Nature of the Carbonyl Semibridge Bond in Coordinatively Unsaturated Metal Carbonyl Compounds. Solvated and Semibridged Forms in Photolysis of $MM'(CO)_{10}$ (M, M' = Mn, Re) in 3-Methylpentane

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Low-temperature flash photolysis of $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$ in 3-methylpentane glass at 93 K leads to loss of CO as the sole net photochemical process. The initial product upon photolysis of $MnRe(CO)_{10}$ is the solvento form $MnRe(CO)_9(S)$ (S = solvent). In contrast with $Mn_2(CO)_9(S)$, which readily loses solvent at 93 K to form the semibridge form $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$, $MnRe(CO)_9(S)$ is stable. Upon warming of the glass, it recombines with CO without formation of the semibridge form. Irradiation with visible light at 93 K causes conversion to the semibridge form, $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$, in which the CO is presumed to be bound in η^1 fashion to Re and in η^2 fashion to Mn. $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ reacts with CO somewhat more readily than does $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$. On irradiation of $Re_2(CO)_{10}$, CO loss results in formation of the solvento form $Re_2(CO)_9(S)$, which upon warming recombines with CO without intermediate formation of the semibridging form. Irradiation with visible light does not result in conversion of the solvento to the semibridging form. Comparisons of IR and reactivity data for dinuclear manganese and rhenium carbonyl semibridging structures suggest that phosphine substitution at the metal stabilizes the semibridge form largely through steric effects. Loss of a CO or other ligand, with subsequent semibridge formation, reduces steric crowding at the metal center. In addition, the semibridge species, once formed, is stabilized by the presence of phosphines, which block access by incoming nucleophiles.

Examples of bonding of carbonyl groups to metals in modes other than the simple terminal (monohapto) form characteristic of mononuclear binary carbonyl compounds have been known since the determination of the structure of $Fe_2(CO)_9$ in 1939.[1] Since then, a myriad of carbonyl bondings to metals in various arrays have been discovered. It has come to be appreciated that changes in carbonyl bonding mode from one form to another often require rather low energies. A variety of empirical generalizations regarding the prevalence of bridging modes for CO groups, related to the presence of ligands such as phosphines, or other factors affecting the electron-richness of the metal cluster core,[2,3] steric crowding,[4,5] and whether the metal is from the first, second, or third row of transition metals,[6] have arisen.

The nature of semibridging CO groups, in which the normal terminal CO group bonding to a metal is disturbed by the interaction between the CO group and one or more other metal centers, has received considerable attention. An early, important analysis is due to Cotton,[7] who considered unsymmetrically bridging CO groups shared between two metal centers. Cotton pointed to the existence of a continuum of bonding modes, ranging from a pure terminal bond at one extreme to the formation of a symmetrically bridging CO at the other. The concerted formation of bridging bonds by two CO groups is of particular interest because of its common role in intramolecular exchanges of CO groups in clusters. The presence of semibridging CO groups in ground state structures can generally be rationalized as a means of achieving equalization of charges on the metal centers. Hoffmann and co-workers analyzed $Cp_2Mo_2(CO)_4$ and $Cp_2Fe_2(CO)_4$ via extended Huckel calculations and concluded that a general characteristic of bridging or semibridging carbonyl arrangements is donation of electron density from the metal d orbitals into the 2π (π^*) orbital of the CO group.[8]

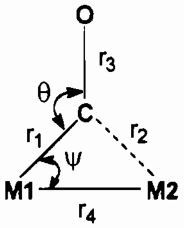

Figure 1. Geometrical parameters of semibridging carbonyl.

Employing the concept of a continuum of structures, coupled with the methods of Bürgi and Dunitz for building models of reaction trajectories from structural data,[9] Crabtree and Lavin have carried out an analysis of the structural parameter changes accompanying the transition from a fully terminal CO to one that is symmetrically bridging.[10] The parameters of the model are illustrated in Figure 1. The angles θ and ψ are of particular importance. As the carbonyl group moves from terminal to bridging, θ decreases from 180° to about 135° and ψ falls from as high as 125° to as low as 40°.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

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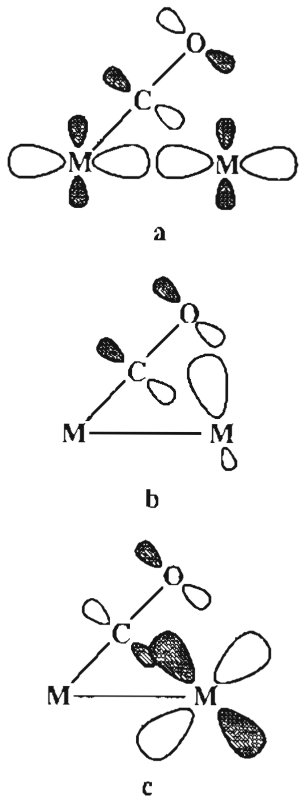

Figure 2. Schematic illustrations of orbital interactions between semibridging carbonyl and metals. In (a) the interaction occurs mainly between the carbon lobe of the carbonyl π^* orbital and the occupied metal−metal bond; in (b), between the occupied π orbital of the CO group and a vacant orbital on the metal; in (c), between an occupied largely nonbonding orbital on M and the π^* orbital of CO.

While the bent semibridging mode of CO bonding has been well recognized for some time, the so-called linear semibridge was more recently identified as a distinctive mode of bonding. The first example of such a bonding mode was provided by Commons and co-workers,[11,12] who discovered an apparently η^2 bonding interaction of a carbonyl group with the second Mn atom in $Mn_2(CO)_5(dppm)_2$. The angle ψ has a value of 43°, but θ is close to 180°. Shortly afterward, Curtis and co-workers reported the structure of $Cp_2Mo_2(CO)_4$,[13] which contains multiple linear semibridges.

The most obvious structural characteristic of the linear semibridge arrangement, a value near 180° for θ, has prompted theoretical analysis. Theoretical treatments of $Cp_2Mo_2(CO)_4$[8,14] and $Mn_2(CO)_5(PH_3)_4$[15] indicate that the primary mode of interaction of the semibridging CO with the two metal centers occurs through a three-center, two-electron bonding involving primarily the carbon lobe of the carbonyl π^* orbital and an occupied, in-phase combination of metal d orbitals. The resulting bond, illustrated schematically in Figure 2a, concentrates charge in the triangular region with the two metal atoms and carbonyl carbon atom as vertices. The theoretical models do not appear to assign a strong role to the intuitively appealing bonding mode illustrated in Figure 2b, which involves donation of electron density from the occupied π orbital of CO into an orbital of M made vacant by the loss of a ligand from that center. A concurrent reciprocal interaction of an occupied orbital on M with the carbonyl π^* orbital, Figure 2c, is also possible,[8,10] depending on the relative electron-richness of the various bonding centers.

In their analysis of bridging and semibridging carbonyl groups, Crabtree and Lavin distinguish linear semibridging forms on the basis of structural features, notably high values of θ. Within the broad category of linear semibridging forms, they further distinguish four types. The compound $Mn_2(CO)_5(dppm)_2$ represents the sole example of their type IV. The authors speculate that this example may be one in which there is significant donation from the metal center to the CO π^* orbital, in a three-center, two-electron interaction, Figure 2c.

In 1983 Hepp and Wrighton reported the photolysis of $Mn_2(CO)_{10}$ in 3-methylpentane (3MP) glass at 77 K.[16] Under these conditions, $Mn(CO)_5$ radicals formed via homolysis of the Mn−Mn bond would be expected to undergo rapid geminate recombination within the solvent cage formed by the 3MP glass. On the other hand, CO molecules lost via dissociative loss of CO from $Mn_2(CO)_{10}$ might, by virtue of their small size, escape the solvent cage with sufficient efficiency to lead to an observable net photochemical change. Indeed, a product of the continuous photolysis, featuring an absorption at 1759 cm^{-1}, was observed. The analogy with $Mn_2(CO)_5(dppm)_2$ led Hepp and Wrighton to propose that the loss of CO from one manganese center had led to formation of a semibridging CO bond of the kind observed by Commons *et al.*

Since Hepp and Wrighton's work, a large number of metal carbonyl species formed via low-temperature photolysis in matrices, glasses, or fluid media have been assigned structures containing a linear semibridging carbonyl. In the absence of detailed structural information on such species of high reactivity, the principal bases for assuming the presence of a bridging carbonyl are a characteristic low-frequency CO stretch in the IR and reactivity patterns, such as formation from a solvento species,[17] recombination with CO to re-form the starting material, or other chemical transformation that might reasonably be imputed to a semibridging species.

Important characteristics of the semibridging forms generated via photochemical loss of CO or other ligand from a metal center are as follows: (i) They are formed as a result of coordinative unsaturation at the metal center. Formation of a bridging or semibridging arrangement in these cases can be viewed as a means of molecular "self-repair", to compensate for the loss of a ligand. (ii) They may be highly reactive species, which react with nucleophiles quite rapidly even at low temperatures. At the same time, however, their stabilities vary considerably, depending on the metals involved and the presence of other ligands (*vide infra*).

It is tempting to assign the type of carbonyl bridging or semibridging bonding in these high-energy intermediates on the basis of their CO stretch frequencies or reactivity patterns relative to those of other species. However, such assignments are necessarily tentative. While it is useful for discussion purposes to assign structures to the intermediates, the most important issues are not structural ones, but rather the patterns of reactivity and stability as a function of such parameters as metal, bond types, ligand environments, and charge.

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In this contribution we discuss the patterns of reactivity observed to date for coordinatively unsaturated manganese and rhenium carbonyl intermediates containing bridging carbonyls. For purposes of discussion we assume that the structures are of the semibridging type and that they are reasonably close to the linear type (i.e., ψ is 160−180°). The observed properties of the systems are considered in light of the alternative bonding modes depicted in Figure 2. Secondly, we present new experimental evidence regarding the relative stabilities and barriers to formation of the semibridging CO form in $MM'(CO)_{10}$ (M, M′ = Mn, Re) via photolysis in 3MP glass at low temperatures.

Experimental Section

All experiments were carried out under an atmosphere of purified argon, employing Schlenk techniques. 3-Methylpentane (3MP, 99+%, Aldrich) was distilled over CaH_2, passed over activated silica, and stored over freshly activated 4 Å molecular sieves. It was subjected to four freeze−pump−thaw cycles before use. $Mn_2(CO)_{10}$ was purchased from Strem and sublimed prior to use. $Re_2(CO)_{10}$ was purchased from Strem and used as received.

$MnRe(CO)_{10}$ was synthesized by a cross-coupling reaction, involving photolysis of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in hexane, using a sunlamp as source. $MnRe(CO)_{10}$ was then separated and purified by passing through a column of activated neutral Al_2O_3, with hexane as eluent. The CO IR stretching bands in hexane, 1947 (w), 1979 (m), 1993 (vw), 2000 (w), 2018 (vs), 2055 (m), and 2126 (w) cm^{-1}, are consistent with those previously reported for $MnRe(CO)_{10}$.[18]

IR spectra were recorded on a Perkin-Elmer 1710 FTIR spectrophotometer. A sealable 1.0 mm CaF_2 variable-temperature solution cell from SPECAC was used. The solution of dinuclear carbonyl (~0.3−0.5 mM) in 3MP was loaded into the IR cell under Ar. A SPECAC Model 21500 variable-temperature system was employed. The cell was cooled to 93 K using liquid nitrogen. After a solution in the cell had been flash-photolyzed by a conventional xenon flash lamp source (broad-band, UV−visible), the apparatus was quickly moved to the IR spectrometer to record spectra. To obtain the desired IR spectra at various temperatures, the solvent background spectra, recorded separately at corresponding temperatures, were subtracted from the solution spectra and saved on computer disks. The data analyses were performed using a combination of ASYST-based programs and SlideWrite Plus version 5.0. A sunlamp (GE, 275 W) was also employed, at times in combination with optical filters (long-pass filters with cutoffs at 450 and 420 nm). In addition to the predominant line at 366 nm, the sunlamp also emits at ~575, 545, 430, 400, and 320 nm.

Results

When $MnRe(CO)_{10}$ in 3MP at 93 K is flash-photolyzed using a conventional xenon flash lamp, the IR difference spectrum following the flash reveals loss in absorbance due to $MnRe(CO)_{10}$ (negative absorptions at 2127, 2055, 2017, and 1976 cm^{-1}) and the appearance of positive absorbances at 2112, 2030, 2002, 1983, 1966, 1955, and 1939 cm^{-1}. Seven consecutive flashes resulted in consumption of about 35% of the $MnRe(CO)_{10}$. Figure 3a shows the difference IR spectrum after and before the flashes. The expanded absorbance scale in the free CO stretching region indicates the presence of free CO (2132 cm^{-1}) resulting from loss of CO from $MnRe(CO)_{10}$. However, there is no evidence for bridging CO in the IR spectrum of the CO-loss product. The IR spectrum is consistent with formation of a solvento species, $MnRe(CO)_{10}(S)$, where S represents a solvent molecule bound to the metal in an equatorial site. For comparison, the N_2-coordinated species *eq*-$MnRe(CO)_9(N_2)$ exhibits IR bands at 2116, 2040, 2016, 2010, 1980, and 1965 cm^{-1} in an N_2 matrix at 20 K and bands at 2112, 2038, 2012, 2008, 1976, and 1965 cm^{-1} in liquid Xe at 193 K.[19]

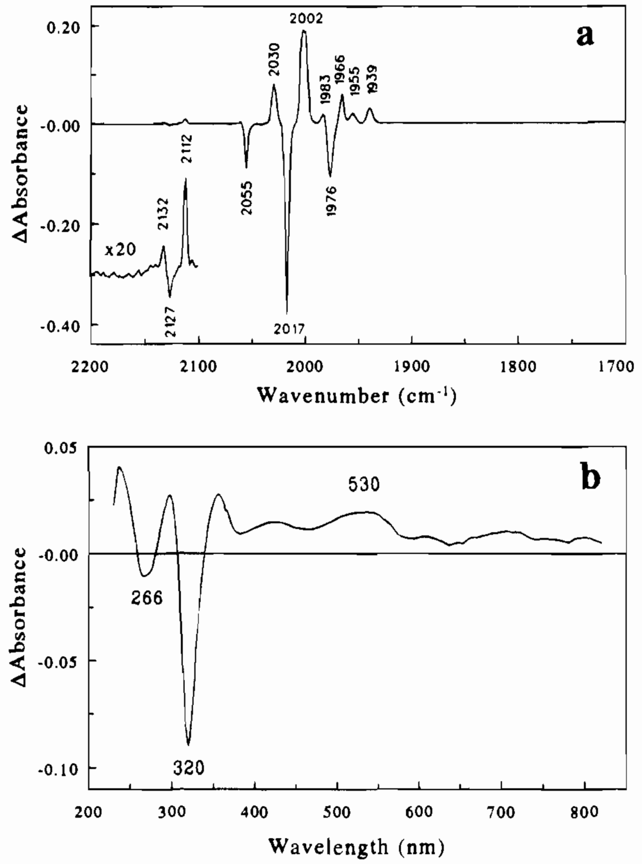

Figure 3. Difference FTIR spectrum (a) and UV−visible spectrum (b) of 0.3 mM $MnRe(CO)_{10}$ in 3MP at 93 K before and after several xenon lamp flashes.

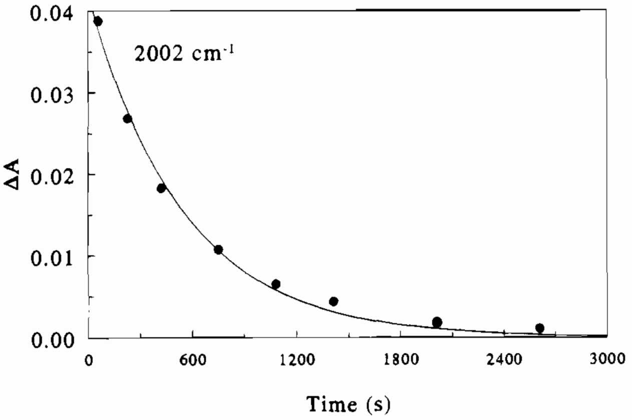

Figure 4. Decay of the IR absorbance at 2002 cm^{-1} in $MnRe(CO)_9(S)$ in 3MP at 123 K, due to reaction with CO. The solid line represents a fit to an exponential decay, with $k = 2 \times 10^{-3}\ s^{-1}$.

An analogous formation of a solvento species has been seen upon flash photolysis of $Mn_2(CO)_{10}$ at 93 K.[17] However, $Mn_2(CO)_9(S)$ converts at 93 K to the semibridged form $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$, with a first-order rate constant of $5 \times 10^{-3}\ s^{-1}$. By contrast, $MnRe(CO)_9(S)$ appears to be stable at 93 K for long times. Upon warming of the glass to 123 K, $MnRe(CO)_9(S)$ recombines with CO to re-form $MnRe(CO)_{10}$, with no sign in the IR spectrum of the intermediate formation of the semibridge form. As shown in Figure 4, the decay of $MnRe(CO)_9(S)$, monitored at 2002 cm^{-1}, can be fitted as a first-

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order decay process, with rate constant of about 2×10^{-3} s^{-1} at 123 K. The process may, however, be bimolecular. An approximate second-order rate constant can be estimated from the expression $k = 1/c_0t_{1/2}$ (where c_0 is the initial concentration of CO and MnRe(CO)$_9$(*S*), $\sim 10^{-4}$ M, and $t_{1/2}$ is estimated from Figure 4 to be about 300 s) as 30 M^{-1} s^{-1}.

Figure 3b shows the difference UV−visible absorption spectrum attendant upon photolysis of MnRe(CO)$_{10}$. There is a weak absorbance in the vicinity of 530 nm associated with formation of MnRe(CO)$_9$(*S*). Irradiation of the glass at 93 K following flash photolysis, using a sunlamp with a >450 nm long-pass filter, causes reaction of MnRe(CO)$_9$(*S*) without notable change in the absorbances due to MnRe(CO)$_{10}$. The difference IR and UV−visible spectra are shown in Figure 5. The positive bands, at 2113,[20] 2061, 2020, 1997,[20] 1979, 1955,[20] 1930, and 1761 cm^{-1} indicate formation of a new species, one involving a CO bridge. Our interpretation of these results is that visible irradiation causes conversion of a solvento species, MnRe(CO)$_9$(*S*), to a semibridged species, MnRe(CO)$_8$(μ-η^1,η^2-CO). However, at the same time, the irradiation may also be producing recombination with CO, as reported earlier by Turner and co-workers for irradiation of MnRe(CO)$_9$ in an Ar matrix at 12 K.[21] Thus, the match of IR bands in our difference spectrum with those associated by Turner *et al.* with MnRe(CO)$_8$(μ-η^1,η^2-CO) is incomplete, possibly in part because of the difference in experimental conditions, in part because their spectra may have contained lines due to MnRe(CO)$_9$(*S*), not recognized by them as such, and in part because visible irradiation on our part produces not only the process shown in eq 1 but those in eq 2 or 3 as well. The most important aspect

$$\mathrm{MnRe(CO)_9}(S) \xrightarrow{h\nu} \mathrm{MnRe(CO)_8}(\mu\text{-}\eta^1,\eta^2\text{-CO}) \quad (1)$$

$$\mathrm{MnRe(CO)_9}(S) + \mathrm{CO} \rightarrow \mathrm{MnRe(CO)_{10}} \quad (2)$$

$$\mathrm{MnRe(CO)_8}(\mu\text{-}\eta^1,\eta^2\text{-CO}) + \mathrm{CO} \rightarrow \mathrm{MnRe(CO)_{10}} \quad (3)$$

of the present results, however, is that under flash photolysis conditions, as opposed to continuous irradiation, it is possible to form a solvento species, MnRe(CO)$_9$(*S*), which has substantial kinetic stability with respect to thermal conversion to the semibridging form, in distinction to Mn$_2$(CO)$_9$(*S*), which readily converts to the semibridging form at 93 K.

Once formed, MnRe(CO)$_8$(μ-η^1,η^2-CO) recombines with CO to form MnRe(CO)$_{10}$ at 148 K. Figure 6a shows the IR spectral change, and Figure 6b shows an exponential fit to the decay of absorbance at 2021 cm^{-1}. (The negative, broad absorptions in Figure 6a are due to formation of solid MnRe(CO)$_{10}$, which falls from solution upon formation at this temperature.) The data are not adequate to permit a full kinetics analysis. The limited data provide a rough fit to a first-order process as shown in Figure 6b, with apparent first-order rate constant 3.8×10^{-3} s^{-1}. Assuming a bimolecular process, the rate constant can be estimated as $k = 1/c_0t_{1/2}$, where $t_{1/2}$ is the half-life, estimated from Figure 6b as 200 s, and c_0 is the initial concentration of CO and MnRe(CO)$_8$(μ-η^1,η^2-CO), $\sim 5 \times 10^{-5}$ M. This yields a second-order rate constant of about 100 M^{-1} s^{-1} at 148 K. For comparison, the decay of absorbance due to Mn$_2$(CO)$_8$(μ-η^1,η^2-CO) upon recombination with CO at 155 K is shown in Figure 7. In this case, the apparent first-order rate constant is 4.0×10^{-3} s^{-1}. We estimate a bimolecular rate constant of 50 M^{-1} s^{-1} at 155 K. These observations suggest that MnRe(CO)$_8$(μ-η^1,η^2-CO) is more reactive than Mn$_2$(CO)$_8$(μ-η^1,η^2-CO), in agreement with the observations of Turner *et al.*

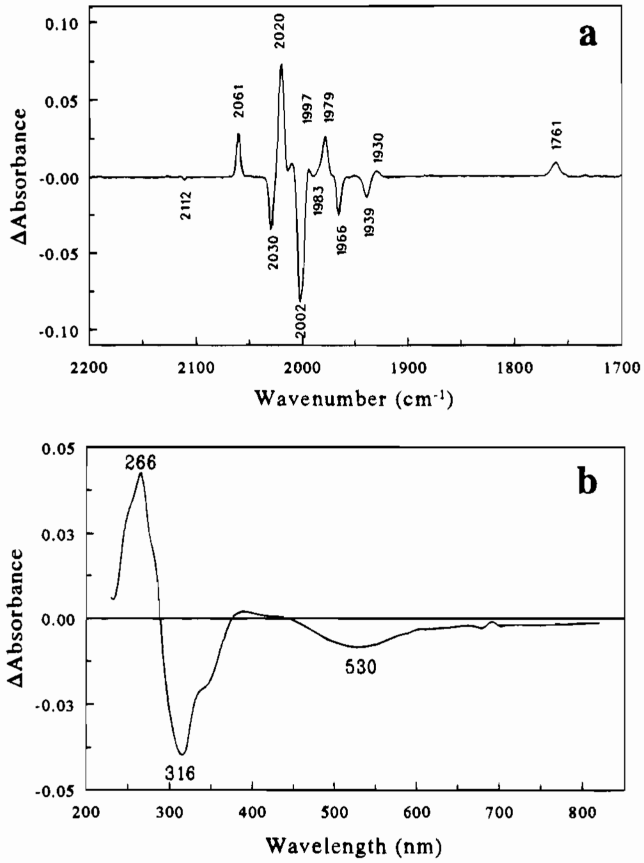

Figure 5. Difference FTIR spectrum (a) and UV−visible spectrum (b) of MnRe(CO)$_9$(*S*) in 3MP at 93 K before and after filtered sunlamp irradiation.

Flash photolysis of Re$_2$(CO)$_{10}$ in 3MP at 93 K yields a CO-loss species to which we assign the structure *eq*-Re$_2$(CO)$_9$(*S*). Figure 8 shows the difference IR and UV−visible spectra before and after several flashes with a xenon flash lamp. There is no evidence in the IR spectrum of a bridging carbonyl, in agreement with the findings of Turner and co-workers.[21] The IR band pattern, 2110, 2052, 2019, 1998, 1991, 1969, and 1941 cm^{-1}, is consistent with an equatorially-substituted solvento species and is in good agreement with the data reported for photolysis in Ar at 20 K.[21] For comparison, the N$_2$-coordinated species, *eq*-Re$_2$(CO)$_9$N$_2$, exhibits IR bands at 2114, 2059, 2013, 2007, 1991, 1982, and 1964 cm^{-1} in an N$_2$ matrix at 20 K and bands at 2111, 2058, 2008, 2007, 1990, 1981, and 1966 cm^{-1} in liquid Xe at 193 K.[19]

Re$_2$(CO)$_9$(*S*) is stable at 93 K. Upon warming to about 173 K, it recombines with CO to regenerate Re$_2$(CO)$_{10}$. There is no evidence for a bridging CO intermediate at any stage in the process. The difference UV−visible absorption spectrum, shown in Figure 8b, indicates that Re$_2$(CO)$_9$(*S*) exhibits an absorption band in the 370−500 nm region. However, in contrast with the behavior of MnRe(CO)$_9$(*S*), subsequent irradiation of the photolyzed glass with visible light (sunlamp with a >420 nm long-pass filter) caused little reaction of Re$_2$(CO)$_9$(*S*). In particular, there was no evidence of a CO-bridged species.

Discussion

A. Semibridge Bonding in Coordinatively Unsaturated Dinuclear Species. For the purposes of the discussion that

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(20) These bands are not evident in Figure 5, because they overlap extensively with bands of MnRe(CO)$_9$(*S*). However, careful measurements of relative intensity changes ensure that they are present.

(21) Firth, S. P.; Hodges, M.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 4608.

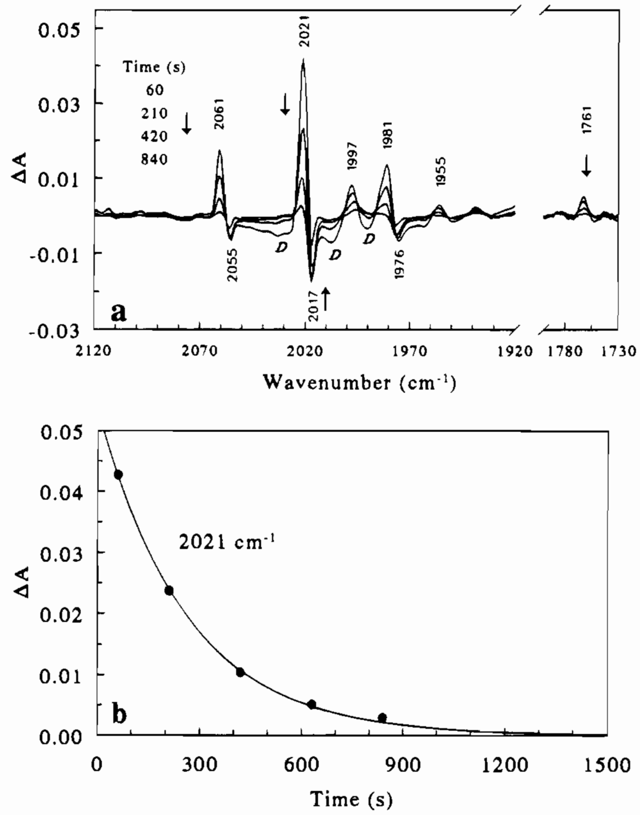

Figure 6. (a) Difference FTIR spectrum of $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ in 3MP as a function of time at 148 K. (b) Difference absorption at 2021 cm^{-1} as a function of time. The solid curve represents a fit to an exponential decay with $k = 3.8(\pm 0.4) \times 10^{-3}\ s^{-1}$.

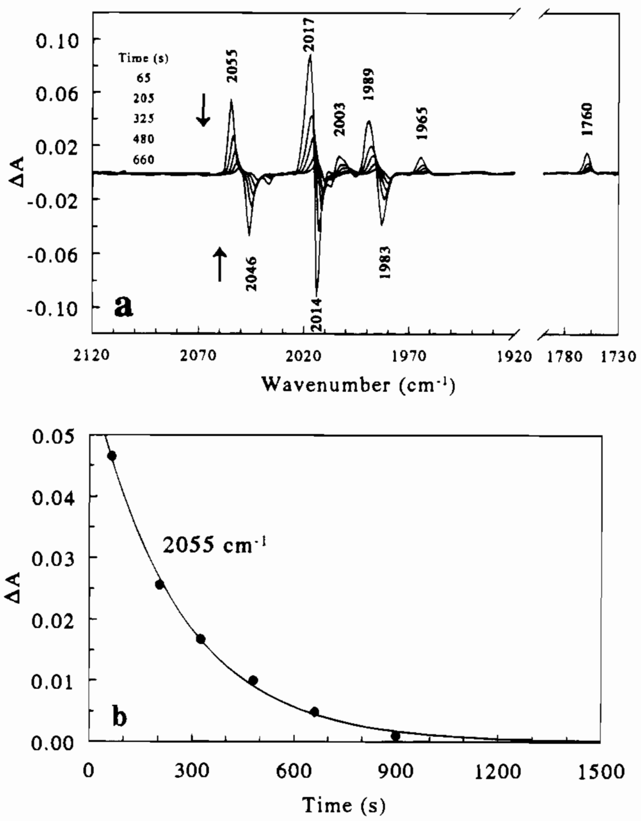

Figure 7. (a) Difference FTIR spectrum of $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ at 155 K in 3MP as a function of time. (b) Graph of the absorbance at 2055 cm^{-1} as a function of time. The solid line represents a fit to an exponential decay with $k = 4.2(\pm 0.4) \times 10^{-3}\ s^{-1}$.

follows, we will assume that the bridging CO bonding arrangements in the dinuclear species under discussion are of the linear semibridging type, unless indicated otherwise. Whether these species are in fact *linear* semibridging is open to question, as pointed out in the introduction. It is not even certain that they are semibridging, but the asymmetry in the structure occasioned by loss of a CO group from one of the metal centers argues for a corresponding asymmetry in the bridging CO arrangement, particularly in the absence of a strongly electron-donating ligands such as C_5H_5. In the case of $Cp_2Fe_2(CO)_4$, photochemical loss of CO gives rise to $Cp_2Fe_2(\mu\text{-}CO)_3$[22] but also to a presumptively semibridging form, $Cp_2Fe_2(CO)_3(\mu\text{-}\eta^1,\eta^2\text{-}CO)$.[23]

So long as the angle θ (Figure 1) does not depart markedly from 180°, the bonding modes illustrated in Figure 2 should serve adequately as a basis for discussion of the effects of structural variations on the nature and stability of the semibridging carbonyl in CO-loss products. With these bonding models in mind, it is useful to consider the data in Table 1, which shows the IR CO stretching frequencies observed for the semibridging CO in several dinuclear manganese and rhenium compounds formed via photolytic loss of CO (or, in the case of $Mn_2(CO)_5$(bidentate phosphine)$_2$ compounds, thermal loss of CO). The semibridging CO stretching frequency decreases markedly with increasing replacement of CO on the metal by phosphorus donors. While this might be taken at first sight as evidence of increasing degree of interaction of the semibridging CO with the second metal center, account must also be taken of the fact that the stretching frequencies of *all* CO groups are shifted to lower frequency by increasing substitution. To take this into account, ν_{ATCO} represents the arithmetic average of all the CO IR stretching modes characteristic of the terminal CO groups in the semibridging molecule. This rather crude measure takes into account increasing electron density at the metal and the fact that π back-bonding is shared among a smaller number of CO groups as the degree of substitution increases. The quantity Δ represents the difference between the frequency of the semibridging CO stretch frequency and ν_{ATCO}. Quite strikingly, the difference is virtually constant throughout the series of Mn_2 compounds, even though the semibridging CO frequency varies by about 100 cm^{-1}. (The frequency of the semibridging CO stretch is affected by the geometrical placement of the phosphines relative to the semibridging group.[24] There might be as much as a 20 cm^{-1} variation in the semibridge frequencies among the phosphine-substituted compounds due to this factor, comparatively small in relation to the values for Δ.) The α-diimine entries are discussed below.

A second line of evidence relates to the stability of the semibridging form with respect to reaction with a nucleophile to form the fully saturated species. $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ reacts with CO at 155 K with a half-life of about 200 s. Under similar concentration conditions, $Mn_2(CO)_6[P(n\text{-}Bu)_3]_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ reacts with CO at 213 K with a half-life of about 300 s.[24] $Mn_2(CO)_6[PCy_3]_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ reacts very slowly with CO at 213 K; at room temperature it has a half-life following formation via photolysis of a few minutes.[24] $Mn_2(CO)_4(dppm)_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)$ reacts slowly with excess CO at elevated temperature, forming $Mn_2(CO)_6(dppm)_2$.[12,25] Further, in the series $Mn_2(CO)_6(R_2PCH_2PPh_2)$ (R = Et, Ph, c-C_6H_{11}), the ease of CO

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[22] (a) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022. (b) Hepp, A. F.; Blaha, J. P.; Lewis, C.; Wrighton, M. S. *Organometallics* **1984**, *3*, 174. (c) Blaha, J. W.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolph, C. L.; Wilson, B. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4561.

[23] Zhang, S.; Brown, T. L. *J. Am. Chem. Soc.* **1993**, *115*, 1779.

[24] Zhang, H.-T.; Brown, T. L. *J. Am. Chem. Soc.* **1993**, *115*, 107.

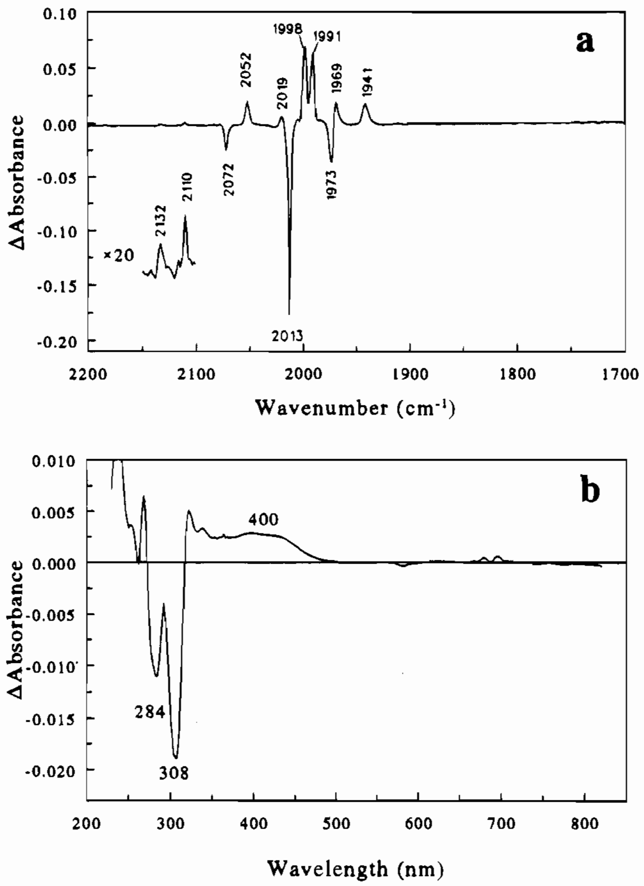

Figure 8. Difference FTIR spectrum (a) and UV−visible spectrum (b) of 0.3 mM Re$_2$(CO)$_{10}$ in 3MP before and after several xenon lamp flashes.

Table 1. Data Relating to Semibridging Carbonyl Groups in Dinuclear Manganese and Rhenium Compounds

species^a	ν(sb)^b	ν_{ATCO}^{b}	Δ^b	ref
Mn$_2$(CO)$_9$*	1760	2005	245	16, *c*
Mn$_2$(CO)$_7$[P(n-Bu)$_3$]$_2$*	1701	1964^d	263	24
Mn$_2$(CO)$_7$(dppm)* ^{e}	1708	1958	250	35
Mn$_2$(CO)$_7$[PCy$_3$]$_2$*	1699	1952^{d,f}	253	24
Mn$_\infty$(CO)$_5$(dppm)$_2$* ^{g}	1654	1900	245	25
Mn$_2$(CO)$_5$(depm)$_2$* ^{g,h}	1646	1891	245	25
Mn$_2$(CO)$_5$(dcpm)$_2$* ^{g,i}	1644	1890	246	25
MnRe(CO)$_9$*	1765	2005	240	21, *c*
Mn$_2$(CO)$_7$(α-diimine)* ^{j}	1816	1947	131	30a
MnRe(CO)$_7$(α-diimine)* ^{k}	1805	1958	153	30b

^{a} The asterisk notation indicates the presence of a semibridging CO (μ-η^1,η^2-CO). ^{b} cm^{-1}. ^{c} Present work. ^{d} The bis(phosphine) compounds exhibit isomerism relating to the location of the phosphine relative to the semibridging bond. The values listed are for the *ax,ax* isomer, which is the one initially formed following photolysis. ^{e} In toluene solution. ^{f} The average value of the doublet at 1898 and 1882 cm^{-1} was counted as a single peak. ^{g} In cyclohexane solution.[25] ^{h} depm = Et$_2$PCH$_2$PPh$_2$. ^{i} dcpm = (c-C$_6$H$_{11}$)$_2$PCH$_2$PPh$_2$. ^{j} Mn$_2$(CO)$_7$(α-diimine)* = Mn(CO)$_4$−Mn(CO)$_2$(α-diimine)(μ-η^1,η^2-CO). That is, CO is coordinated η^2 to the metal atom bearing the α- diimine ligand. ^{k} MnRe(CO)$_7$(α-diimine)* = Re(CO)$_4$−Mn(CO)$_2$(α-diimine)(μ-η^1,η^2-CO). That is, CO is coordinated η^2 to the metal atom bearing the α-diimine ligand.

loss is enhanced with increasing steric requirement of R.[25] These comparative results suggest that there is a strong *steric* component to the decreasing reactivity toward CO recombination that attends substitution by phosphines of varying steric requirement at the Mn centers, in accord with earlier flash photolysis studies of CO recombination of CO with Mn$_2$(CO)$_7$(PR$_3$)$_2$* at room temperature.[26] Whether *any* of the variation in reactivity can be associated with an increased stability of the semibridge due to electronic influences as the extent of phosphorus substitution increases is not clear.[27,28]

Of the three bonding modes illustrated in Figure 2, (a) is the one which should take on increasing importance with increasing electron density at the metal centers. Indeed, this is the bonding mode proposed on the basis of theoretical work to be of principal importance in Mn$_2$(CO)$_4$(dppm)$_2$(μ-η^1,η^2-CO)[15]. Bonding mode (c) may also be of importance in this case, as suggested by Crabtree and Lavin. In Mn$_2$(CO)$_8$(μ-η^1,η^2-CO), at the other extreme, the manganese center from which the CO has been lost is clearly a strong Lewis acid, as evidenced by its high reactivity in binding to even weak nucleophiles such as 3MP or other hydrocarbon solvents, rapid reaction with CO or other nucleophiles, and ready oxidative addition of HSnBu$_3$ and addition of HSiR$_3$[29]. The bonding mode represented by (b) seems the more appropriate model for such a case. The various Mn$_2$(CO)$_6$[PR$_3$]$_2$(μ-η^1,η^2-CO) intermediates represent intermediate cases between these two extremes.

It is a characteristic of all three modes of binding shown in Figure 2 that they result in a lowering of the CO bond order. Each should therefore result in a lowering of the CO stretching frequency observed in the IR, as compared with that expected for a terminal CO group in the compound in question. The relative constancy in the frequency difference measure Δ shown in Table 1 is therefore understandable; though the bonding mode by which the semibridging CO is held in place may vary with the degree of phosphine substitution at the metals, each component of the bonding mix contributes to a lowering of CO stretching frequency.

The two α-diimine-substituted compounds shown in Table 1 represent exceptions to the empirical generalization outlined above.[30] In these cases, the replacement of CO groups occurs at only one of the metal centers whereas, in the other examples, the two metal centers are roughly equivalent. Replacement of CO groups at the metal to which the semibridging CO is coordinated in η^2 fashion by groups which, through their electron donation, lower the acidity of that metal center reduces the extent of interaction of CO with that metal. Thus, if bonding mode (b), Figure 2, is of importance in Mn$_2$(CO)$_9$* and MnRe(CO)$_9$*, as we believe it is, α-diimine substitution should reduce Δ, as observed (Table 1).

This conclusion implies that there is not a great deal of variation in the electronic component of the factors that contribute to the stabilities of the semibridging CO bonds in the cases in which substitution occurs symmetrically at both metal centers. On the other hand, increased steric crowding enhances the stability of semibridge bonding. This probably occurs in two ways. Increasing steric crowding about the metal centers impedes the approach of reagents which might react at the metal center. Secondly, the semibridge structure is less crowded overall than the structure that results from addition of

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(25) Wolff, T. E.; Klemann, L. P. *Organometallics* **1982**, *1*, 1667.

(26) Herrick, R. S.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 4550.

(27) While the replacement of semibridged CO by external reagents is slow, it is noteworthy that there exists a fairly facile *intra*molecular exchange involving the interchange of two CO groups in the η^2 semibridge bonding, with an activation energy of 17 kcal/mol.[28] The exchange involves a kind of wagging motion, in which one CO group replaces the other in a concerted manner, so this activation energy does not represent the energy required to entirely disrupt the semibridge.

(28) Marsalla, J. A.; Caulton, K. G. *Organometallics* **1982**, *1*, 274.

(29) (a) Sullivan, R. J.; Brown, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 9155. (b) Sullivan, R. J.; Brown, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 9162.

(30) (a) van der Graaf, T.; Stufkens, D. J.; Oskam, A.; Goubitz, K. *Inorg. Chem.* **1991**, *30*, 599. (b) Rossenaar, B. D.; van der Graaf, T.; van Eldik, R.; Langford, C.; Stufkens, D. J.; Vlček, A., Jr. *Inorg. Chem.* **1994**, *33*, 2865.

CO or any other nucleophile. Thus, there is likely to be a thermodynamic component to the stabilization in addition to the kinetic one. This is most evident in $Mn_2(CO)_6(dppm)_2$, which loses CO very readily. The illustration of the structure of $Mn_2(CO)_4(dppm)_2(\mu\text{-}\eta^1,\eta^2\text{-CO})$[11] reveals that the phenyl groups bound to phosphorus on the Mn center that is η^2-bonded to CO lie directly over the metal, occupying the volume of space that would be occupied by a terminal CO and more or less blocking access on the part of a nucleophile that might displace the semibridging CO. Indeed, Commons *et al.* allude to steric pressures as the origin of the ready extrusion of CO from $Mn_2(CO)_6(dppm)_2$.[11,12]

B. Semibridging Bonds in MM′(CO)₉ (M, M′ = Mn, Re). Turner and co-workers have studied the photochemical properties of $MnRe(CO)_{10}$[31] and have shown via elegantly designed experiments that (a) CO loss is accompanied by formation of a semibridging CO bond, both in an Ar matrix at 20 K and in *n*-heptane at 297 K, (b) photochemical loss of CO occurs exclusively from Mn, and (c) there is no exchange of the semibridging CO, which is coordinated η^1 to Re and η^2 to Mn, with the terminal CO groups on Mn during the lifetime of the intermediate in *n*-heptane at 297 K. Turner and co-workers also reported the absence of any evidence for a semibridging CO upon photolysis of $Re_2(CO)_{10}$, either in a matrix or in solution or the gas phase.[19]

In the present work we have shown that flash photolysis of $MnRe(CO)_{10}$ in a 3MP glass at 93 K results in CO loss, with formation of a solvento species, $MnRe(CO)_9(S)$. In contrast to the corresponding species formed upon photolysis of $Mn_2(CO)_{10}$, $MnRe(CO)_9(S)$ does not undergo ready thermal conversion to the semibridging form, $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$. Upon warming of the matrix, the sole process observed is recombination with CO in the temperature range up to about 123 K. Irradiation of the glass containing $MnRe(CO)_9(S)$ with visible light results in conversion to the semibridging form. $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$ undergoes reaction with CO upon warming of the matrix, at a rate faster than that for its analog, $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$.

In agreement with Turner *et al.*, we find no evidence for formation of a semibridging form upon photolysis of $Re_2(CO)_{10}$, neither initially following flash photolysis nor upon subsequent irradiation with visible light. The species formed upon photochemical loss of CO is assigned as an equatorially-substituted solvento species, *eq*-$Re_2(CO)_9(S)$.

These various observations lead to the following conclusions:

(i) Upon loss of CO from a Mn center in either $Mn_2(CO)_{10}$ or $MnRe(CO)_{10}$, there is a competition between solvation and semibridge formation for satisfying the coordinative unsaturation at the metal center.

(ii) The semibridge form, once formed, is thermodynamically more stable than the solvento species, in hydrocarbon solvents.

(iii) Upon formation of a solvento species, the thermal reaction leading to semibridge formation is probably a concerted displacement, rather than one rate-determined solely by the dissociation of solvent. This conclusion is based in part on the following considerations: In both $Mn_2(CO)_9(S)$ and $MnRe(CO)_9(S)$, the solvents occupies sites at the Mn atoms, which are electronically very similar in the two species. One would therefore expect that solvent dissociation would occur at about the same rate in both species, assuming that the steric properties of the Mn binding site are closely similar in the two cases, as seems reasonable. However, while replacement of solvent by the semibridge occurs readily at 93 K in $Mn_2(CO)_9(S)$, it is not observed over a long period under the same conditions in $MnRe(CO)_9(S)$. An additional source of activation energy other than that required for solvent dissociation is therefore required, at least in $MnRe(CO)_9(S)$.[32,33]

(iv) Visible light excitation of $MnRe(CO)_9(S)$ provides the activation energy required for replacement of solvent by the semibridge. Presumably, shorter wavelength irradiation would also suffice, via internal energy conversion processes. The distinction between the present results and those of Turner *et al.* lies in that they employed continuous photolysis in generating their matrix species whereas we employed only a few to several xenon lamp flashes. The latter procedure would minimize secondary conversion of the solvento species to the semibridge. Secondly, Turner *et al.* worked in Ar matrices. Ar is a much weaker base than 3MP and thus should not compete as well for the initially-formed unsaturated species during the short time that the molecule is reaching thermal equilibrium following the photochemical event. Turner *et al.* observed the semibridged species within 10 μs following flash photolysis of $MnRe(CO)_{10}$ at room temperature, a result which is consistent with a barrier to semibridge formation sufficiently high to preclude rapid reaction at 20 or even 93 K.

(v) $Re_2(CO)_{10}$ does not form a semibridge species upon photochemical CO loss, either upon initial CO loss or upon visible light irradiation of the solvento species. Although it might be argued that the observations can be accounted for in terms of a high barrier to semibridge formation, it seems most likely that the semibridge form is not thermodynamically stable relative to a solvento species, even in Ar.

In comparing the variations in stabilities and barriers to formation of semibridge bonding in the Mn_2, MnRe, Re_2 series, it is useful to begin with a comparison of $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$ and $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$. As shown in Table 1, the two species have comparable values for the semibridging CO stretch and roughly the same value for Δ. While $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$ reacts more rapidly with CO, the difference in reactivities of the two semibridging species is not great. Roughly speaking, then, the two semibridging species, once formed, are of comparable stabilities. They differ primarily in that the thermal barrier to formation from the solvento species is substantially greater for $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$. This difference is not ascribable to a difference in the ease of displacement of solvent from Mn, for the reasons discussed above. It might be ascribed to a higher M−M′−CO bending force constant when M′ = Re as compared with Mn or to differences in the ways the bonding overlaps develop with the bending motion of the CO resulting from differences in bond distances.

The question arises as to whether the varying stability of semibridge bonding in the series is related to variations in metal−metal bond distance. Coville and co-workers recently discussed bond length data in Mn_2, MnRe, and Re_2 carbonyl compounds.[34] The metal−metal bond distances vary in the order Mn−Mn = 2.90 Å, Mn−Re = 2.96 Å, Re−Re = 3.04 Å. At the same time, the Mn−CO distance to the carbonyl groups *cis* to the metal−metal bond averages 1.82−1.83 Å whereas the corresponding Re−CO distances average around 1.98 Å. Thus, while the metal−metal distance increases in the series, the substantially larger value for the Re−C bond distance more than compensates for an increase in M−M′ distance in

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[31] Firth, S. P.; Hodges, M.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1987**, *331*, 347.

[32] Further evidence comes from unpublished observations that the reaction of $Mn_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-CO})$ with CO follows second-order kinetics, first order each in CO and metal complex.[33]

[33] Zhang, H.-T.; Brown, T. L. Unpublished observations.

[34] Leins, A. E.; Billing, D. G.; Levendis, D. C.; du Toit, J.; Coville, N. J. *Inorg. Chem.* **1992**, *31*, 4756.

[35] Liu, X.-Y.; Riera, V.; Ruiz, M. A. *Organometallics* **1994**, *13*, 2925.

$MnRe(CO)_{10}$ and comes close to doing so in $Re_2(CO)_{10}$. We do not know the bond distances in the semibridging structure, but in $Mn_2(CO)_5(dppm)_2$ there is little change in the M−M′ distance as compared with that of the parent compound.[11] Thus, it does not seem likely that the failure to form a stable semibridge in $Re_2(CO)_9$ is due to the incapacity of the Re−CO grouping to span the larger M−M distance.

We noted above that the solvento form $Re_2(CO)_9(S)$ reacts with CO to re-form $Re_2(CO)_{10}$ at a much higher temperature than $MnRe(CO)_9(S)$ (173 K vs 123 K for comparable rates). It might be argued that the failure to form the semibridge is simply due to stronger binding of solvent at Re as compared with Mn. However, Turner also failed to observe a semibridge species in Ar matrices, even upon visible irradiation. Given that an Re−CO linkage does form a stable semibridge in $MnRe(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CO)$, the absence of such a stable form in $Re_2(CO)_9$ suggests that the spatial extent of the orbitals on the coordinatively unsaturated Re in the latter compound does not admit of a sufficiently stable semibridge, a consideration that should apply rather generally to third-row transition metal systems.

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