(terminal) = 1.19 Å, B–B = 1.80 Å, B–H(bridge) = 1.32 Å with all borons and terminal hydrogens lying in a plane and the dihedral angle of the boron plane with the B–H–B plane being 90°. For $B_4H_9^-$, the B–B–B angle was chosen to be 120°.

The Fenske–Hall calculations[15] employed single-ζ Slater basis functions for the 1s and 2s function of B, C, and O. The exponents were obtained by curve fitting the double-ζ functions of Clementi[25] while maintaining orthogonal functions; the double-ζ functions were used directly for the 2p orbitals. For hydrogen, an exponent of 1.16 was used which corresponds to the minimum energy exponent for methane.[26] The iron 1s–3d functions were taken from the results of Richardson et al.[27] and were all single-ζ except the 3*d* function which is double-ζ and was chosen for the 1+ oxidation state. Both the 4s and 4p exponents were chosen to be 2.0. For all the atoms used here, these are the basic functions typically employed by Fenske and Hall in their studies using this quantum chemical approach.

The extended Hückel calculations[28] employed Slater functions, and the orbital exponents and diagonal matrix elements used are the same as those used previously.[29] The arithmetic mean Wolfsberg–Hemholz approximation with $K = 1.75$ was used.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged as is the computing time provided by the Notre Dame Computing Center.

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Mechanisms of $Re_2(CO)_{10}$ Substitution Reactions: Crossover Experiments with $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$

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Abstract: $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ were prepared separately and then utilized in combination in crossover experiments to probe for fragmentation to mononuclear rhenium species in thermal and photochemically initiated substitution reactions. For the CO–$Re_2(CO)_{10}$ exchange reaction, a reaction separately analyzed for ^{13}CO–^{12}CO interchange, no crossover was observed at 150 °C after 14 half-lives of reaction (14 h). Similarly, the thermal reaction sequences of $Re_2(CO)_{10} + P(C_6H_5)_3 \rightleftharpoons Re_2(CO)_9P(C_6H_5)_3 + CO$ and $Re_2(CO)_9P(C_6H_5)_3 + P(C_6H_5)_3 \rightleftharpoons Re_2(CO)_8[P(C_6H_5)_3]_2 + CO$ were examined at 150 °C (maintaining a CO pressure of ~560–640 mm). No crossover was detectable in either $Re_2(CO)_{10}$ or $Re_2(CO)_9P(C_6H_5)_3$ (relative to blank experiments). Hence, phosphine substitution reactions proceed without a detectable formation of mononuclear rhenium species. These observations support a CO dissociative mechanism. A model based upon this mechanism can accurately reproduce the mass spectra observed during ^{13}CO–^{12}CO interchange. In the absence of a CO atmosphere, $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ formed $^{185}Re^{187}Re(CO)_{10}$, and this interchange was nearly complete at 150 °C within 14–16 half-lives. All photochemically initiated reactions with the two labeled decacarbonyls led to complete crossover within short reaction times. It appears then that the primary mode of reaction for $Re_2(CO)_{10}$ under photolysis conditions involves Re–Re bond scission as an early elementary step. Also, the reversible steps leading to the precursor(s) to $Re_2(CO)_{10}$ decomposition include scission of the rhenium–rhenium bond.

Important to a full development of metal cluster chemistry is a basic understanding of reaction mechanism. Because of the very complexity of these polynuclear species, the number of chemically plausible reaction pathways for a given system can be relatively large.[1] In metal carbonyl clusters, the average metal–metal and metal–carbonyl bond energies appear comparable, Hence, scission of *either* type of bond can be an elementary step in even simple reactions like ligand replacement, We address here the mechanism of $M_2(CO)_{10}$ reactions.

Despite substantial efforts, the mechanism of substitution reactions of group 7 metal carbonyl dimers remains an unresolved question.[1a] Two different mechanisms have been advanced. One involves reversible CO dissociation, Scheme I; the other reversible metal–metal bond homolysis, Scheme II. Both mechanisms predict rate expressions that are first order in metal–carbonyl dimer concentration and independent of entering ligand concentration (when the concentration of the entering ligand is sufficiently large that the reverse of the activation step is negligible). In contradistinction to the CO dissociative mechanism, the radical mechanism requires the dependence on metal–carbonyl dimer concentration to decrease from first to half-order for less than limiting rates. Less than first-order kinetic behavior has not yet been observed for any ligand substitution reaction. However, Poë and co-workers have reported such behavior for the presumedly related decomposition reactions of $M_2(CO)_{10}$ that occur at the same rates as ligand substitution and therefore favor a radical mechanism.[2-11] Sonnenberger and Atwood favor a CO disso-

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ciative mechanism, in part on the basis of their failure to observe any homonuclear dimeric products during substitution reactions of $MnRe(CO)_{10}$.[12,13] In a recent complementary study, Schmidt and co-workers have demonstrated that the reaction of $Mn_2(CO)_{10}$ with $Re_2(CO)_{10}$ at 130 °C does not yield significant amounts of $MnRe(CO)_{10}$.[14] This experiment establishes that the absence of homonuclear dimeric products is a consequence of kinetic rather than thermodynamic features. Collectively, these observations also imply the absence of a significant concentration of metal free radical intermediates for rhenium, if not for manganese as well.

Scheme I

$$M_2(CO)_{10} \rightleftharpoons M_2(CO)_9 + CO$$

$$M_2(CO)_9 + L \rightarrow M_2(CO)_9L$$

Scheme II

$$M_2(CO)_{10} \rightleftharpoons 2M(CO)_5$$

$$M(CO)_5 + L \rightarrow M(CO)_4L + CO$$

$$2M(CO)_4L \rightarrow M_2(CO)_8L_2$$

$$M(CO)_5 + M(CO)_4L \rightarrow M_2(CO)_9L$$

We report here the results of the first of a series of crossover experiments with metal carbonyl complexes prepared from separated metal isotopes. The interpretation of these experiments are not complicated by disparate reaction rates for the two labeled components or by changes in equilibria induced by the presence of the label. Our experiments unequivocally demonstrate that metal–metal bond homolysis is unimportant as an activation process for all known thermally initiated substitution reactions of rhenium carbonyl dimers. In marked contrast, our experiments show that photolysis of $Re_2(CO)_{10}$ generates significant concentrations of mononuclear rhenium carbonyl intermediates.

Experimental Section

General Information. $Re_2(CO)_{10}$ was obtained from Pressure Chemical Co. and was used without further purification. Natural abundance Re metal powder, 99.997%, was obtained from Alfa Chemicals. ^{185}Re, 96.25% enriched, and ^{187}Re, 99.22% enriched, were obtained as metal powders from Oak Ridge National Laboratory. Natural abundance C.P. grade carbon monoxide, prepurified argon and extra-dry oxygen were used as obtained from Matheson Co. ^{13}C-enriched carbon monoxide of 99.59% carbon monoxide purity with isotope percentages of 91.2% ^{13}C, 8.1% ^{17}O, and 0.22% ^{18}O, was obtained from Bio-Rad Laboratories. Triphenylphosphine was recrystallized from absolute ethanol. $Re_2(CO)_9P(C_6H_5)_3$ and $Re_2(CO)_8[P(C_6H_5)_3]_2$ were prepared by literature procedures.[6] *n*-Octane, 99.0% (Aldrich Gold Label), was stored under vacuum over sodium benzophenone ketyl and triethylene glycol dimethyl ether (triglyme). The octane was vacuum-transferred into reaction vessels as needed. Impurities were detected (<0.1%) neither by gas chromatography nor by a color test for unsaturated molecules (Br_2 in CH_2Cl_2).

All reaction conditions and synthetic procedures were developed by using natural abundance materials and by comparison to authentic compounds. Separate sets of equipment were used for each separated isotope and for natural abundance materials where possible in order to minimize the possibility of cross-contamination. Precautions taken, where this was not possible, are described below.

Mass spectra were obtained with an AEI-MS 12 system interfaced with an INCOS data system. Solutions as dilute as 500 μg/mL could be directly introduced and analyzed. After removal of the octane solvent in vacuum in the mass spectrometer, $Re_2(CO)_{10}$ sublimed into the ionization chamber at room temperature and operating pressure. $Re_2(CO)_9P(C_6H_5)_3$ could not be detected until the inlet temperature was raised to 80 °C. Thus, it was possible to independently analyze these two complexes in a mixture. $Re_2(CO)_8[P(C_6H_5)_3]_2$ proved insufficiently volatile to permit analysis by conventional mass spectrometry. Raw data for all relevant mass spectra are included in the supplementary material. Infrared spectra were recorded with a Perkin-Elmer 283 spectrometer. Elemental analyses were performed by V. Tashinian of the U.C.B. Chemistry Department Microanalytical Laboratory.

Conversion of Rhenium Metal to $Re_2(CO)_{10}$. Rhenium metal was initially converted to Re_2O_7 by the literature procedure of combustion of the metal at 450 °C in a closed system containing excess extra-dry oxygen.[15] Reactions were run on a 200-mg scale. The yellow product was sublimed into a constricted section of the reaction tube and sealed into that section.

Re_2O_7 was converted to $Re_2(CO)_{10}$ by a modification of the literature procedure.[16] The presence of a metallic copper surface appeared to be beneficial. The ampule of Re_2O_7 and a spatula tip full of copper metal powder were placed in a length of $^1/_2$-in. diameter copper tube with a drilled $^3/_{32}$-in. hole in the side. Both ends of the tube were capped, and the tube was placed into a 110-mL capacity stainless steel Aminco Superpressure micro series reaction vessel. The sealed vessel was flushed with CO and the ampule crushed under CO pressure. After the vessel was pressurized to 2700 psi, it was heated to 250 °C for 16 h. Then the vessel head was opened after cooling and venting of the reaction system. White solids, dispersed on surfaces near the head of the vessel, were collected by washing all exposed surfaces with CH_2Cl_2. The collected washings were filtered through Celite, and the solvent was removed under vacuum. The resulting solid was purified by sublimation. Yields were 80–85% on the basis of rhenium metal. Mass spectra of products prepared from natural abundance rhenium metal and infrared spectra of products prepared from all materials were identical with those of authentic $Re_2(CO)_{10}$. The mass spectra of products prepared from ^{185}Re and ^{187}Re metals matched those expected and permitted a determination of the actual enrichments of products, which were 97.1% and 99.6%, respectively. Anal. Calcd for $Re_2(CO)_{10}$ (natural abundance Re): C, 18.41; H, 0.0; Cl, 0.0. Found: C, 18.71; 18.87; H, 0.00; 0.08; Cl, 0.07; <0.2 (error margin of the sample).

Separate copper tubes and high-pressure connectors were used for each separated isotope and for natural abundance materials. It was not practical to use separate high-pressure vessels and valves. The empty vessel was subjected to the same reaction conditions as in the $Re_2(CO)_{10}$ preparation, at least twice, before a sample of different isotopic composition was used in the vessel to preclude contamination.

Crossover Experiments. All manipulations were performed under subdued lights. Reactions were conducted in sealed Pyrex tubes, approximately 24 mL in volume. The main body of the tube was attached to a standard taper joint through a length of smaller diameter tubing which had a constriction on it. Solid compounds were introduced through the joint and were shaken down to the bottom of the tube. Typically, 10.0 mg each of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ were employed, as well as varying amounts of $P(C_6H_5)_3$, as required by the specific experiment. The tube was next attached to a vacuum line, through an adaptor with a Teflon Kontes valve, and was thoroughly evacuated. *n*-Octane (~4 mL) was vacuum-transferred into the tube. Catalysis of reactions of metal carbonyls by transition metals and their oxides has recently been reported.[17] Therefore, a special effort was made to wash all solids out of the constricted tube in order to prevent the potential formation of a catalyst by decomposition of solids upon sealing the tube. The contents of the tube were freeze–thaw–degassed and refrozen with a dry ice–isopropyl alcohol slush bath. An appropriate pressure of gas was introduced, as required by the specific experiment, and the tube was sealed at the constriction (decomposition products were not noted at any seal). The reaction vessel was allowed to warm to ~20 °C and then was agitated until all solids dissolved. All tubes used in the thermal reactions were wrapped in aluminum foil and were totally immersed in a thermostated, 150 °C (±1 °C) oil bath for an appropriate period of time. Tubes were immediately quenched in cold water after removal from the oil bath. Photochemically initiated reactions were run at 0 °C and irradiated by a Hanovia medium-pressure mercury lamp with a 450-W power supply. All samples were analyzed by mass spectrometry (within 30 min) after removing and opening the tube unless otherwise noted. A computer program was employed to analyze the parent ion regions of $Re_2(CO)_{10}$ and $Re_2(CO)_9P(C_6H_5)_3$ in the mixtures. Correcting for the natural isotope distribution and the actual enrichment of the $^{185}Re_2(CO)_{10}$ and

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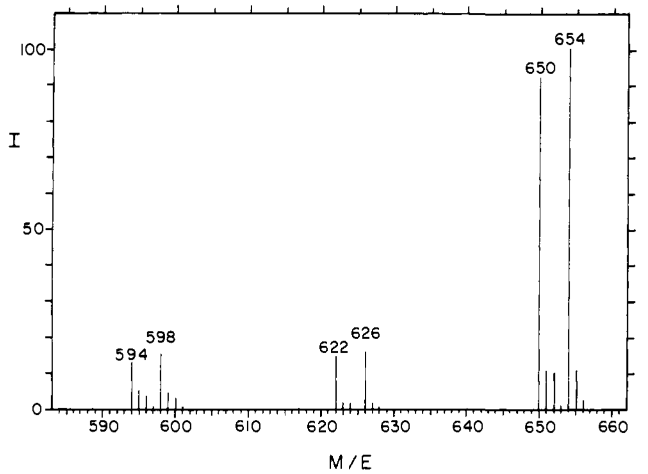

Figure 1. Mass spectrum of a mixture of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ in *n*-octane after 16 h in the dark at room temperature. This represented the blank for all subsequent tests for a crossover reaction.

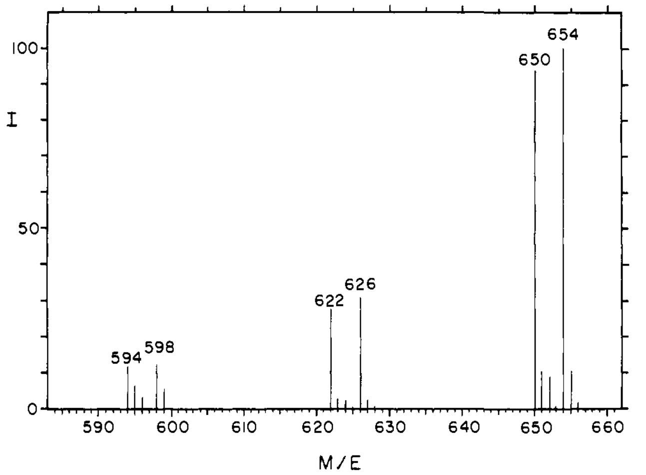

Figure 2. Calculated mass spectrum of a 1:1 mixture of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$.

$^{187}Re_2(CO)_{10}$, the program calculated the ratio of the amounts of the two carbonyl complexes initially present, the fraction of label crossover, and the predicted mass spectrum based upon these two parameters. Agreement between predicted and observed spectra was good.

Rate of ^{13}CO Incorporation into $Re_2(CO)_{10}$. Natural abundance $Re_2(CO)_{10}$ (36 mg) was placed in a Kontes valve equipped reaction tube. This was placed on the vacuum line, and 40 mL of *n*-octane was vacuum-transferred into the tube. The tube was brought into an argon atmosphere drybox, and six reaction tubes (described in the crossover experiment section) were each charged with 4 mL of the solution. Each reaction tube was fitted to an adaptor, placed on the vacuum line, freeze-thaw-degassed, and sealed under 560-mm pressure of ^{13}CO, while immersed in a dry ice-isopropyl alcohol slush bath. This represented roughly 170 mol of CO per mol of $Re_2(CO)_{10}$. All tubes were wrapped in aluminum foil and were placed in a thermostated 150 °C (±1 °C) oil bath. At appropriate times, tubes were removed and quenched in cold water. Tubes were stored at 0 °C until all had been removed from the oil bath (exchange is insignificant at room temperature[18]). Tubes were opened and the contents were analyzed by both infrared and mass spectrometry. All solutions remained clear. No solids were present.

Results

Reactions of $Re_2(CO)_{10}$. A solution of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ in *n*-octane was sealed under vacuum and stored for 16 h in the dark at room temperature in order to provide a control for later experiments. The mass spectrum of this mixture is shown in Figure 1. By way of comparison, a theoretical spectrum of a 1:1 mixture of the two carbonyls, assuming no crossover, is presented in Figure 2. The apparent crossover in the control was calculated to be 1.6%.

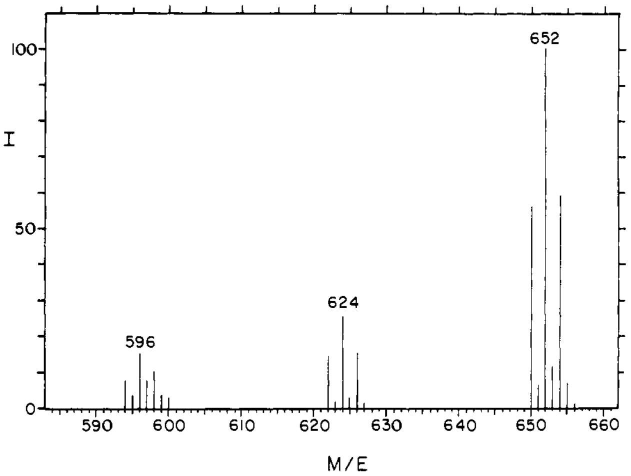

Figure 3. Mass spectrum of dirhenium decacarbonyl recovered from a mixture of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ that had been heated in *n*-octane to 150 °C for 16 h. The reaction mixture initially was frozen and sealed under vacuum. In this thermal reaction, crossover was nearly complete (93%) as evidenced by the high-intensity parent ion mass of 652 for $^{185}Re^{187}Re(CO)_{10}$.

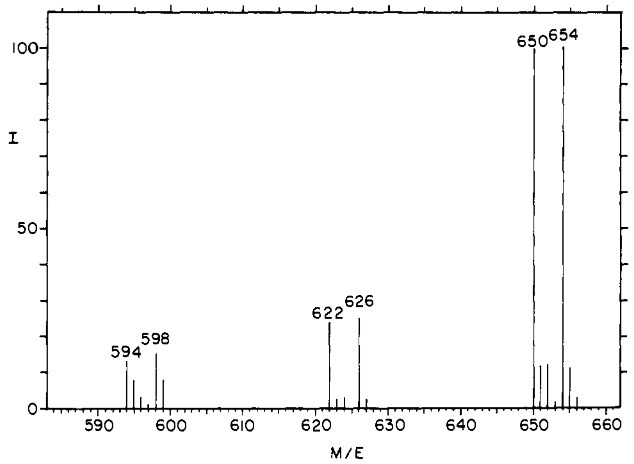

Figure 4. Mixture of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ in *n*-octane, sealed under 560 mm of CO, was heated for 14 h at 150 °C. Shown above is the mass spectrum of the recovered dirhenium decacarbonyl from the reaction mixture. No significant crossover was observed (2.6%) as evidenced by the low intensity of the 652 mass ion.

The ligand substitution reactions of $Re_2(CO)_{10}$ are reported to have a conveniently short half-life of approximately 1.9 h at 150 °C.[6] A reaction tube was prepared as above, sealed under 560-mm pressure of argon, and heated in a 150 °C oil bath for 14 h. At the end of this time, the solution was slightly opalescent, but no solid was discernable. Analysis of the mass spectrum of this material established that nearly complete crossover, 96.2%, had occurred. To preclude the possibility that trace impurities in the argon were responsible for the crossover either through catalysis or creation of decomposition products, another reaction tube was prepared and sealed under vacuum. After 16 h at 150 °C, this solution was also opalescent. Analysis of the mass spectrum, Figure 3, established that the extent of crossover was 93%. In contrast to these results, a solution sealed under 560-mm pressure of CO remained clear after 14 h at 150 °C. More importantly, only a 2.6% crossover occurred. The mass spectrum is presented in Figure 4.

Because carbon monoxide suppressed crossover, the interactions of $Re_2(CO)_{10}$ and ^{13}CO were examined. Solutions of $Re_2(CO)_{10}$ were allowed to react with ^{13}CO at 150 °C for from 1 to 22 h. The infrared spectra of these samples established that substantial ^{13}CO incorporation had occurred in times as short as 1 h. The frequencies of the C–O stretching vibration in the substituted

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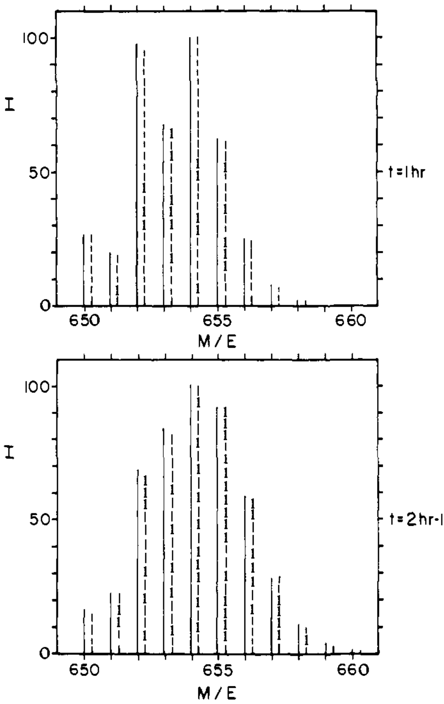

Figure 5. Comparison of mass spectra observed for ^{13}CO incorporation by $Re_2(CO)_{10}$ at 150 °C (solid line) with spectra predicted by a model based on CO dissociation with $t_{1/2} = 0.99$ h (dashed line).

species were in reasonable agreement with those predicted by force field calculations.[18,19] It was not possible to quantitatively analyze for extent of exchange from the infrared spectra due to the overlap of ^{12}CO and ^{13}CO bands and to the presence of mixtures which may contain complexes with from 0 to 10 ^{13}CO groups. The mass spectra were amenable to quantitative analysis, however, Predicted mass spectra were calculated from the known isotopic distributions of each substituted complex and the calculated proportion of each in the mixtures at different times. The latter was calculated with the assumption of a first-order CO dissociative process with successive dissociation rates statistically corrected for the number of natural abundance CO groups remaining. If replacement of ^{13}CO by ^{12}CO is assumed to be insignificant, a valid assumption for short reaction periods, the problem reduces to that of a 10-step radioactive decay chain for which a general solution exists.[20] The agreement of observed and predicted spectra at reaction times of 1 h and of $^{13}/_{6}$ h, Figure 5, was excellent when an initial half-life for CO dissociation of 0,99 was chosen. This half-life agrees with that for phosphine substitution reactions of $Re_2(CO)_{10}$ within a factor of 2. Choice of other half-lives, including that reported for phosphine substitution, resulted in poor agreement. A model based on rate limiting metal–metal bond homolysis cannot reproduce the observed spectra unless unreasonable assumptions are made: such assumptions require that only one radical of each pair derived from $Re_2(CO)_{10}$ reacts with precisely one ^{13}CO before recombining with a radical that did not react with ^{13}CO.

Reaction of $Re_2(CO)_{10}$ with $P(C_6H_5)_3$. The investigations were complicated by the existence of the CO suppressable crossover pathway. All experiments were conducted under CO pressure to prevent crossover by this pathway. An undesired consequence of this was a substantial decrease in the rate of reaction, unless a large phosphine concentration was present.

Two tubes were prepared containing 0.6 mol of $P(C_6H_5)_3$ (3×10^{-3} M) per mol of total $Re_2(CO)_{10}$. Both were sealed under 560-mm pressure of CO and heated to 150 °C. Half-lives for reaction were expected to increase approximately by a factor of 10 under these conditions. One tube was removed after 16 h, The solution was clear, Analysis of the mass spectra established that 1.2% crossover had occurred in the $Re_2(CO)_{10}$. Crossover was not detected in the $Re_2(CO)_9P(C_6H_5)_3$ product. After 56 h, the second tube was removed. Once again, the solution had remained clear, A 1.4% crossover was established for $Re_2(CO)_{10}$ and ~2% crossover for $Re_2(CO)_9P(C_6H_5)_3$.

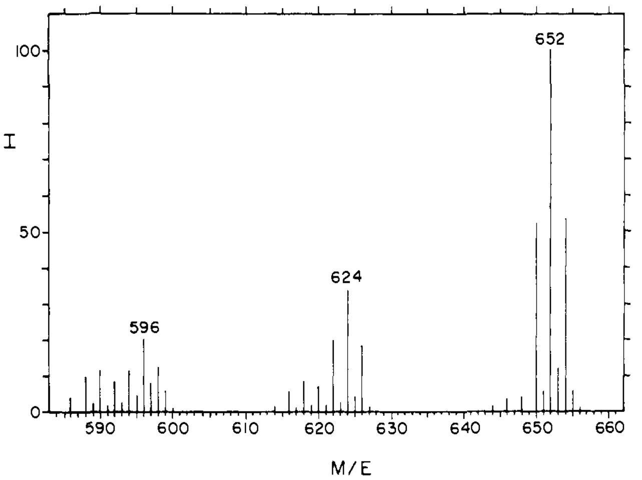

Figure 6. Mixture of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ in *n*-octane, sealed in Pyrex glass under 560 mm of CO, was photolyzed at 0 °C for 20 min. Crossover was extensive (98%) as shown by the above mass spectrum of recovered dirhenium decacarbonyl with the large intensity mass ion (652) for $^{185}Re^{187}Re(CO)_{10}$.

An experiment was performed with a triphenylphosphine concentration of 5×10^{-2} M, which was sufficiently large to reverse inhibition by CO but did not greatly affect the equilibrium product distribution under a CO atmosphere.[6] This represented a 10-fold molar excess of phosphine relative to total $Re_2(CO)_{10}$. The tube was sealed under 640-mm pressure of CO and heated to 150 °C for 16.5 h, The solution remained clear. An examination of the solution by infrared spectroscopy and by thin-layer chromatography confirmed that the major product was $Re_2(CO)_9P(C_6H_5)_3$. Only minor amounts of $Re_2(CO)_{10}$ and $Re_2(CO)_8[P(C_6H_5)_3]_2$ were present. The 650 and 654 peaks were the only peaks detected in the mass spectrum of $Re_2(CO)_{10}$, establishing that significant crossover had not occurred in this complex, Similarly, the mass spectrum of the $Re_2(CO)_9P(C_6H_5)_3$ gave no evidence of crossover.

Photochemical Reactions. A reaction tube was prepared as above and sealed under 560-mm pressure of CO. Irradiation for as little as 20 min resulted in a yellowing of the solution and precipitation of substantial amounts of an off-white solid, which was a $Re_4(\mu_3\text{-}OH)_4(CO)_{12}$ cluster that resulted from reaction of reaction intermediates with traces of water. A sample of solution that was free of solids was analyzed. The mass spectrum, Figure 6, established that 98% crossover had occurred. Small extraneous peaks were noted at masses slightly lower than the parent ion of $Re_2(CO)_{10}$. The sources of these peaks became apparent when the inlet temperature of the mass spectrometer was increased. A new species was detectable that contained two rhenium atoms (with complete crossover), had a parent ion centered at mass 708, and fragmented by loss of 30 mass units. These data are consistent with a $Re_2(CO)_8$(octene) complex, but identification must await the results of a more definitive investigation of this reaction, currently in progress.

The photoinitiated $Re_2(CO)_{10} + P(C_6H_5)_3$ reaction was also examined, using 1.1 mol of phosphine per mol of the metal carbonyl. The reaction tube was sealed under vacuum and irradiated for 20 min. Substantial yellowing and solid formation were noted. Analysis of the mass spectra disclosed that 91.4% crossover had occurred in the $Re_2(CO)_{10}$. Nearly complete crossover was noted in the $Re_2(CO)_9P(C_6H_5)_3$ product.

In an effort to gauge the effects of room lighting, a reaction tube was sealed under vacuum and stored on a lab bench. After 3 days, the solution remained clear. Exposure to sunlight for 10 min, at this point in time, led to a very slight yellowing of the

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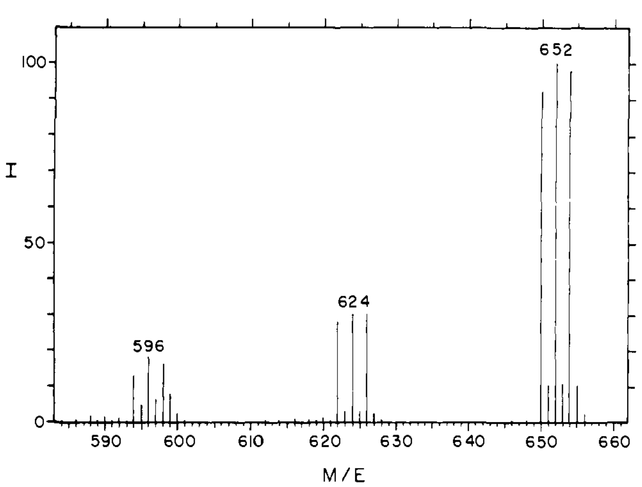

Figure 7. Mass spectrum of dirhenium decacarbonyl recovered from a mixture of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$, sealed under vacuum in Pyrex glass after 4-days exposure to room lights and 10-min exposure to sunlight. Crossover was about 66% complete (note 652 mass ion intensity for the crossover species).

solution. The tube was opened and analyzed 1 day later. A small amount of solid was present. Analysis of the mass spectrum, Figure 7, established that 66.4% crossover had occurred.

Discussion

Because there is evidence[1] that reaction mechanism for phosphine substitution in metal carbonyl clusters may change after the introduction of the first, or second, phosphine ligand, ostensibly the ideal protocol for our study would have comprised separate experiments specific to each of the following reactions:

$$Re_2(CO)_{10} + L \rightleftharpoons Re_2(CO)_9L + CO \qquad (1)$$

$$Re_2(CO)_9L + L \rightleftharpoons Re_2(CO)_8L_2 + CO \qquad (2)$$

$$Re_2(CO)_8L_2 + L \rightleftharpoons \text{steps leading to mononuclear species}^{21} \qquad (3)$$

with mass spectrometric characterization of the reaction product in each case. However, this was not experimentally feasible because of the involatility of $Re_2(CO)_8[P(C_6H_5)_3]_2$, the low isolated yields of the monophosphine complex and our limited quantities of the pure rhenium isotopes.

The reversibility of reactions 1 and 2, as established by Poë and co-workers, provided a very simple experimental solution: (i) If reaction 1 proceeds by a rhenium–rhenium bond scission, crossover in a mixture of $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ must occur at a rate identical with ligand substitution. (ii) Should crossover not occur in the above experiment thereby defining the mechanism in reaction 1, reaction 2 can be examined by the addition of less than 1 mol of phosphine per mol of total $Re_2(CO)_{10}$ since by the principle of microscopic reversibility the reverse of reaction 1 cannot lead to crossover. Therefore, given a sufficiently long reaction time, reaction 2 can be characterized by the mass spectrometric analysis of the decacarbonyl and the $Re_2(CO)_9P(C_6H_5)_3$ product. (iii) If crossover does not occur in reactions 1 and 2, reaction 3 can be monitored by adding sufficient phosphine to result in partial conversion to the bis(phosphine) complex at equilibrium.

In these experiments, the presence of carbon monoxide is beneficial in that it increases the back-reaction rates. Moreover, the presence of carbon monoxide would not have much effect upon rate of crossover, were the rhenium–rhenium bond cleaved, even though the forward rate of ligand substitution might be decreased. In addition to reactions 1–3 a fourth reaction should be considered, namely the reversible steps that precede thermal decomposition of $Re_2(CO)_{10}$.

$$Re_2(CO)_{10} \rightleftharpoons \text{precursor(s) to } Re_2(CO)_{10} \text{ decomposition} \qquad (4)$$

Reaction 1 does not proceed thermally by rhenium–rhenium bond scission as established by our studies. There was no crossover in the $^{185}Re_2(CO)_{10} + {}^{187}Re_2(CO)_{10} + CO$ reaction at 150 °C after a 14-half-lives reaction time, and mass spectrometric analysis of $Re_2(CO)_9P(C_6H_5)_3$ formed in the $^{185}Re_2(CO)_{10} + {}^{187}Re_2(CO)_{10} + P(C_6H_5)_3$ reaction showed no evidence of crossover. Furthermore, the study of the $^{13}CO + Re_2(CO)_{10}$ established that the distribution of ^{13}C in the product was fully consistent with a substitution mechanism based on CO dissociation (eq 5). The

$$Re_2(CO)_{10} \rightleftharpoons Re_2(CO)_9 + CO \qquad (5)$$

rate of ^{13}CO incorporation was faster within a factor of two of the reported rate of phosphine substitution in $Re_2(CO)_{10}$.

Reaction 2 also must proceed by a CO dissociative mechanism. No crossover was seen in $Re_2(CO)_9P(C_6H_5)_3$ after either 16 h or 56 h of reaction (150 °C) of $Re_2(CO)_{10}$ with 0.6 mol of $P(C_6H_5)_3$. This period of 40 h between observations represents at least 90 half-lives of reaction time for reaction 2 in the absence of CO.[6] Substantial crossover during this period would be required by a radical mechanism. Additional evidence supporting a CO dissociative mechanism was found in the absence of crossover, in either $Re_2(CO)_{10}$ or $Re_2(CO)_9P(C_6H_5)_3$, in the reaction with a 10-fold excess of phosphine at 150 °C.

The latter experiment also provides evidence for a CO dissociative mechanism for reaction 3. Under the conditions of the reaction, $Re_2(CO)_9P(C_6H_5)_3$ should have had sufficient time to cycle through reaction 2 several times. The time of reaction represents several half-lives for reaction 3. The absence of crossover in $Re_2(CO)_9P(C_6H_5)_3$ is inconsistent with a radical mechanism for initial phases of reaction 3.

Having established that reactions 1 and 2 proceed by a CO dissociative mechanism, one must conclude then that reverse reactions proceed by ligand dissociation. There is no expectation that the reactions of $Re_2(CO)_9P(C_6H_5)_3$ with CO and $P(C_6H_5)_3$ proceed at the same rate, which is required by a homolytic fission mechanism. The observed rates differ.[6]

Elementary steps that lead to precursors to the thermal decomposition of $Re_2(CO)_{10}$, reaction 4, include reversible scission of the rhenium–rhenium bond as established by the extensive crossover for the $^{185}Re_2(CO)_{10}$–$^{187}Re_2(CO)_{10}$ reaction at 150 °C in the absence of carbon monoxide. This crossover in the absence of added CO or phosphine is consistent with earlier observations by Schmidt et al.[14] and may provide a possible explanation for the half-order dependence observed in the rates of thermal decomposition of dimetal decacarbonyls and their reaction with oxygen. Suppression of crossover by CO or phosphine establishes that cleavage to mononuclear fragments occurs only after formation of an unsaturated $M_2(CO)_9$ intermediate. This is consistent with the observation that clean phosphine substitution of $MnRe(CO)_{10}$ still occurs under O_2 and at the same rate as either substitution or oxidation alone.[11] Upon cleavage, two mononuclear fragments[22] will form in equal concentration proportional to $[M_2(CO)_{10}]^{1/2}$. The equality of concentration will be maintained if both fragments decompose or react with oxygen at similar rates. Thus, the overall rate of these equations will have a half-order dependence upon the concentration of $M_2(CO)_{10}$, at less than

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[21] Products include isomers of $HRe(CO)_3[P(C_6H_5)_3]_2$ and $HRe(CO)_4[P(C_6H_5)_3]$. See: Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1980**, *186*, 339.

[22] The identity of the two fragments is not known. One possibility is that the $Re_2(CO)_9$ fragments to yield $Re(CO)_5$ and $Re(CO)_4$. The rate of fragmentation must be low relative to trapping of the $Re_2(CO)_9$ by CO or phosphine. In the presence of CO, $Re(CO)_4$ should react to form $Re(CO)_5$. Two $Re(CO)_5$ radicals can recombine to form $Re_2(CO)_{10}$. The reverse of recombination (homolysis) provides a pathway for crossover in the presence of CO, contrary to our observations. Thus, the fragmentation of $Re_2(CO)_9$ must be an activated process or else either $Re(CO)_4$ does not react with CO or the two $Re(CO)_5$ radicals do not escape from a solvent cage. Neither of the last two assumptions is reasonable in view of previous photolytic investigations.[23] Alternatives include heterolytic fragmentation and dimerization of an $Re_2(CO)_9$ or $Re_2(CO)_8$ species.

[23] Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095.

limiting rate. The rate of these reactions will be equal to the rate of substitution at limiting rates.[24]

The results of the photochemical experiments could indicate that different mechanisms are operative than for thermal reactions. In all cases, substantial crossover occurred. Photoinduced metal–metal bond homolysis of $Re_2(CO)_{10}$ is a reasonable activation step for these reactions. There is precedent in flash photolysis studies[23] and other photochemical investigations.[25] The possibility exists that the crossover in our systems could have resulted from other reactions or have been catalyzed by the solid formed in these reactions. The latter does not seem likely in light of the incomplete crossover observed when a solution was allowed to stand over this solid for a day under room lights. Resolution of this issue requires a more complete understanding of the basic photochemical reactions. *On the basis of our data alone*, we cannot exclude the possibility that there are two fast steps in the photochemical reaction; the first involving CO dissociation and the second Re–Re bond scission in $Re_2(CO)_9$.

Summary

These crossover experiments have provided an incisive and definitive characterization of the reaction mechanisms for $Re_2(CO)_{10}$ substitution reactions. Thermally initiated ligand substitution reactions proceed by reversible CO dissociation and not by scission of the rhenium–rhenium bond as the primary activation step in thermally initiated substitution reactions of $Re_2(CO)_{10}$ and of its substituted complexes. In contrast, photoinitiated reactions proceed with a substantial degree of metal–metal bond scission.

Our conclusions rigorously apply only to the $Re_2(CO)_{10}$ system. An extension of these conclusions to the $MnRe(CO)_{10}$ system appears reasonable on the basis of the results of previous investigations[12,14] and the similar bond energies of Re–Re and Mn–Re in the corresponding decacarbonyls,[26-29] An analogous extension to the $Mn_2(CO)_{10}$ system appears more tenuous because of the very small Mn–Mn bond energy but compensatorily the average Mn–CO bond energy is substantially smaller than the average Re–CO bond energy in the respective dimetal decacarbonyls.[29] In any case, our experiments raise significant questions about the interpretation of the kinetic evidence for the $Mn_2(CO)_{10}$ system. The homolytic fission mechanism that was advanced for all $M_2(CO)_{10}$ systems was predicated on the observed half-order rate behavior of decomposition at less than limiting rates and the congruence of limiting rates of ligand substitution and decomposition.[4,11] Our results for the rhenium system permit a reinterpretation of these observations that is consistent with rate-limiting CO dissociation followed by fragmentation of the unsaturated dimer. Although the lack of two stable isotopes for manganese precludes experiments analogous to those presented here for the $Re_2(CO)_{10}$ system, an analysis of the ^{13}CO + $Mn_2(CO)_{10}$ reaction could be insightful.[30]

With a sufficient supply of pure metal isotopes, we plan analogous crossover studies of reactions for ruthenium, iridium, and iron carbonyl complexes. We are now characterizing the mechanistic pathways of $Ru_3(CO)_{12}$ substitution reactions and of ostensibly cluster-based $H_4Ru_4(CO)_{12}$ catalytic sequences.

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Registry No. Re, 7440-15-5; $Re_2(CO)_{10}$, 14285-68-8; $Re_2(CO)_9P(C_6H_5)_3$, 27770-63-4; $P(C_6H_5)_3$, 603-35-0.

Supplementary Material Available: Mass spectrometric data for the exchange studies (33 pages). Ordering information is given on any current masthead page.

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(24) Decomposition of $Re_2(CO)_{10}$ was found to proceed at low rates at 150 °C in the absence of added CO. The initial products of decomposition were less soluble in alkanes than in $Re_2(CO)_{10}$. Although thermal decomposition has been a kinetically investigated reaction, the products are uncharacterized. We are presently attempting a characterization of this decomposition reaction for group 7 dimetal decacarbonyl molecules.

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(30) Additionally, we plan a mass spectrometric study of the $Mn_2(^{12}CO)_{10}$ and $Mn_2(^{13}CO)_{10}$ reactions with CO and with phosphines, a study that is a viable alternative to the metal-labeled crossover study. (**Note Added in Proof**: This study is partially completed. Thermally initiated substitution reactions of $Mn_2(CO)_{10}$ do not involve Mn–Mn bond scission. Coville, N.; Stolzenberg, A. M.; Muetterties, E. L., submitted for publication.)