_{PH} = 10.7 Hz)		

[a] Taken in toluene. [b] Taken in $CDCl_3$. [c] Taken in CD_2Cl_2. [d] Carbonyl region. [e] Molecular ion peak based on ^{187}Re. [f] Not taken.

Table III. Spectroscopic Data for $(\mu\text{-H})Re_2(CO)_6(\overset{\frown}{L\,L})(\mu\text{-CH=CHR})$, 5 and 6

$\overset{\frown}{L\,L}$	R	IR ν_{CO},[a] cm^{-1}	^1H NMR δ[b]	$^{13}C\{^1H\}$ NMR δ[b,c]	MS,[d] *m/e*
dppe	H	2078 (m)	7.24–7.78 (m, 20 H)	194.9 (dd, 1 C, *J* = 53.4 and 10.0 Hz)	968
		2026 (w)	6.86 (dd, 1 H, J_{HH} = 13.9 and 9.5 Hz)	194.1 (t, 1 C, *J* = 5.9 Hz)	
		1978 (s)	5.03 (d, 1 H, J_{HH} = 9.5 Hz)	190.2 (s, 1 C)	
		1968 (sh)	3.66 (dd, 1 H, J_{HH} = 13.9 Hz, J_{PH} = 10.2 Hz)	187.7 (s, 1 C)	
		1955 (m, sh)	2.54 (m, 2 H), 2.77 (m, 2 H)	185.9 (s, 1 C)	
		1931 (s)	−14.11 (t, 1 H, J_{PH} = 12.8 Hz)	184.8 (s, 1 C)	
		1892 (m)			
	CH_3	2077 (m)	7.30–7.68 (m, 20 H)	*e*	982
		2026 (w)	6.40 (d, 1 H, J_{HH} = 14.0 Hz)		
		1979 (s)	4.16 (ddq, 1 H, J_{HH} = 14.0 and 5.3 Hz, J_{PH} = 10.6 Hz)		
		1967 (m, sh)	2.55–2.85 (m, 4 H)		
		1930 (s)	1.27 (d, 3 H, J_{HH} = 5.3 Hz)		
		1888 (m)	−13.93 (t, 1 H, J_{PH} = 11.6 Hz)		
dmpe	H	2075 (m)	6.79 (dd, 1 H, J_{HH} = 13.7 and 9.5 Hz)	196.5 (dd, 1 C, *J* = 50.8 and 9.5 Hz)	720
		2010 (w, br)	4.90 (d, 1 H, J_{HH} = 9.5 Hz)	194.9 (t, 1 C, *J* = 7.4 Hz)	
		1975 (s)	3.47 (t, 1 H, J_{PH} = 13.1 Hz, J_{HH} = 13.7 Hz)	190.6 (s, 1 C)	
		1961 (s)	1.88 (d, 3 H, J_{HH} = 9.4 Hz)	189.5 (s, 1 C)	
		1944 (s)	1.87 (d, 3 H, J_{HH} = 9.4 Hz)	185.5 (s, 1 C)	
		1931 (s)	1.70 (d, 3 H, J_{HH} = 8.1 Hz)	183.6 (s, 1 C)	
		1880 (s, br)	1.38 (d, 3 H, J_{HH} = 8.0 Hz)		
			−15.0 (t, 1 H, J_{PH} = 15.0 Hz)		
	CH_3	2071 (m)	6.38 (d, 1 H, J_{HH} = 13.3 Hz)	*e*	734
		2020 (w, br)	4.14 (ddq, 1 H, J_{HH} = 13.3 and 5.4 Hz, J_{PH} = 12.5 Hz)		
		1976 (s)	1.93 (d, 3 H, J_{HH} = 5.4 Hz)		
		1958 (s)	1.87 (m, 6 H)		
		1944 (m)	1.66 (d, 3 H, J_{HH} = 8.1 Hz)		
		1930 (s)	1.38 (d, 3 H, J_{HH} = 8.1 Hz)		
		1877 (s, br)	−14.76 (t, 1 H, J_{PH} = 14.9 Hz)		
		1856 (m, sh)			

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

moval of solvent under reduced pressure, the products were separated as yellow solids on silica gel coated preparative TLC plates using hexane and methylene chloride (1:1) and recrystallized from the same solvent system. The yields for **2** and **3b** were 15 and 65%, respectively. Anal. Calcd for $C_{44}H_{34}O_6P_2Re_2$ (**3b**): C, 48.35; H, 3.14; P, 5.67. Found: C, 47.34; H, 3.01; P, 5.73. IR (toluene): ν_{CO} 2096 (w), 2014 (vs), 1995 (w), 1963 (m), 1925 (m), 1903 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ −11.99 (dd, 1 H, J_{PH} = 21.8 and 11.2 Hz), 7.16–7.55 (m, 30 H), 6.80 (t, 1 H, *J* = 6.8 Hz), 6.59–6.65 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 194.2 (t, 1 C, J_{PC} = 6.1 Hz), 193.9 (d, 1 C, J_{PC} = 9.0 Hz), 192.2 (d, 1 C, J_{PC} = 57.0 Hz), 185.1 (s, 1 C), 183.9 (d, 1 C, J_{PC} = 5.9 Hz), 183.4 (d, 1 C, J_{PC} = 7.3 Hz). FDMS, M^+ at *m/e* 1094 based on ^{187}Re.

The corresponding reaction of 1,2-*dieq*-$Re_2(CO)_8(PMe_3)_2$ (0.100 g, 0.134 mmol) for 18 h was also carried out as in the previous procedure. **1** (17%) and **3a** (66%) were the major products. **3a**: IR (toluene) ν_{CO} 2085 (w), 1999 (s), 1943 (s), 1920 (s), 1892 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.21 (ddd, 1 H, J_{HH} = 15.8 and 9.6 Hz, J_{PH} = 11.0 Hz), 5.80 (dd, 1 H, J_{HH} = 9.6 and 3.2 Hz), 4.04 (dd, 1 H, J_{HH} = 15.8 and 3.2 Hz), −14.01 (dd, 1 H, J_{PH} = 19.0 and 11.1 Hz); FDMS, M^+ at *m/e* 722 based on ^{187}Re.

Photochemical Reactions of Mixtures of Dinuclear Carbonyl Compounds with Ethylene. $Re_2(CO)_{10}$ (0.066 g, 0.101 mmol), 1,2-*dieq*-$Re_2(CO)_8(PMe_3)_2$ (0.075 g, 0.100 mmol) and toluene (10 mL) were added into a 50-mL Schlenck. The solution was degassed and saturated with ethylene (1 atm). The solution was then irradiated at ambient temperature for 3 h. The solvent was removed under reduced pressure. Analysis by ^1H NMR shows 16% of $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$, 57% of **1**, and 7.6% of **3a**. The corresponding reaction of the 3:2 mixture of $Re_2(CO)_{10}$ and 1,2-*dieq*-$Re_2(CO)_8(PMe_3)_2$ gives 41% of $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$ and 46% of **1**.

The corresponding reaction of the 1:1 mixture of $Re_2(CO)_{10}$ and 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$ was also carried in the same manner. Analysis by ^1H NMR shows 16% of $(\mu\text{-H})Re_2(CO)_8(\mu\text{-CH=CH}_2)$, 55% of **2**, and 17% of **3b**.

The corresponding reaction of the 1:1 ratio of 1,2-*dieq*-$Re_2(CO)_8(PMe_3)_2$ (0.083 mmol) and 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$ (0.093 g, 0.083 mmol) was analyzed by ^1H NMR using $(\mu\text{-H})Re_2(CO)_7(\mu\text{-NC}_5H_4)py$ [^1H NMR (CD_2Cl_2) δ −11.36 (s)][13] as internal standard to yield 6.7% of **1**, 8.4% of **2**, 17% of **3a**, 24% of **3b**, and 19% of **3c**. Spectral data for the mixture permit the following assignments to **3c**: ^{1}H NMR ($CDCl_3$) δ −12.42 (dd, J_{PH} = 25.6 and 12.1 Hz). FDMS, M$^+$ at *m/e* 908 based on ^{187}Re.

Photochemical Reactions of $Re_2(CO)_8(\mu$-L$^\frown$L) (L$^\frown$L = dmpm, dppe, dmpe) with Alkenes. $Re_2(CO)_8(\mu$-dmpm) (0.095 g, 0.130 mmol) and toluene (10 mL) were added into a 50-mL Schlenk flask. After being degassed and saturated with ethylene or propylene, the solution was irradiated at ambient temperature for 48 h. The liquid portion was removed under reduced pressure. The pure product **4** was separated as a yellow solid on silica gel coated preparative TLC plates using methylene chloride and hexane (3:1) and recrystallized from the same solvent system. The yields are 40% for **4a** and 30% for **4b**. The spectroscopic data for **4** are listed in Table II. Anal. Calcd for $C_{13}H_{18}O_6P_2Re_2$ (**4a**): C, 22.16; H, 2.57; P, 8.79. Found: C, 22.06; H, 2.56; P, 8.77. UV (CH_2Cl_2): λ_{max} 297 nm (ϵ 6800, sh).

The corresponding reactions of $Re_2(CO)_8(\mu$-dppe) and $Re_2(CO)_8(\mu$-dmpe) were also carried out for 9 and 24 h, respectively. The pale yellow solid products were separated on preparative TLC plates using methylene chloride and hexane (1:1) and recrystallized from the same solvent system. The yields of **5a**, **5b**, **6a**, and **6b** are 50, 38, 45, and 30%, respectively. The spectroscopic data for **5** and **6** are listed in Table III. Anal. Calcd for $C_{34}H_{28}O_6P_2Re_2$ (**5a**): C, 42.23; H, 2.92; P, 6.41. Found: C, 43.77; H, 3.03; P, 6.38. Anal. Calcd for $C_{14}H_{20}O_6P_2Re_2$ (**6a**): C, 23.40; H, 2.81; P, 8.62. Found: C, 23.62; H, 2.98; P, 8.96.

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Registry No. **1a**, 96041-48-4; **1b**, 96148-97-9; **1c**, 96148-98-0; **1d**, 96148-99-1; **2a**, 96041-49-5; **2b**, 96094-63-2; **2c**, 96094-64-3; **2d**, 96094-65-4; **3a**, 96041-50-8; **3b**, 96041-51-9; **4a**, 96041-52-0; **4b**, 96041-53-1; **4c**, 96094-66-5; **5a**, 96041-54-2; **5b**, 96041-55-3; **6a**, 96041-56-4; **6b**, 96041-57-5; $(\mu$-H)$Re_2(CO)_8(\mu$-CH=CH_2), 82621-42-9; $Re_2(CO)_9(PMe_3)$, 51371-62-1; H_2C=CH_2, 74-85-1; $Re_2(CO)_9(PPh_3)$, 51371-62-1; 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$, 27770-64-5; $Re_2(CO)_{10}$, 14285-68-8; $Re_2(CO)_8(\mu$-dmpm), 88271-76-5; H_3C-CH=CH_2, 115-07-1; $Re_2(CO)_8(\mu$-dppc), 88271-77-6; $Re_2(CO)_8(\mu$-dmpe), 88271-78-7; 1,2-*dieq*-$Re_2(CO)_8(PMe_3)_2$, 88035-63-6.

Organotin Compounds. 6. Hydrostannation of Methyl (*E*)-Disubstituted Propenoates with Trimethyltin Hydride and Dimethyltin Chlorohydride

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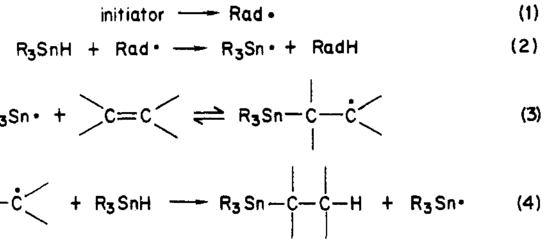
A series of (trimethylstannyl)- and (chlorodimethylstannyl)propyl derivatives having the carboxymethyl functional group has been prepared via free radical additions of trimethyltin hydride and dimethyltin chlorohydride to methyl (*E*)-2,3-disubstituted propenoates giving high yields of mixtures of diastereomeric products. The relationship between the diastereomers obtained in both reactions is demonstrated by quantitative conversion of the (trimethylstannyl)propyl derivatives into the corresponding (chlorodimethylstannyl)propyl derivatives by methyl/chlorine exchange with trimethyltin chloride. The chlorostannyl esters showed intramolecular coordination with the carbonyl group. Evidence concerning the reversibility of the free radical forming step, resulting in a rapid *Z* → *E* isomerization of the olefin, is presented. The high predominance of one diastereomer in the product might be governed by the preferred conformation of the intermediate radicals.

Hydrostannation is still the most useful reaction for the synthesis of organotin compounds containing organic functional groups. Commonly the reaction proceeds by a well-established free radical mechanism[2,3] according to Scheme I. Besides our interest in the synthesis of organotin esters in order to use them in biochemical studies, the organofunctional organostannes are also of interest because of structure-reactivity relationships like, for example, intramolecular donor–acceptor interactions.[4]

Scheme I



$$\text{initiator} \longrightarrow \text{Rad}\cdot \quad (1)$$

$$R_3SnH + \text{Rad}\cdot \longrightarrow R_3Sn\cdot + \text{RadH} \quad (2)$$

$$R_3Sn\cdot + \text{>C=C<} \rightleftharpoons R_3Sn\text{—C—}\dot{C}\text{<} \quad (3)$$

$$R_3Sn\text{—C—}\dot{C}\text{<} + R_3SnH \longrightarrow R_3Sn\text{—C—C—H} + R_3Sn\cdot \quad (4)$$

Following our studies[5,6] on the synthesis of new functionally substituted organotin compounds, we now report

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[1] Part of the forthcoming Dr. in Chem. Thesis.

[2] Neumann, W. P. "The Organic Chemistry of Tin"; Wiley: London, 1970.

[3] Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47.

[4] Kuivila, H. G.; Karol, T. J.; Swami, K. *Organometallics* **1983**, *2*, 909.

[5] Podestá, J. C.; Chopa, A. B.; Ayala, A. D. *J. Organomet. Chem.* **1981**, *212*, 163.