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Ultrafast Infrared Studies of the Role of Spin States in Organometallic Reaction Dynamics

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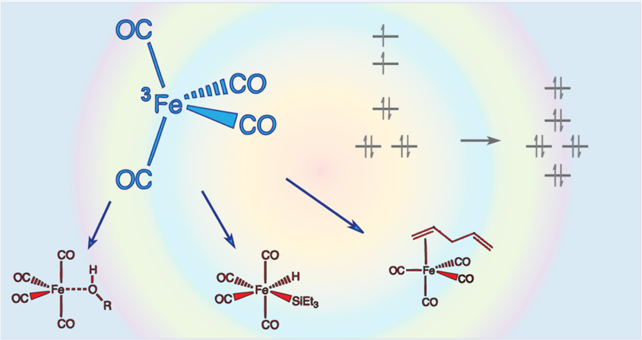

CONSPECTUS: The importance of spin state changes in organometallic reactions is a topic of significant interest, as an increasing number of reaction mechanisms involving changes of spin state are consistently being uncovered. The potential influence of spin state changes on reaction rates can be difficult to predict, and thus this class of reactions remains among the least well understood in organometallic chemistry. Ultrafast time-resolved infrared (TRIR) spectroscopy provides a powerful tool for probing the dynamics of spin state changes in organometallic catalysis, as such processes often occur on the picosecond to nanosecond time scale and can readily be monitored in the infrared via the absorptions of carbonyl reporter ligands. In this Account, we summarize recent work from our group directed toward identifying trends in reactivity that can be used to offer predictive insight into the dynamics of coordinatively unsaturated organometallic reaction intermediates.

In general, coordinatively unsaturated 16-electron (16e) singlets are able to coordinate to solvent molecules as token ligands to partially stabilize the coordinatively unsaturated metal center, whereas 16e triplets and 17-electron (17e) doublets are not, allowing them to diffuse more rapidly through solution than their singlet counterparts. Triplet complexes typically (but not always) undergo spin crossover prior to solvent coordination, whereas 17e doublets do not coordinate solvent molecules as token ligands and cannot relax to a lower spin state to do so. 16e triplets are typically able to undergo facile spin crossover to yield a 16e singlet where an associative, exothermic reaction pathway exists. The combination of facile spin crossover with faster diffusion through solution for triplets can actually lead to faster catalytic reactivity than for singlets, despite the forbidden nature of these reactions.

We summarize studies on odd-electron complexes in which 17e doublets were found to display varying behavior with regard to their tendency to react with 2-electron donor ligands to form 19-electron (19e) adducts. The ability of 19e adducts to serve as reducing agents in disproportionation reactions depends on whether the excess electron density localized at the metal center or at a ligand site. The reactivity of both 16e and 17e complexes toward a widely used organic nitroxyl radical (TEMPO) are reviewed, and both classes of complexes generally react similarly via an associative mechanism with a low barrier to these reactions.

We also describe recent work targeted at unraveling the photoisomerization mechanism of a thermal—solar energy storage complex in which spin state changes were found to play a crucial role. Although a key triplet intermediate was found to be required for this photoisomerization mechanism to proceed, the details of why this triplet is formed in some complexes (those based on ruthenium) and not others (those based on iron, molybdenum, or tungsten) remains uncertain, and further exploration in this area may lead to a better understanding of the factors that influence intramolecular and excited state spin state changes.

INTRODUCTION

Spin state changes can play an important role in any area of chemistry, and, in organometallic catalysis, these very often occur with low energetic and spin barriers such that their dynamics can be probed on the ultrafast time scale. Ultrafast time-resolved infrared (TRIR) spectroscopy has become established as a powerful tool for studying the dynamics of such processes, as the high structural sensitivity offered by carbonyl reporter ligands allows changes in the spin state, structure, and ligand coordination environment to be monitored directly. The impact of these formally spin-forbidden processes on reaction rates and the formation (or lack thereof) of products can be difficult to predict, and, as such, nonadiabatic reactions are generally less understood than those occurring on a single potential energy surface.

Much of the work in our research group in recent years has focused on elucidating correlations between spin state and reactivity that will be widely applicable in the field of organometallic chemistry. These include fundamental processes like diffusion kinetics or the coordination of a solvent molecule to coordinatively unsaturated reaction intermediates as well as

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catalytically important reactions such as the activation of chemical bonds. The majority of the complexes that we study are widely used, prototypical organometallic regents whose chemistry is intended to serve as a model for a broad range of complexes. We have sought to investigate the relationship between electronic structure and reactivity with the goal of being able to offer predictive insight into the behavior of complexes whose reactivity has not yet been studied directly.

This Account will focus on work from our lab using ultrafast infrared spectroscopy in conjunction with computational chemistry methods to probe the role of spin states and electronic structure in organometallic reaction mechanisms. Where relevant, work occurring concurrently in other groups will also be highlighted.

■ EVEN-ELECTRON PHOTOPRODUCTS: SOLVENT COORDINATION AND IMPLICATIONS FOR BOND ACTIVATION REACTIONS

Coordination of Solvent Molecules as Token Ligands

Dissociation of a 2-electron (2e) ligand from a stable 18-electron (18e) complex yields a reactive, coordinatively unsaturated 16-electron (16e) reaction intermediate. Although the majority of such species adopt a singlet ground state, many also possess triplet ground states. Photochemical excitation can often be used to generate these coordinatively unsaturated intermediates, allowing for time-resolved spectroscopic interrogation. This is the approach used in the studies described in this section: a one picosecond duration UV or visible laser pulse is used to photochemically dissociate a 2e ligand, yielding an intermediate whose structure and reactivity is subsequently probed using another ultrafast pulse in the infrared. The spin state of a complex can be characterized, in principle, by a variety of techniques including magnetic susceptibility measurements, electron paramagnetic resonance, and temperature-dependent magnetic circular dichroism, although for many of the complexes described in this Account, the spin state was determined by simple molecular orbital theory arguments, computational chemistry, and/or comparison to less-direct experimental results surrounding the reactivity of the complex.

Coordinatively unsaturated 16e intermediates often coordinate solvent molecules as token ligands at the vacant coordination site to partially offset the electron deficiency at the metal center.[1] The energetic favorability of such interactions is in the range of ca. 11 kcal/mol for alkanes to ca. 25 kcal/mol for THF; these values depend largely on the coordinating strength of the solvent.[2]

Interestingly, coordination of a solvent molecule as a token ligand typically occurs only with ground-state singlet 16e photoproducts but not for those with triplet spin multiplicity.[3,4] In addition to experimental evidence based on reaction kinetics,[3] computational investigations have correctly predicted this behavior with regard to coordination to alkyl moieties. It has been suggested that open-shell singlets possess an empty sd-hybridized orbital, localized at the vacant coordination site, allowing for electron donation from an alkyl moiety into this orbital; the lack of alkyl coordination to triplets has been attributed to the inability of their valence atomic orbitals to efficiently form these sd hybrids.[4] In the presence of coordinating solvents (e.g., alcohols), the spin state of a triplet photoproduct typically changes upon coordination to the electron-donating functional moiety (e.g., the hydroxyl group of an alcohol).[5] In noncoordinating alkane solvents, coordinatively unsaturated 16e triplets may encounter an energetic barrier to spin crossover and solvent coordination, or the ground-state triplet may be more stable than the putative alkyl-solvated singlet.[6,7] Additional studies, such as those described regarding bond activation in the next section, have also verified the behavior described with regard to coordination of alkyl moieties as token ligands.

Ultrafast TRIR experiments performed in primary *n*-alcohols of varying chain lengths were used to explore the rearrangement dynamics of singlet and triplet 16e photoproducts en route to formation of the singlet hydroxyl-coordinated adducts (Figure 1).[5] For the prototypical 16e triplet $^{3}\text{Fe(CO)}_4$, the rearrangement kinetics to yield the hydroxyl-coordinated adduct were more rapid than those observed for the singlet photoproduct $^{1}\text{Cr(CO)}_5$. These differences can be attributed to coordination, or lack thereof, to alkyl moieties: for singlets, coordination and rearrangement among alkyl-coordinated intermediates significantly hinders diffusion through the solvent, whereas triplets diffuse more rapidly and are unhindered by intermediate coordination to alkyl moieties. Importantly, upon encountering the more strongly coordinating hydroxyl group, the barrier for $^{3}\text{Fe(CO)}_4$ to change spin states appears to be essentially negligible,[5] despite the fact that spin crossover for the same complex in alkanes involves a significant barrier.[6]

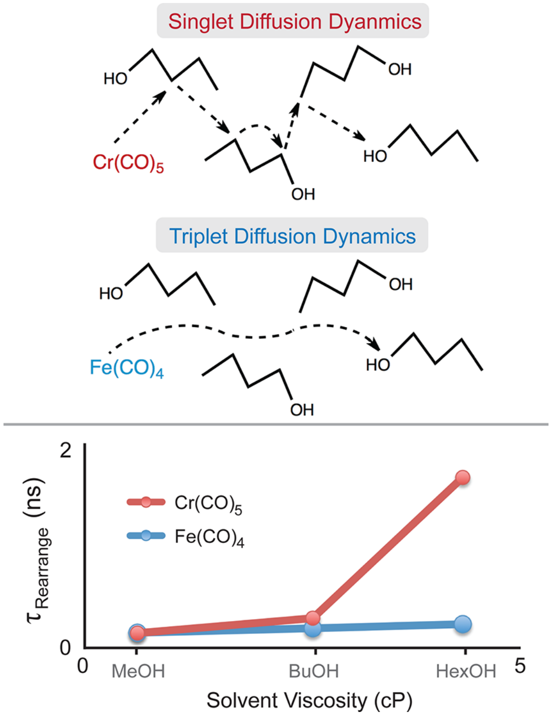

Figure 1. Rearrangement dynamics of singlet and triplet intermediates to form hydroxyl-coordinated adducts in alcohol solutions. $\tau_{\text{rearrange}}$ indicates the time constant measured for formation of the hydroxyl-coordinated metal carbonyl adduct. Adopted from ref 5. Copyright 2001 American Chemical Society.

Effects of Spin State Changes on Bond Activation in Silanes and Stannanes

Having established the behavior of singlet and triplet 16e complexes with regard to solvent coordination, the next relevant step is to explore the implications of these observations for chemical reactions. Accordingly, our group investigated the reactivity of singlet and triplet organometallic photoproducts toward the activation of Si−H (silane)[8−10] and Sn−H (stannane)[11] bonds in solution. Our findings indicate behavior similar to that observed in alcohols, where the Si−H or Sn−H moiety facilitates spin crossover, analogous to the hydroxyl group. 16e singlets undergo rearrangement among alkyl-coordinated intermediates until encountering the more coordinating Si−H or Sn−H bond, at which point bond activation can occur. For 16e triplets, the lack of formation of alkyl-coordinated intermediates allows for more rapid diffusion through the alkyl chains in the solvent, but upon encountering the more coordinating Si−H or Sn−H moiety, spin crossover and bond activation are facile. Figure 2 presents representative results regarding the activation of silanes.[8−12] A marked difference exists between the time scale for bond activation with and without formation of alkyl-coordinated intermediates. In a neat silane or stannane solvent, the reactivity of the singlet is partitioned into two channels, with a minor amount of bond activation occurring prior to formation of alkyl-coordinated intermediates.

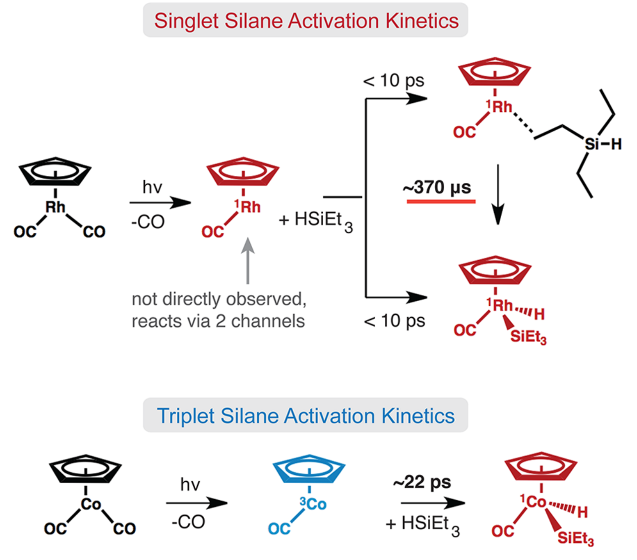

Figure 2. Silane activation by singlet and triplet photoproducts in neat $HSiEt_3$ solution.

Extension of the trends in reactivity observed in alcohols, silanes, and stannanes is not difficult to envision, and, indeed, we expect that the behavior described thus far can be readily generalized to many other chemical reactions. It is relevant to point out that the experiments carried out on the femtosecond to microsecond time scale were in neat solutions of alcohols, silanes, and stannanes. In synthetic applications, a reagent is typically used as a dilute solution in another solvent. Where alkanes or other noncoordinating solvents are used, it is expected that the effects of slowed reactivity for coordinatively unsaturated singlets because of intermediate alkyl coordination would be significantly more pronounced. Conversely, where coordinating solvents are used, both coordinatively unsaturated singlet and triplet intermediates can be expected to form solvent-coordinated singlets and thus will likely behave similarly with regard to their diffusion kinetics.

For readers interested in a detailed theoretical treatment of nonadiabatic reactions, Harvey and co-workers have published several excellent articles,[13−16] and we refer the reader to those publications. Although the bulk of the work in our group has been experimental in nature, we have found such a treatment helpful in our studies on bond activation reactions, as is discussed in several of the publications reviewed in this Account. For example, the spin−orbit coupling (SOC) associated with many transition-metal complexes is relatively high such that the probability of changing spin states at the crossing point between triplet and singlet potential energy surfaces is typically fairly large (ca. 5% for first-row transition-metal complexes, although this number may vary widely, and approaching unity for many second- and third-row transition-metal complexes).[13−16] Thus, the free energy barrier to reaching the crossing point between triplet and singlet surfaces often plays a significant role in the spin-barrier in organometallic reactions involving a change of spin state.

Coordination of CpCo(CO) to Solvents in Singlet and Triplet Spin States

In the studies described thus far, we have undertaken detailed investigations of a necessarily limited number of complexes, which we believe provide a representative picture of general trends in singlet and triplet reaction dynamics. Of course, there will likely be exceptions to any rule, such as that regarding solvent coordination to singlet and triplet intermediates. Indeed, we have recently uncovered the first known exception to the rule described thus far concerning lack of solvent coordination to 16e triplets. CpCo(CO) is able to coordinate to the sp^3-hybridized oxygen atom of alcohols and THF (and likely other solvents as well, though in most solvents studied it does not coordinate a token ligand in the triplet state) in both singlet and triplet spin states (Figure 3).[17] DFT calculations support the notion that coordination of these solvents to ^{3}CpCo(CO) is unusually favorable. It is interesting that CpCo(CO) was discovered as the first known exception to this rule, as CpCo(CO) was also the first coordinatively unsaturated triplet for which the tendency for solvents to not coordinate to triplet intermediates was established.[3,4]

This exception to the rule can likely be attributed to the unusually high stability of the triplet state of CpCo(CO). DFT calculations indicate that in the gas phase the triplet state is favored over the singlet by ca. 13−26 kcal/mol (depending on the choice of functional used). For comparison, the triplet state of $Fe(CO)_4$ is calculated to be favored by 0−9 kcal/mol.[11] Thus, it is possible that the greater intrinsic stability of the triplet state of CpCo(CO) may play a role in the ability of this species to coordinate to a select set of solvent molecules in the triplet state. No singlet alkyl coordinated CpCo(CO) complex has ever been observed (and indeed may likely not exist), further validating that the triplet state of CpCo(CO) is unusually stable.[7] The ability of CpCo(CO) to coordinate to solvent molecules in the triplet state suggests that it may be worth re-examining previous assertions that triplet states are inherently unable to coordinate to ligands without a change of spin state, as other exceptions to this rule may very well exist.

Because $CpCo(CO)_2$ is widely used as a catalyst for alkyne cyclotrimerization, subsequent experiments investigated the reactivity of the CpCo(CO) photoproduct in neat alkyne and alkene solutions.[18] These experiments uncovered that the nascent CpCo(CO) photoproduct first coordinates to the carbon−carbon π bond(s) of 1-hexyne and 1-hexene in the triplet state and rapidly undergoes spin crossover to form the coordinated singlet species (Figure 4). This spin crossover was observed to occur on the time scale of 30−40 ps, and as such, it

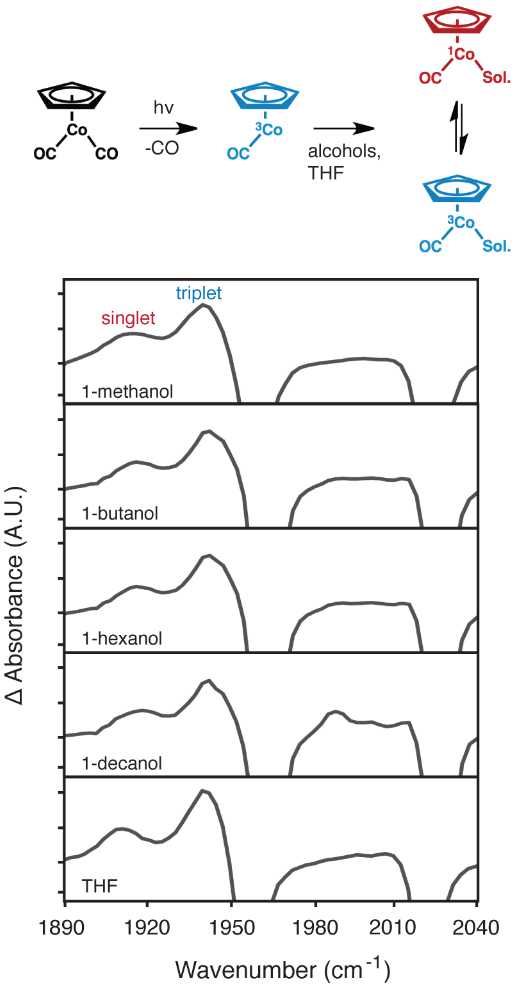

Figure 3. CpCo(CO) coordinates to certain solvents in both singlet and triplet states. TRIR spectra are shown at a UV pump−IR probe delay time of 50 ps. The excitation wavelength used was 267 nm.

occurs on a time scale similar to that of vibrational cooling, making it possible that coordination to the alkyne/alkene in the triplet state may be tied to the presence of excess vibrational energy. In a related vein, spin crossover of other triplet species (e.g., $CpV(CO)_3$ and $CpMn(CO)_2$) to form alkyl-coordinated singlets has been observed to occur during the period of vibrational cooling.[8,11]

Reactivity of the Triplet 14e Photoproduct $Fe(CO)_3$

The solution-phase photochemistry of $Fe(CO)_5$ is unusual in that the corresponding dicarbonyl-loss product, $Fe(CO)_3$, can be generated via a single-photon process.[6] This afforded the opportunity to study the coordination behavior of a 14-electron (14e) intermediate generated from an 18e precursor. As it happens, $Fe(CO)_3$ possesses a triplet ground state,[19,20] and interestingly, in alcohol solutions, $Fe(CO)_3$ forms a hydroxyl-solvated adduct in the triplet state.[20] TRIR experiments in neat *n*-alcohols of varying chain lengths (analogous to those described with $Fe(CO)_4$, Figure 1) suggest that nascent $Fe(CO)_3$ rearranges rapidly to coordinate to the hydroxyl moiety of these solvents. Thus, on the basis of the results of our ultrafast experiments, $^3Fe(CO)_3$ would appear not to coordinate to alkyl moieties in solution. However, experiments by George et al. carried out under a CO atmosphere demonstrated that $Fe(CO)_3$ recombined with CO more slowly in heptane solution than when the solvent was supercritical xenon or argon.[6] This implies that $^3Fe(CO)_3$ does coordinate to alkyl groups in the solvent to some extent, at least to some extent (an apparent contradiction).[6] One possible resolution to this discrepancy would be that, on the ultrafast time scale in our experiments, $Fe(CO)_3$ was still vibrationally hot and that this excess vibrational energy inhibited a weak coordination to alkyl moieties on the time scale of our experiments, with the longest taking 46 ps to rearrange. Another (nonmutually exclusive) possibility is that $^3Fe(CO)_3$ interacts with alkanes only to a slight extent, but enough to slow the reaction with CO relative to when a noble-gas solvent is used. This study represents the only detailed investigation into the behavior of a triplet 14e reaction intermediate to date and demonstrates that the behavior of 14e intermediates may differ from that of 16e intermediates.

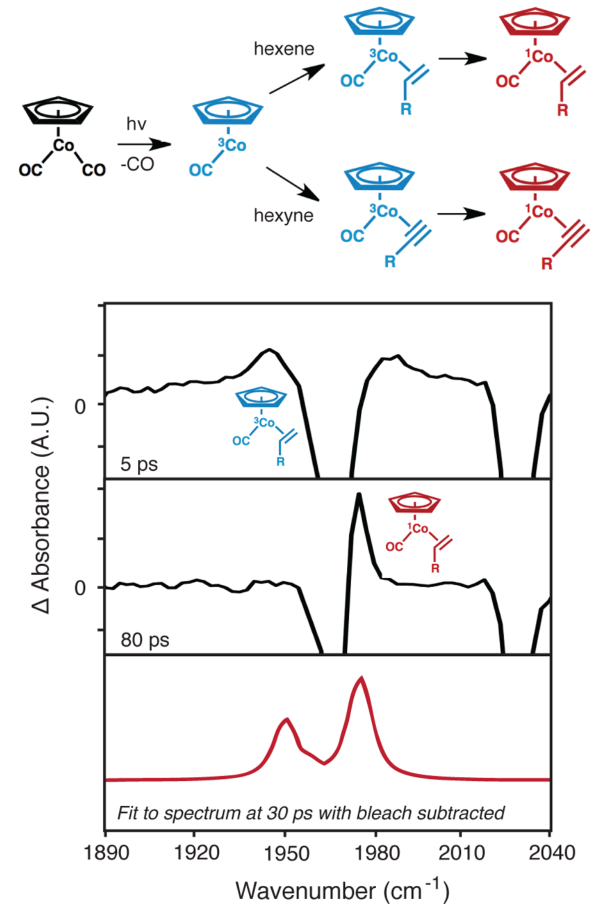

Figure 4. TRIR spectra of $CpCo(CO)_2$ in neat 1-hexene solution and corresponding structural assignments. Similar results were obtained in 1-hexyne solution. The excitation wavelength used was 267 nm.

■ ODD-ELECTRON PHOTOPRODUCTS: REACTIVITY TOWARD 2E DONOR LIGANDS AND DISPROPORTIONATION REACTIONS

Odd-Electron Intermediates and Their Behavior with Regard to Solvent Coordination

So far, we have examined the reactivity of even-electron complexes. Although these comprise the majority of reactive intermediates in organometallic catalysis, odd-electron complexes are also frequently encountered, and their reactivity patterns differ greatly from those of even-electron complexes.

Homolysis of a metal−metal bond is one process that commonly leads to the formation of odd-electron transition-metal complexes, and we have used photochemical excitation to generate 17-electron (17e) photoproducts in this manner. Such species adopt a doublet ground state, and with regard to these species, we will be focusing on trends in reactivity of doublet species alone, as their reactivity does not typically involve changes in spin state to the same extent as that observed for 16e complexes.

In contrast to coordinatively unsaturated 16e intermediates, 17e species do not coordinate to solvent molecules as token ligands.[21] This is readily verified by comparing the infrared spectrum of such complexes in widely varying solvent environments, where the spectrum does not change significantly with variation in solvent conditions. This behavior can be rationalized by noting that 17e complexes are only deficient by a single electron relative to the stable 18e precursor. Thus, they do not have a fully vacant frontier bonding orbital into which an electron pair can be accepted, either from a lone pair of nonbonding electrons or via sigma/pi donation from a chemical bond.

Reactivity toward Strong 2e Donors and Disproportionation Reactions

Although 17e complexes do not tend to coordinate solvents as token ligands, a strong 2e donor (e.g., a phosphine or phosphite) may be able to coordinate to the 17e metal center to yield a 19-electron (19e) product.[22−27] These 19e species (also doublets) are electron-rich and may serve as good reducing agents. Alternatively, they may tend to displace their excess electron density onto a ligand to mitigate the unfavorable energy associated with placing an electron into an antibonding metal-centered orbital. We will discuss examples of both types of behavior for 19e species.

Tyler et al. were among the first to investigate the mechanisms by which 19e organometallic intermediates behave as reducing agents in disproportionation reactions,[22,23] proposing that transfer of the excess electron from a 19e adduct to another parent dimer molecule leads to cleavage of the dimer and formation of disproportionation products (we have previously termed this the “dimer mechanism”).

Ultrafast and longer time scale TRIR experiments in our group uncovered two additional mechanisms termed the “radical mechanism” and the “in-cage mechanism”.[24−26] In the radical mechanism, a 19e complex diffusively encounters a 17e radical, at which point an electron is transferred to yield the disproportionation products. The in-cage mechanism is similar in spirit to the radical mechanism except that both formation of the 19e species and electron transfer take place before diffusion out of the solvent cage (i.e., within a few hundred picoseconds of cleavage of the metal−metal bond). Such a mechanism can outcompete the radical mechanism only at high concentrations of the 2e donor ligand, although it can serve as a contributing mechanism under essentially any conditions.

As suggested in Figure 5, the in-cage disproportionation mechanism was observed to take place (at high phosphine/phosphite concentrations) upon photolysis of $[CpW(CO)_3]_2$. We investigated the applicability of this mechanism for several other transition-metal dimers in a solvent of 1:4 molar $P(OMe)_3/CH_2Cl_2$.[27] Figure 6 shows representative TRIR data for a complex that undergoes in-cage photochemical disproportionation on the ultrafast time scale. Table 1 summarizes the results of our investigation into the tendency of various metal carbonyl dimers to undergo in-cage photochemical disproportion.[27]

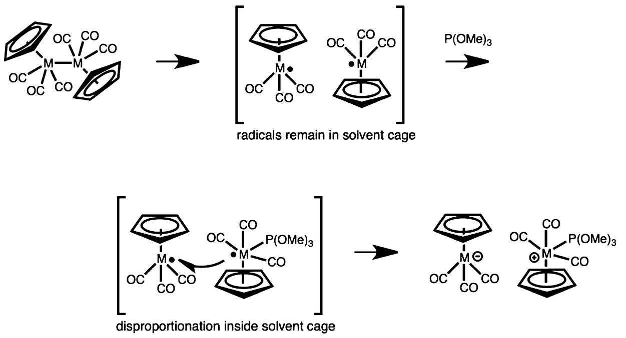

Figure 5. In-cage disproportionation mechanism.

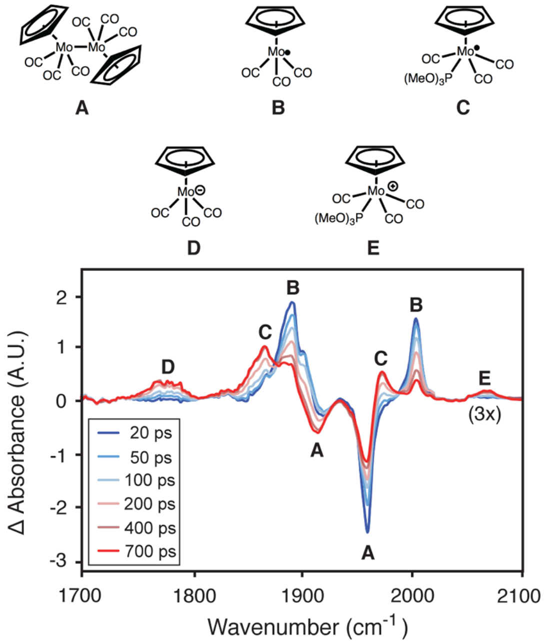

Figure 6. TRIR data for $[CpMo(CO)_3]_2$ undergoing in-cage photochemical disproportion in 1:4 molar $P(OMe)_3/CH_2Cl_2$ solution following 400 nm excitation.

Table 1. Summary of Reactivity Observed for Various Metal Carbonyl Dimers in Ultrafast TRIR Experiments in 1:4 Molar $P(OMe)_3/CH_2Cl_2$ Solution

photolysis generates	19-electron adduct observed?	ultrafast in-cage disproportionation observed?
2 $Mn(CO)_5$ or 2 $Re(CO)_5$	no	no
2 $CpFe(CO)_2$ or 2 $CpRu(CO)_2$	yes	no
2 $CpMo(CO)_3$ or 2 $CpW(CO)_3$	yes	yes

For $Mn(CO)_5$ and $Re(CO)_5$, no formation of a 19e product was detectable, indicating either a 17e/19e equilibrium strongly favoring the 17e species or an energetic barrier to coordination of the phosphite ligand. For $CpFe(CO)_2$ and $CpRu(CO)_2$, coordination of the phosphite to generate a 19e adduct was observed, but no electron transfer to the corresponding 17e fragment was observed on the ultrafast time scale. For $CpMo(CO)_3$ and $CpW(CO)_3$, both formation of the 19e adduct and in-cage disproportionation were observed.

The lack of disproportionation for the Fe and Ru complexes can be readily rationalized by noting that these 19e species actually localize their excess electron density onto a ligand: 19e $CpFe(CO)_2L$ complexes have been previously shown to delocalize the excess electron onto the Cp ring, causing it to adopt an η^4 geometry,[28] whereas for the Ru complex, our TRIR and DFT results indicate delocalization of the excess electron onto a CO ligand, resulting in a bent CO ligand.[29] Each of these complexes are thus better described as $18 + \delta$ species, explaining the lack of electron transfer observed prior to diffusion out of the solvent cage.

To summarize briefly the ultrafast results surrounding odd-electron reactivity, these complexes do not coordinate solvent molecules as token ligands and are thus expected to diffuse rapidly through solution, similar to triplet 16e complexes. However, 17e complexes are not as reactive toward addition of most 2e donor solvents/ligands as the 16e triplets, likely because addition of a 2e ligand to a 17e complex does not lead to a stable 18e configuration. Reactions to yield 19e adducts may proceed with strong 2e donors, and the reactivity of such 19e adducts will depend sensitively on whether the complex is truly a 19e species at the metal center or whether these are better characterized as $18 + \delta$ complexes with the excess electron density localized on a ligand.

Reactivity of Even and Odd Transition-Metal Complexes with TEMPO, a Nitroxyl Radical

Having examined the reactivity of even- and odd-electron intermediates toward 2e donors, it is also of interest to know how these intermediates react toward radical reagents. (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) is a stable nitroxyl radical that has been employed for a truly extensive array of chemical applications ranging from alcohol oxidations to serving as a structural probe in biological systems via EPR measurements.[30,31] Its coordination behavior is quite varied, with at least three distinct binding modes possible at a single metal center.[32,33] Hence, we undertook a TRIR study of its reactivity toward 16e and 17e reaction intermediates, providing the first ultrafast study of the reaction dynamics of a radical (doublet) organic molecule with coordinatively unsaturated metal centers. DFT calculations were used to facilitate interpretation of the experimental results.[34]

In each case studied, TEMPO was observed to coordinate to the metal center in the η^1 anionic coordination mode, reflecting an oxidation of the metal center. With regard to developing a predictive picture of the coordination chemistry of TEMPO, it was thus concluded that TEMPO initially coordinates to low-valent 16e and 17e reaction intermediates via an associative mechanism in the anionic coordination mode. Figure 7 shows TRIR spectra collected following photolysis of $CpCo(CO)_2$ and $[CpFe(CO)_2]_2$ (yielding 16e and 17e photoproducts, respectively) in a solution of TEMPO in cyclohexane. Photolysis of $Fe(CO)_5$ and $Mn_2(CO)_{10}$ to yield the corresponding 16e ($Fe(CO)_4$) and 17e ($Mn(CO)_5$) photoproducts yielded similar results (not shown).

With regard to the spin states of the complexes involved, the rates of these reactions, along with the simple fact that a reaction was consistently observable on the ultrafast time scale, are both of interest. At TEMPO concentrations ranging from 0.16 to 0.64 M in cyclohexane, a reaction was clearly observable on the picosecond time scale for each of the 16e and 17e intermediates studied. For the 16e species, the reactions proceeded at rates approaching the diffusion limit. The rates for the 17e complexes were slower, although the reactions were still observable on the picosecond time scale; it was not clear whether the reactions were still proceeding or were reaching an equilibrium between the 17e species and the corresponding TEMPO adducts on the time scale studied.

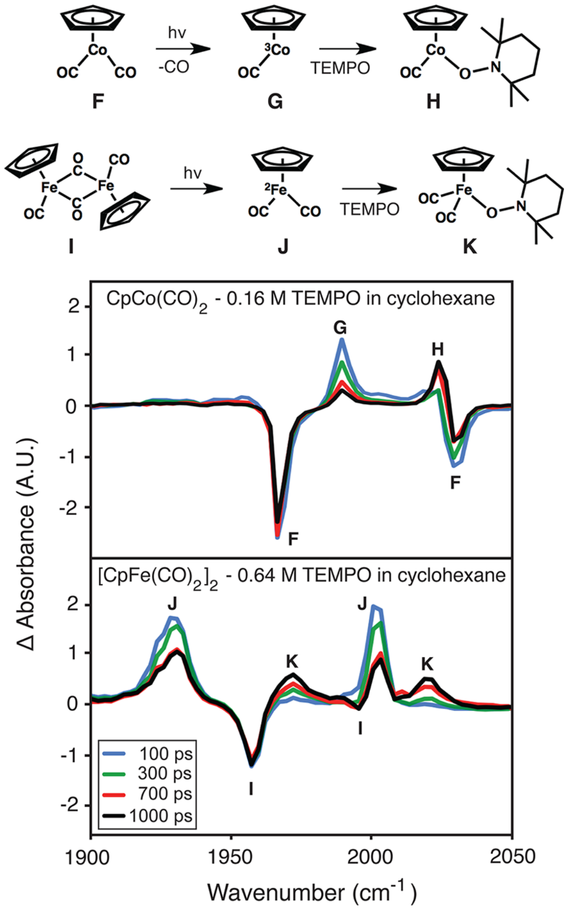

Figure 7. TRIR spectra of $CpCo(CO)_2$ and $[CpFe(CO)_2]_2$ following 400 nm photolysis in 0.16 and 0.64 M solutions, respectively, of TEMPO in cyclohexane.

Notably, both even- and odd-electron complexes reacted rapidly with TEMPO. Although 17e species tend to be less reactive toward 2e donors than their 16e counterparts, they appear to react fairly readily with TEMPO. An intuitive explanation for this observation exists: the tendency to react appears to be determined by whether the reaction will cause the metal center to exceed an 18e count. In the reactions between TEMPO and 17e radicals, the resulting adduct possesses only 18 electrons at the metal center, such that the electron count does not become excessively high, as would tend to be the case with coordination of a 2e donor ligand to a 17e species.

Finally, it is worth pointing out that the 16e species studied were each triplets and this selection was made deliberately such that intermediate alkyl-coordinated species would not slow the reaction, allowing its observation on the ultrafast time scale. We would like to carry out additional studies on singlets, although at the time of the study we were primarily interested in the products that form rather than the reaction rates. Nonetheless, this study provides important insight into the reactivity of organic radicals toward organometallic reaction intermediates.

PHOTOISOMERIZATION REACTIONS OF DIMETALLIC FULVALENE COMPLEXES

Fulvalene Diruthenium Complexes for Solar Energy Storage

In addition to the studies described thus far, we wish to touch briefly on related work involving spin state changes in a photoisomerization reaction, as photoisomerization reactions represent another widely studied class of organometallic reactions that may often involve changes in spin state. $FvRu_2(CO)_4$ has received significant attention for its potential as a solar−thermal energy storage molecule because of its ability to undergo photoisomeriation in sunlight,[35] storing 20.8 kcal/mol of energy that can be readily released in the presence of an appropriate catalyst. The forward photoisomerization reaction can proceed quantitatively, and a working proof-of-principle device has been constructed.[36]

The mechanism for the photoisomerization process has been investigated using TRIR experiments (Figure 8) in conjunction with X-ray transient absorption experiments and DFT calculations.[37] A long-lived triplet biradical intermediate was found to be crucial to the forward photoisomerization reaction, as depicted in Figure 9.

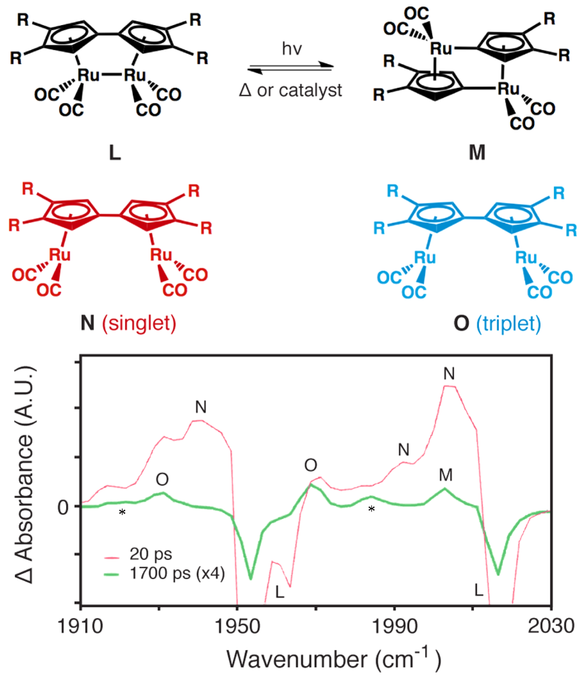

Figure 8. TRIR spectra of $Fv'Ru_2(CO)_4$ in heptane following 400 nm excitation (Fv′ = 2,2′,3,3′-tetra-*tert*-butylfulvalene). * denotes a CO-loss product.

The long-lived triplet biradical, whose lifetime extends beyond the time scale accessible via the ultrafast TRIR or X-ray transient absorption setups, was confirmed to be the syn biradical via TRIR and DFT results in conjunction with fits to X-ray transient absorption data. It is somewhat surprising that the syn triplet biradical (particularly in a second-row transition-metal complex) can exhibit such a long lifetime (>1700 ps, as determined by TRIR experiments), and it seems possible that the biradical spin density localizes on the fulvalene ring, reducing SOC between singlet and triplet substates and preventing the spin crossover (to the ground singlet state) needed to reform the M−M bond.

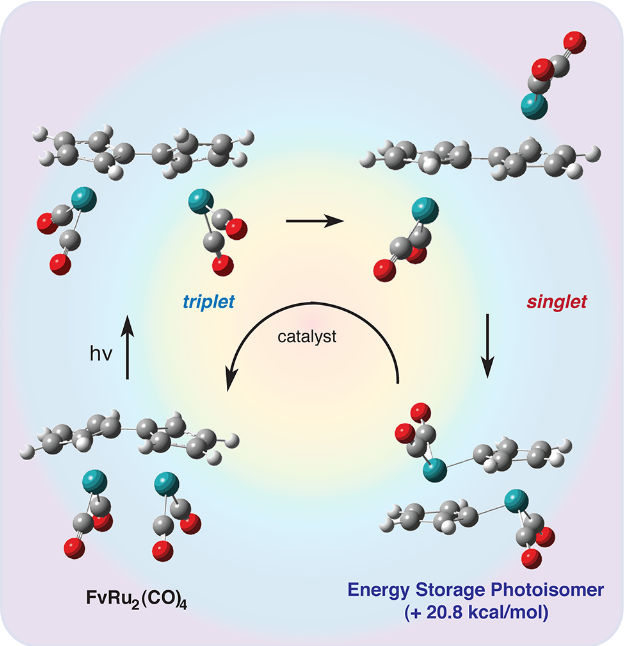

Figure 9. Photoisomerization mechanism for $FvRu_2(CO)_4$.

Toward the Development of an Affordable Iron Analogue

In light of the early successes of the diruthenium fulvalene systems for energy storage, further work has been carried out to synthesize an iron analogue, as iron is substantially cheaper and more naturally abundant.[38] However, no photoisomerization reaction analogous to that shown in Figures 8 and 9for the ruthenium congener has been realized. TRIR experiments carried out on the iron congener were unable to detect the presence of any long-lived triplet species analogous to that observed for the Ru dimer. The reason for the lack of formation of the putative triplet remains unclear. To add to the mystery, the analogous group VI fulvalene carbonyls based on Mo and W ($FvMo_2(CO)_6$ and $FvW_2(CO)_6$) have been synthesized and also fail to undergo the analogous photoisomerization,[39] and TRIR experiments also have been unable to detect any triplet intermediate upon photoexcitation of these complexes. The lack of photoisomerization for the Fe, Mo, and W complexes is all the more surprising in light of the fact that over 20 substituted derivatives based on the $FvRu_2$ framework have been synthesized and demonstrated to undergo the photoisomerization reaction to date. Clearly, there is something unique about the $FvRu_2$ framework that supports the formation of the triplet biradical necessary for the forward photoisomerization reaction to take place. Other examples can certainly be found in the literature in which intramolecular spin state changes do not proceed as expected or can be difficult to rationalize,[40] and at this point, the reasons for which only the $FvRu_2$ framework supports the key triplet intermediate needed for photoisomerization remain uncertain.

Taken as a whole, our work on dimetallic fulvalene complexes highlights the sensitivity of intramolecular spin crossover processes to details of molecular or electronic structure whose effects may be difficult to isolate or identify, motivating further work toward achieving a rational or predictive understanding of these processes.

SUMMARY AND OUTLOOK

As we have explored, the spin states of organometallic reaction intermediates correlate to trends in reactivity that can be used to offer predictive insight into their behavior.

With regard to solvation dynamics, we find that coordinatively unsaturated singlets coordinate solvent molecules as token ligands, whereas their doublet and triplet counterparts do not tend to do so. Although this trend appears quite general on the basis of the available evidence, we have also uncovered a couple of exceptions, suggesting that this should be treated as a guideline rather than a hard-and-fast rule. The implications of these differential solvation dynamics have been explored with regard to the reactivity in bond activation (for 16e complexes) and disproportionation reactions (for 17e complexes).

The reactivity of both odd- and even-electron intermediates toward a widely used organic radical reagent, TEMPO, was also explored. Both classes of intermediates were found to react readily with this organic radical with little energetic barrier, suggesting that addition of organic radicals to either type of coordinatively unsaturated metal center is a facile process.

Lastly, we described a series of recent investigations uncovering the role of spin state changes in the photoisomerization of dimetallic fulvalene complexes, and we found that a key triplet intermediate was crucial to allowing the energy storage photoisomerization reaction to proceed.

In recent years, an increasing number of studies have uncovered key roles played by spin state changes in reactions of transition-metal complexes. These include synthetically and industrially useful reactions catalyzed by inorganic and organometallic species, reactions occuring in electronically excited-states, and enzyme-catalyzed and other bioinorganic reactions crucial to biological function. The rates and outcomes of such reactions have been shown to depend critically on the spin states of catalysts, reactants, intermediates, and/or products. The observations described in this Account are intended to serve as representative examples of the influence of spin states on the reaction dynamics of organometallic complexes, and the trends uncovered are expected to be broadly applicable to transition-metal chemistry occurring under both photochemical and thermal conditions.

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Notes

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