Femtosecond Infrared Study of the Dynamics of Solvation and Solvent Caging

Haw Yang,† Preston T. Sneé, Kenneth T. Kotz, Christine K. Payne, and Charles B. Harris*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720, and Chemical Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, California 94720

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Abstract: The ultrafast reaction dynamics following 295-nm photodissociation of Re2(CO)10 were studied experimentally with 300-fs time resolution in the reactive, strongly coordinating CCl4 solution and in the inert, weakly coordinating hexane solution. Density-functional theoretical (DFT) and ab initio calculations were used to further characterize the transient intermediates seen in the experiments. It was found that the quantum yield of the Re−Re bond dissociation is governed by geminate recombination on two time scales in CCl4, ~50 and ~500 ps. The recombination dynamics are discussed in terms of solvent caging in which the geminate Re(CO)5 pair has a low probability to escape the first solvent shell in the first few picoseconds after femtosecond photolysis. The other photofragmentation channel resulted in the equatorially solvated dirhenium nonacarbonyl eq-Re2(CO)9(solvent). Theoretical calculations indicated that a structural reorganization energy cost on the order of 6−7 kcal/mol might be required for the unsolvated nonacarbonyl to coordinate to a solvent molecule. These results suggest that for Re(CO)5 the solvent can be treated as a viscous continuum, whereas for the Re2(CO)9 the solvent is best described in molecular terms.

Introduction

The reactivity of multinuclear compounds can generally be photochemically activated, creating one or multiple coordinatively vacant sites at the metal.† Dinuclear metal complexes such as MM′(CO)10 (M, M′ = Mn, Re) can be viewed as prototypical compounds for organometallics of higher nuclearity in potential catalytic applications.2−4 The primary photochemical reaction of MM′(CO)10 in solution has been shown to result in (i) homolytic fission of the metal−metal σ-bond to form M(CO)5 radicals, (ii) dissociation of a CO ligand to form MM′(CO)9, and (iii) nondissociative relaxation to the electronic ground state: 2.5−8

![Chemical Equation]

The branching ratios have been found to depend on the excitation wavelength by which pathway (i) is favored by lower energy excitation whereas pathway (ii) is favored by higher energy excitation.9−12 Experimentally, the short-lived photofragments MM′(CO)9 and M(CO)5 have been identified and characterized in the gas phase,12,13 in low-temperature matrix isolation studies,14−19 in liquid Xe,17 and in room-temperature solutions.20−22 These studies have been instrumental in establishing our current understanding of the photochemistry of MM′(CO)10. However, the influence of the surrounding solvent over reaction pathways (i), (ii), and (iii) remains to be characterized. This work examines how the solvent participates in the chemical processes that follow photofragmentation of Re2(CO)10. For Re2(CO)10 a UV pulse may cleave the Re−Re bond to form two formally 17-electron Re(CO)5 radicals or the UV pulse may remove a CO ligand to form the coordinatively unsaturated Re2(CO)5. The chemistry that follows the generation of the reactive species Re(CO)5 or Re2(CO)9 is quite different. The rhenium pentacarbonyl Re(CO)5 that follows dissociation

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pathway (i) has been shown to assume a C4v, square-pyramidal geometry from solid CO matrix studies.18,19 Such a 17-electron Re(CO)5 radical is capable of abstracting a halogen atom from halogenated alkanes.21-23 This type of one-electron oxidative addition to a metal center has been thought to be one of the crucial steps in many catalytic reactions.24 One of the central questions regarding the reactivity of 17-electron species is the possible involvement of a 19-electron precursory complex of the form (CO)3Re...Cl–CR3 during the course of reaction. This question has been addressed in a recent study and it was found that for the abstraction of a Cl atom from CH3Cl–a by Re(CO)5, the rhodium radical is best viewed as an unsolvated 17-e- species.25 Due to the weak interaction between a Re(CO)5 radical and the surrounding solvent molecules, a geminate Re₂(CO)₁₀ radical pair may recombine to reform the parent Re₂(CO)₁₀ molecule on an ultrafast time scale. It will be shown that for this dissociation pathway, the competition of Cl- abstraction and geminate recombination is regulated by solvent caging.

For dissociation pathway (ii), Firth et al. have shown in a low-temperature study that the primary photoproduct Re₂(CO)₁₀ has a coordinatively vacant site in the equatorial position, denoted eq-Re₂(CO)₁₀.17 Irradiation with 546-nm light converts eq-Re₂(CO)₁₀ to the other isomer a-Re₂(CO)₁₀ with an axial vacant site. One possible reaction following CO photolysis is ligand substitution at the vacant site of Re₂(CO)₁₀. Coville and co-workers have studied a series of substituted Re₂(CO)₉L (L = ligand) and concluded that there is a delicate balance in the electronic and steric effects in the relative stability of the axially or equatorially substituted isomers.25-29 In room-temperature solutions, it is observed that a solvent molecule enters the coordinatively vacant site to form a solvated complex Re₂(CO)₁₀(solvent) within a few picoseconds following photodissociation. However, as will be shown later, such solvation may require structural reorganization of the Re₂(CO)₁₀ metal fragment. If the complexation energy of a solvent molecule and the metal center is not sufficient to compensate for the energy cost for structural reorganization, the unsolvated Re₂(CO)₁₀ complex may appear thermodynamically more stable in weak-coordinating solvents. For instance, the unsolvated eq-Re₂(CO)₁₀ complex has been observed in the Ar and N₂ matrices.17 With the aid of quantum-chemical calculations, the picture of reorganization/solvation will be used to explain the experimental results.

Methods

Samples. Dirhenium decaacyl Re₂(CO)₁₀ (98%) and carbon tetrachloride CCl₄ (99.9%, d = 1.589 g/cm³) were purchased from Aldrich, Inc. Hexane (C₆H₁₄, 99.9%, d = 0.664 g/cm³), trichloromethane (CH₂Cl₂, 99.9%, d = 1.484 g/cm³), and dichloromethane (CHCl₃, 99.9%, d = 1.325 g/cm³) were purchased from Fisher Scientific, Inc. All chemicals were used without further purification. The sample was enclosed in an airtight, demountable liquid IR flow cell (Harrick Scientific Corporation). The concentrations of the Re₂(CO)₁₀ solutions were approximately 7 mM in hexanes and 4 mM in chlorinated-substituted methanes.

Femtosecond Infrared Spectroscopy. Details of the femtosecond IR (fs-IR) spectrometer setup have been published elsewhere.20 Briefly, the output of a Ti:sapphire oscillator was amplified in a series of dye amplifiers pumped by a 30-Hz Nd:YAG laser. The UV and IR beams used to initiate and probe the reaction were generated through nonlinear crystals. The resulting 295-nm UV photons (with energy of ~5 µJ/pulse) were focused into a disk of ~200 µm diameter at the sample to initiate chemical reactions. The ~1-µJ IR pulses having a temporal full-width-half-maximum of about 70 fs and a spectral bandwidth of about 200 cm⁻¹ were split into a signal and a reference beam to minimize the shot-to-shot fluctuation and transient heating of the detector. These two beams were then focused into an astigmatism-corrected spectrographic monochromator (SpectraPro-150, Acton Research Corp., 150 g/mm, 4.0 µm blazed) to form two spectrally resolved images on a focal-plane-array (FPA) IR detector. The two femtosecond-resolved images were digitized by two windows of 12 × 200 pixels, which allowed simultaneous normalization of a ~70-cm⁻¹ spectrum. The censoring chip of the detector was an engineering grade, (256 × 256)-element HgCdTe matrix of dimensions 1.28 × 1.28 cm² (or 50 × 50 µm² per pixels). During the course of an experiment, the sensing chip and its immediate circuits were kept in contact with a 4-L liquid nitrogen dewar to increase its sensitivity in the IR range. The long-time temperature drift was minimized by normalizing the gain against the FPA readouts from a small region far away from the illuminated area. Rejection of bad laser shots further improved the S/N ratio. With a data acceptance ratio of about 0.5 and a 30-Hz laser repetition rate, it took about 1 min to acquire signals on the order of 1% absorbance change with a 10:1 S/N ratio after signal averaging for 1000 valid laser shots. The typical spectral and temporal resolution for this setup were ~4 cm⁻¹ and ~300 fs, respectively. The polarizations of the pump and the probe pulse were set at the magic angle (54.7°) to ensure that all signals were due to population dynamics. All kinetic data have been corrected for a positive chirp of ~1.4 fs/cm⁻¹, measured from pump-probe cross correlation with use of a silicon wafer. A broadband, wavelength-independent background signal from CaF₂ windows has also been subtracted from the transient spectra and kinetic traces.

Nanosecond Step-Scan FTIR. These measurements were made by using a Step-Scan FTIR spectrometer described elsewhere.30 The instrument was based on a Bruker IFS-88 FTIR with a special scanner module to allow step scanning. An InSb detector with a 40-ns temporal full-width-half-maximum (fwhm) measured from the IR scatter of 1064-nm light from a YAG laser was used. The IR light was focused in the cavity with two 10-mm focal length BaF₂ lenses, which gave beam sizes smaller than comparable curved mirrors, allowing increased IR throughput. The sample was photoexcited with 10-ns pulses at 295 nm from the second harmonic of a dye laser.

Theoretical. To represent the chemical species in a practically tractable way, the solvent molecule in the complexes Re₂(CO)₉(solvent) was represented by CH₄ for alkane or by CHCl₃ for solvation through the Cl atom in halogenated solvents. For density-functional theoretical (DFT) calculations, the commercial JAGUAR package was used.32 The exchange-correlation functional employed was the Becke’s three-parameter hybrid functional33 combined with the Lee–Yang–Parr (LYP) correlation functional,34 commonly denoted as B3LYP.35 This functional has been shown to give very good results for transition metal complexes.36,37 Except for molecules with apparent symmetry such as CH₄ or Re₂(CO)₁₀, no constraint was imposed during geometry optimization. The basis set consisted of the 6-31G basis functions for H, C, O, and Cl atoms,38 and the Los Alamos Effective Core Potential.
(ECP) for Re with the outermost core orbitals included in the valence description (ECP+5s5p6s5dp).\(^{(40)}\) To make certain that a proper energy extremum had been located each geometry optimization was followed by a frequency calculation at the same level of theory. The resulting frequency analyses were used to calculate thermodynamic properties such as the zero-point energy (ZPE) and enthalpy (H) at 298 K. The interaction energy between a metal fragment and a model solvent molecule was also calculated, using the counterpoise technique to account for basis set superposition error (BSSE).\(^{(41,42)}\)

Results and Discussions

The Reaction Dynamics following Dissociation Pathway (i): Photolysis of the Re–Re Bond. It has been shown in a previous Communication that the Re(CO)\(_5\) radical is only weakly solvated in alkane or chlorinated alkane solvents.\(^{(43)}\) The interaction energies for Re(CO)\(_5\)/CH\(_4\) and Re(CO)\(_5\)/CCl\(_4\) have been calculated to be ca. 0.2 kcal/mol and ca. 0.6 kcal/mol, respectively.\(^{(43)}\) The weak interaction allows the chemically active Re bond to recombine with another Re(CO)\(_5\) radical to form the parent Re\(_2\)(CO)\(_{10}\) without much energy cost in displacing the solvent molecule. In the reactive CCl\(_4\) solution, the parent Re\(_2\)(CO)\(_{10}\) molecule exhibits two reformation time scales of ~50 and ~500 ps. The Re(CO)\(_5\) radicals are also capable of abstracting a Cl atom from CCl\(_4\) to form Re(CO)Cl on a time scale of ~1.3 ns. In this section, it will be shown that the competing geminate-recombination and CI-atom abstraction are regulated by solvent caging, and that treating the solvent as a viscous continuum is sufficient to account for the observed dynamics.

The kinetic traces of the Re(CO)\(_5\)Cl and Re\(_2\)(CO)\(_{10}\) are reproduced in Figure 1. The biphasic recovery of the parent bleach shown in Figure 1b has been explained by a modified diffusion model in the literature.\(^{(44)}\) For clarity, the model and required parameters are briefly restated below. The reaction is considered to follow the diffusion equation in a continuous medium,

\[
\frac{\partial}{\partial t} w(r,t;r_0,R) = D \nabla^2 w(r,t;r_0,R) \tag{2}
\]

where \(w(r,t;r_0,R)\) is the time-dependent survival probability density of a pair of monomers and \(D\) is the diffusion coefficient of the monomer in the solvent. The model assumes that a pair of Re(CO)\(_5\) radicals rest at \(r_0\) apart at time \(t \to 0\). The two radicals can react to form Re\(_2\)(CO)\(_{10}\) when their separation \(r\) is equal to or smaller than a critical distance \(R\). To account for the finite recombination rate, an additional boundary condition at \(r = R\) is imposed,

\[
D \frac{\partial}{\partial t} w(r,t;r_0,R)_{r=R} = bw(r,t;r_0,R) \tag{3}
\]

Known as the “radiation boundary condition”, eq 3 states that the recombination rate is proportional to the concentration at the contact distance \(R\). The relation of the proportionality \(b\) in eq 3 to the recombination rate constant can be expressed by,

\[
k_r = 4\pi R^2 b \tag{4}
\]

The physical parameters needed for the analysis of the experimental data are the branching ratio \(Q_i\) for pathway (i), the solvent viscosity \(\eta\), the contact distance \(R\), the initial separation \(r_0\), and the recombination rate constant \(k_r\). The contact distance \(R\) is assigned as twice the distance from the center of the Re–Re bond to the center of the axial Re–C–O line. Similar treatments for the contact distance have been employed in the analysis of geminate pair dynamics of disulfides.\(^{(45,46)}\) By using the crystallographic data of Re\(_2\)(CO)\(_{10}\),\(^{(47)}\) \(R\) is estimated to be 6.3 Å. To verify this estimate, the DFT geometry for the Re(CO)\(_5\) radical and the Lennard-Jones parameters for the C and O atoms are used to construct a Lennard-Jones Re(CO)\(_5\) molecule suitable for classical molecular simulation.\(^{(46)}\) The contact distance in this approach is defined as the diameter of a sphere that encloses the Lennard-Jones Re(CO)\(_5\). This procedure gives a contact distance of 6.2 Å, consistent with the first estimate.

For the Cl-atom abstraction reaction in CCl\(_4\) solution (\(\eta_{CCl_4} = 0.97\) cp), the product kinetics and parent bleach signal are fitted simultaneously since they both draw from the same Re(CO)\(_5\) source. Three processes are considered to contribute to the observed product kinetics: vibrational cooling, nonequilibrium barrier crossing to form the product, and equilibrium barrier crossing. Incorporating these ideas, the normalized product signal is described as,

\[
I_{\text{prod}}(t) = A_{\text{vib}} \exp(-t/\tau_{\text{vib}}) + A_{\text{neq}}(1 - \exp(-t/\tau_{\text{neq}})) + \int_0^t dt' k_r M(t'/r_0,R) \tag{5}
\]

The first term of eq 5 describes the relaxation of vibrationally excited low-frequency modes (hot bands) that overlap with the product band; the second term models the nonequilibrium product formation with a phenomenological rise time \(\tau_{\text{neq}}\) and the last term relates the time-dependent Re(CO)\(_5\) concentration \(M(t,r_0,R)\) to the macroscopic, pseudo-
first-order rate constant $k_0$. To account for the nonequilibrium barrier crossing in the CCl₄ case, the normalized parent signal can be written as,

$$I_{\text{parent}}(t) = -1 + (1 - A_{\text{neq}}) \times Q_i \times \int_0^t 4\pi R^2 d\omega (r = R, r', \omega, R)$$ (6)

With $R$ fixed (=6.256 Å) and $Q_i$ (=0.8) obtained from experiments, the recombination rate is found to be $k_r = (1.0 \pm 0.2) \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, an order of magnitude greater than the literature value measured in CH₃CN, $(1.0 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This is not surprising since in the current simplified model, a single parameter $k_0$ is used to encompass all fast dynamics such as nondissociative energy relaxation and primary geminate recombination. The initial separation of the two Re(CO)₅ monomers was found to be $r_0 = 8.6 \pm 0.2$ Å, about 2.3 Å away from their contact distance. The Cl-atom abstraction rate $k_a = (7.5 \pm 0.4) \times 10^7 \text{ s}^{-1}$ is in very good agreement with the literature value, which is calculated to be $(1.8-9.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ from a set of Arrhenius parameters. The time constant for the fast rise of product kinetics $\tau_{\text{neq}}$ is found to be approximately 2–3 ps, with an amplitude $A_{\text{neq}} = 0.10 \pm 0.01$. That is, about 10% of the product is produced through nonequilibrium barrier crossing. Finally, the hot band amplitude $A_{\text{vib}}$ is found to be $0.13 \pm 0.01$ with a vibrational-cooling time $\tau_{\text{vib}} = 35 \pm 14$ ps. The resulting traces for the product and parent kinetics are plotted on top of the experimental data displayed in Figure 1.

Within the framework of the diffusion model, the physical origin of the experimental observation is illustrated in Figure 2. In Figure 2, the abscissa is the separation of the two Re(CO)₅ monomers, in units of Å. The equilibrium Re–Re distance $R_{\text{eq}} \approx 3.0$ Å, the contact distance $R \approx 6.3$ Å, and the initial separation $r_0 \approx 8.6$ Å are also marked. The portion to the left of $R$ is a schematic potential energy surface plot depicting dynamics that are not susceptible to the current model. To the right of $R$ are plots of the spatial distribution of a monomer around a recombination center at various time delays. At short time delays such as 1 and 5 ps, the distribution maxima still linger around the initial separation $r_0$. By comparing the 8.6-Å initial separation with the Lennard-Jones radius of CCl₄ of 5.8 Å, one can envision that following photodissociation the monomers are trapped in the first solvent shell for a few picoseconds. Furthermore, the initial distribution also broadens significantly on the 1–5 ps time scale. The broadening results in a fast buildup of the monomer concentration at $R$. Recall that the recombination rate $k_r$ is defined to be proportional to the concentration at the contact distance $R$ (eq 3). Consequently, the fast broadening of the distribution contributes to the experimentally observed fast recovery of the parent bleach. Driven by the accumulating population around $R$, the distribution diffuses away from the recombination center until the system reaches equilibrium. This is shown in Figure 2 for time delays longer than ca. 20 ps, where the distribution maximum starts to diffuse away noticeably. This diffusion process is identified with the longer recovery in the parent bleach data.

The Reaction Dynamics following Dissociation Pathway (ii): Photolysis of the Equatorial Re–CO Bond. The infrared spectra in the CO stretch region are presented in the form of difference absorbance in which positive bands indicate the appearance of new species while negative bands (bleaches)

![Figure 2. Illustration of the diffusion model for geminate recombination. On the abscissa, $R_{\text{eq}}$ is the equilibrium Re–Re bond length of Re₂(CO)₁₀. $R$ the contact distance, and $r_0$ the initial separation of the two Re(CO)₅ monomers. The schematic potential curve for the ground-electronic state and for the dissociative excited state are on the left. In this simplified model, the rate constant $k_r$ encompasses energy relaxation processes resulting from nondissociative energy relaxation and primary geminate recombination. Time evolution of the probability distributions (dashed curves) for the geminate pair are on the right. Inset: An illustration of solvent caging. The thick circles represent the Re(CO)₅ monomers and the thin circles CCl₄ molecules. A dashed circle roughly shows the extent of the first solvent shell.](Image 335x489 to 540x744)

represents the depletion of parent molecules. In the stronger coordinating CCl₄ solution, the 1945, 1985, 1998, 2005, and 2055 cm⁻¹ bands are assigned to the equatorially solvated nonacarbonyl species $eq$-Re₂(CO)₉(CCl₄). The CO stretching peaks of Re(CO)₅Cl also appear on the ultrafast spectra as a result of Cl-atom abstraction. The nonacarbonyl solvate $eq$-Re₂(CO)₉(CCl₄) is found to be stable up to the experimental time window of 2.5 μs.

In the weaker coordinating hexane solution, the early-time spectra (for example, the 10–ps panel of Figure 3) are typically broad and featureless which results from spectral overlap and excitation of low-frequency bands. As the photoproducts dissipate excess vibrational energy at later time delays, the IR bands narrow in and rise to reveal several identifiable bands. For the Re₂(CO)₁₀ molecules that dissociate through channel (i) in eq 1, the nascent Re(CO)₅ radicals appear as the most intense broad peak centering on 1992 cm⁻¹ in the 660-ps panel of Figure 3. This assignment is in very good agreement with the previously reported Re(CO)₅ band (1990 cm⁻¹) in cyclohexane solution.

On the basis of matrix-isolation experiments, the peaks at 1942, 1973, 1984, 1999, and 2051 cm⁻¹ on the same panel are attributed to the equatorially solvated dirhenium nonacarbonyl $eq$-Re₂(CO)₉(hexane), in which a solvent molecule occupies the equatorially vacant site left behind by the leaving CO ligand. The kinetic trace of $eq$-Re₂(CO)₉(hexane) at 2051 cm⁻¹ exhibits a single-exponential rise of 69 ± 5 ps and is attributed to

vibrational relaxation of the binuclear eq-Re₂(CO)₉(hexane) complex. As indicated by the nanosecond spectra in Figure 3, the eq-Re₂(CO)₉(hexane) solvate is stable on the ultrafast time scale up to 1 ns. But at longer time delays (>50 ns), the eq-Re₂(CO)₉(hexane) thermally transforms to another species that has discernible CO stretches at 1990, 1999, and 2043 cm⁻¹ as shown in the last panel of Figure 3. This species is assigned as unsolvated eq-Re₂(CO)₉, denoted [eq-Re₂(CO)₉]bare, based on theoretical considerations to be discussed below. Although the current experimental setup does not permit an accurate measurement of the transformation rate from the solvated eq-Re₂(CO)₉(hexane) to the unsolvated [eq-Re₂(CO)₉]bare, the time constraints (1 ns < rate < 50 ns) allow for an evaluation of the lower and upper bounds of the free-energy barrier, which is estimated to be 5.2 < ΔG‡ < 7.5 kcal/mol.

Quantum-Chemical Characterizations, Geometry Optimization. A series of DFT calculations were carried out in efforts to identify and further characterize the transient species that appear in the time-resolved IR spectra. Shown in Figure 4 are the optimized structures of the parent molecule Re₂(CO)₁₀ and the unsolvated Re(CO)₅ and Re₂(CO)₉. Compared to X-ray diffraction data, the calculations reproduce reasonably well the Re–C bond lengths in Re₂(CO)₁₀, which are on the average about 0.02 to 0.03 Å longer than experimental values. When the dissociation proceeds through pathway (ii) in eq 1, the resulting coordinatively unsaturated Re₂(CO)₉ can assume two different conformations that belong to different symmetry point groups. The structure of the ax-Re₂(CO)₉ conformer is located by removing an axial CO ligand from Re₂(CO)₁₀ as the initial guess for geometry optimization. The other eq-Re₂(CO)₉ conformer is located by removing an equatorial CO ligand from

Re₂(CO)₁₀ as the initial guess. For the addition of alkanes, the structures of ax-Re₂(CO)₉(CH₄) and eq-Re₂(CO)₉(CH₄), ax-Re₂(CO)₉(ClCH₃), and eq-Re₂(CO)₉(ClCH₃), Important geometrical parameters (in Å) are also shown in the figure.

Figure 3. Transient difference spectra in the CO stretching region for Re₂(CO)₁₀ in hexane solution at 10, 33, 66, 198, and 660 ps following 295-nm UV photolysis. The last panel is an averaged spectrum for pump-probe delay greater than 50 ns. The equatorially solvated eq-Re₂(CO)₉(hexane) is indicated by asterisks, and the Re(CO)₅ radical is marked by an arrow. IR bands due to the proposed [eq-Re₂(CO)₉]bare are marked by open circles. It is very likely, however, that the last panel is a spectrum of [eq-Re₂(CO)₉]bare and eq-Re₂(CO)₉(hexane) in equilibrium, considering the similar stability of the two species (see main text). No discernible spectral features were observed in the region 2080–2130 cm⁻¹ (not shown).

Figure 4. Schematic representations of Re₂(CO)₁₀, ax-Re₂(CO)₉, and eq-Re₂(CO)₉. Important geometrical parameters (in Å) and symmetry groups are also shown in the figure. Experimental values are included in parentheses.

Figure 5. Schematic representations of ax-Re₂(CO)₉(CH₄), eq-Re₂(CO)₉(CH₄), ax-Re₂(CO)₉(ClCH₃), and eq-Re₂(CO)₉(ClCH₃). Important geometrical parameters (in Å) are also shown in the figure.


Table 1. Summary of Relative Stability of the Axial and Equatorial Conformers at Various Levels of Theorya

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>B3LYP + ΔZPE</th>
</tr>
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<tbody>
<tr>
<td>Re2(CO)9</td>
<td>16.9</td>
<td>16.3</td>
</tr>
<tr>
<td>Re2(CO)9(CH4)</td>
<td>10.8</td>
<td>10.1</td>
</tr>
<tr>
<td>Re2(CO)9(CICl3)</td>
<td>11.1</td>
<td>11.0</td>
</tr>
</tbody>
</table>

a In the table, ΔZPE is the zero-point energy correction. The energies shown here correspond to (Eax - Eeq) in units of kcal/mol.

Quantum-Chemical Characterizations, Energetics. One next turns to the energetics of the species discussed above. The relative stability of the axial and equatorial form of dirhenium complexes is summarized in Table 1. The unsolvated eq-Re2(CO)9 is energetically 16.3 kcal/mol more stable than the unsolvated ax-Re2(CO)9, in accordance with the proposition that the electronic effect is the dominating factor for equatorial substitution in Re2(CO)9 complexes.27 Such electronic influence is somewhat lessened after solvation, as indicated by the 10.1 and 11.0 kcal/mol ax to eq stabilization energies for Re2(CO)9- (CH4) and Re2(CO)9(CICl3), respectively. The decrease in the (Eax - Eeq) energy gap upon solvation (∼6.2 or ∼5.3 kcal/mol) can be understood by two factors: the energy requirement for the aforementioned structural reorganization and the energy cost due to steric interaction of the solvent molecule and the metal fragment. While the steric interaction is difficult to evaluate with these calculations, the reorganization energy can be estimated by (Epicl - Ebare), where Ebare is the energy of the optimized, unsolvated dirhenium fragment ax-Re2(CO)9 (or eq-Re2(CO)9) and Epicl is the energy of the dirhenium fragment at the solvated geometry. Calculations show that there is almost no energy difference (<0.3 kcal/mol) for the conformational change in the dirhenium fragment from the unsolvated [ax-Re2(CO)9]bace to the axially solvated form [ax-Re2(CO)9]sol in either CICl3 or CH4. On the other hand, a minimum energy of 5.5 or 7.1 kcal/mol is required for the unsolvated [eq-Re2(CO)9]bace to rearrange to the equatorially solvated form [eq-Re2(CO)9]sol in CH4 or CICl3, respectively.35 The results suggest that the energy requirement for structural reorganization contributes significantly to the reduction of the (Eax - Eeq) energy gap upon solvation.

To examine whether the solvation energy is sufficient to compensate for structural reorganization, the binding energies for ax- and eq-Re2(CO)9...(solvent) are also calculated and summarized in Table 2. One sees in Table 2 that the binding energies for ax- and eq-Re2(CO)9...(CH4) are similar in magnitude; however, the energy cost for structural reorganization of the equatorially solvated species (5.5 kcal/mol) is approximately equal to the equatorially solvated species’ binding energy. As a result, the overall binding energy of eq-Re2(CO)9...(CH4) is on the order of 1–2 kcal/mol. Table 2 also shows that the binding energy of eq-Re2(CO)9...(CICl3) is about 9 kcal/mol greater than that of eq-Re2(CO)9...(CH4), providing a qualitative rationale for experimental observations that the equatorial solvate eq-Re2(CO)9(CICl3) is stable up to the experimental window 2.5 μs. The calculations predict their relative stability of dirhenium nonacarbonyl solvates to be, in order of increasing stability, ax-Re2(CO)9 ≪ ax-Re2(CO)9(CH4) ≈ eq-Re2(CO)9(CH4) ≈ eq-Re2(CO)9(CH3) ≈ eq-Re2(CO)9(CICl3). The relative stability of the ax-Re2(CO)9(CH4) and eq-Re2(CO)9(CH3), the weak binding energy of eq-Re2(CO)9(CH4), and an estimated minimal barrier of 6–7 kcal/mol for solvation of eq-Re2(CO)9 with CH4 lead one to propose the unsolvated eq-Re2(CO)9 as the thermodynamically more stable species in hexane solution.

Proposed Solvation Process. Within the context of the unsolvated eq-Re2(CO)9 being the most stable species, the experimental observations are explained in Figure 6. Photodissociation of an equatorial CO ligand creates a coordinatively vacant site at the metal, which is quickly occupied by a solvent molecule in the dense liquid environment within a few picoseconds to form the eq-Re2(CO)9(hexane) solvate. The equatorial solvate then vibrationally cools on a time scale of 69 ps. The vibrationally cooled equatorial solvate is stable on the ultrafast time scale (<1 ns), but transforms to the unsolvated eq-Re2(CO)9 within 50 ns after photolysis. That is, the hexane solvate may traverse a free-energy barrier in the range of 5.2 < ΔG‡ < 7.5 kcal/mol to become an unsolvated eq-Re2(CO)9. The theoretically estimated reorganization energy of 6–7 kcal/mol provides a reasonable rationale for the minimum free-energy barrier, although the nature of the transition state is not clear at this point. The experimentally observed greater stability of eq-Re2(CO)9(CCl4) over eq-Re2(CO)9(hexane) then can be understood by the much greater solvation energy exhibited by eq-Re2(CO)9(CCl4).

Conclusion

The ultrafast events that follow 295-nm photolysis of Re2(CO)10 have been studied in detail in the reactive, stronger-coordinating CCl4, and in the inert, weaker-coordinating hexane solvents. The experimental results for the Re2(CO)9/CCl4 system show that 22.5% of the initially excited Re2(CO)10 molecules dissociate to Re(CO)5 radicals that are able to escape cage recombination and abstract a Cl atom from the CCl4 solvent. About 2.5% of the excited Re2(CO)10 molecules dissociate to form Re(CO)5 radicals and react further to cross the energy barrier to abstract a Cl atom on a time scale faster than vibrational cooling. Such a nonequilibrium barrier crossing can be understood by considering the excess energy the initiation UV photon deposits on the Re(CO)5/solvent system. About 20% of the excited Re2(CO)10 molecules revert to
their electronic ground state, either via an internal relaxation or through geminate recombination.

In hexane solution, the recombination of Re(CO)\textsubscript{5} radicals is also regulated by solvent caging but without the competing channel of atom abstraction as in the case of CCl\textsubscript{4}. Following dissociation pathway (ii), the equatorial solvate eq-Re\textsubscript{2}(CO)\textsubscript{9}-(hexane) is found to further react to form another species on a time scale between 1 and 50 ns, or equivalently a free-energy requirement of 5.2 to 7.5 kcal/mol. With the aid of quantum-chemical calculations, this thermodynamically more stable species is attributed to the unsolvated eq-Re\textsubscript{2}(CO)\textsubscript{9}. In this picture, the energy requirement can be understood to stem from the necessary structural rearrangement for eq-Re\textsubscript{2}(CO)\textsubscript{9} to accommodate a solvent molecule in the equatorial position.

This work may suggest that for metal radical species the solvent can be treated as a viscous continuum, whereas for the dinuclear complexes the solvent is best described in molecular terms. This conclusion together with the notion of reorganization-solvation may help to better understand the roles of solvent in photoactivation of multinuclear organometallic compounds.

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**Supporting Information Available:** The Cartesian coordinates for structures optimized at the DFT-B3LYP level of theory (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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\(\Delta E\) Note that the structural reorganizational energies for the Re\textsubscript{2}(CO)\textsubscript{9} fragments are not included. See the text. In the table, \(\Delta ZPE\) is the zero-point energy correction, \(\Delta H\) is the correction term for finite temperature (298 K) enthalpy, and CP is the counterpoise procedure for correcting the basis set superposition error.

**Table 2. Summary of the Binding Energies\(^a\)**

\(^a\) Note that the structural reorganizational energies for the Re\textsubscript{2}(CO)\textsubscript{9} fragments are not included. See the text. In the table, \(\Delta ZPE\) is the zero-point energy correction, \(\Delta H\) is the correction term for finite temperature (298 K) enthalpy, and CP is the counterpoise procedure for correcting the basis set superposition error.