THE JOURNAL OF PHYSICAL CHEMISTRY B LETTERS

2006, *110,* 20−24
Published on Web 12/15/2005

Time-Resolved Infrared Dynamics of C−F Bond Activation by a Tungsten Metal−Carbonyl

Matthew C. Asplund,* Aaron M. Johnson, and Jared A. Jakeman

Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602

Received: September 26, 2005; In Final Form: November 23, 2005

Chemical reactions that break, or activate, C−H and C−F are of tremendous synthetic interest. The intramolecular C−F bond activation of a tungsten carbonyl system has been studied by time-resolved infrared spectroscopy. The formation of solvent complexes and the final product are monitored using time-resolved infrared spectroscopy of the CO stretches. The rate of the reaction is shown to be limited by the formation of an intermolecular complex between the tungsten metal center and a solvent molecule. Comparison with DFT calculations shows that in the absence of solvent molecules the intramolecular complex with the tethered perfluorobenzene ring is energetically favorable, but is not the primary kinetic product because of the initial geometry of the complex.

Introduction

C−F bonds are among the strongest in all of chemistry, and so chemical reactions that can break these bonds are of particular interest. Since the first demonstration of activating C−H bonds using organometallic molecules[1,2] there has been intense interest in understanding the reaction mechanisms involved. Studies of C−H, Si−H, and C-halide activation reactions have been made with nanosecond and microsecond time resolution in liquefied noble gases[3−5] and low-temperature matrices[6−8] and with femtosecond time resolution[6−15] in room-temperature liquids. Infrared spectroscopy of these reactions has focused on the CO stretching modes of the metal carbonyls, which have large absorption cross-sections and are very sensitive to the oxidation state of the metal atom.

The first organometallic system for activating C−F bonds at room temperature was reported by Richmond and co-workers.[16,17] This original C−F bond activation system was based on a $W(CO)_3(PrCN)_3$ which is coupled to a dinitrogen ligand **1** which has a tethered perfluorobenzene ring. A reaction mechanism was proposed[18] in which the first step was to couple the ligand onto the metal center, displacing two of the nitrile ligands. This is followed by dissociation of the third nitrile ligand and addition of the tethered perfluorobenzene ring across the tungsten metal center to form the final product **2**. Of particular interest, C−F activation occurs only with the tethered ring, and not with perfluorobenzene in the solution. This reaction proceeds by thermal dissociation of the nitrile ligand, and so cannot be studied by pump−probe time-resolved spectroscopy to get information on a sub-millisececond time scale. By coupling the dinitrogen ligand on a $W(CO)_4$ fragment, we can create a model compound of a key intermediate of the reaction. For this work a modified version of the dinitrogen ligand was used. This structure of the ligand is shown in molecule **3**. The CO ligand is more strongly bound than the PrCN, and the reaction does not proceed thermally at room temperature. Absorption of a UV photon causes dissociation of the CO, and begins the C−F bond activation process.

Experimental Section

Transient infrared measurements were made using a Bruker IFS-66 FTIR spectrometer, with the necessary modifications for step-scan and rapid-scan experiments. Step-scan measurements used a fast MCT detector with a 10 ns rise time, and signals were digitized with a 12-bit, 100 MS/s digitizer. Laser pulses for UV excitation were generated as the frequency tripled (355 nm) or quadrupled (266 nm) output of a Nd:YAG laser (Coherent Infinity). All excitations on compound **3** were done at 355 nm. Excitations on compound **6** were done at 266 nm because its absorbance is shifted to shorter wavelengths, and so it did not show any reaction with 355 nm excitation. The pump and probe beams were 8 mm in diameter and were completely overlapped in the sample, with an angle of approximately 20 degrees between the two beams. Excitation energy was kept at 3−5 mJ per pulse to minimize sample degradation during the experiment.

The dinitrogen ligand in compound **3** was synthesized according to a previously published procedure.[19] The ligand was coupled to $W(CO)_6$ under an inert atmosphere to form **3**. Purity was confirmed by NMR and IR spectroscopy. Sample concentrations were 5 mM in the metal carbonyl and were made with dry, oxygen-free solvents and kept under a positive pressure of argon during experiments to minimize sample degradation.

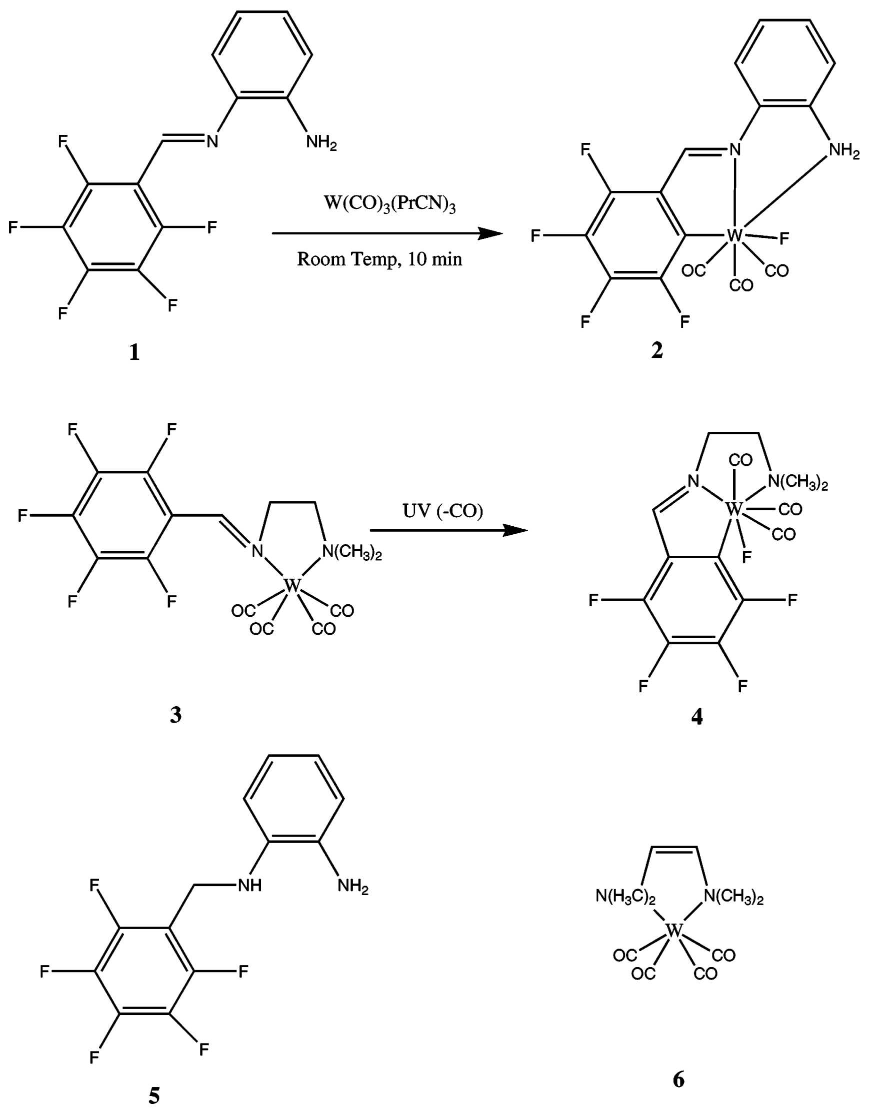
Ab initio calculations were performed using the NWChem computational chemistry package.[20] DFT calculations were performed using the B3LYP hybrid functional, using the LANL2DZ effective core potential basis set on W atoms and 6-31G basis sets on all other atoms. Geometry calculations were minimized using the standard tight convergence criteria, and correct minimization was tracked by vibrational analysis to eliminate negative frequencies.

---

* Corresponding author. E-mail: Asplund@chem.byu.edu.

10.1021/jp055465w CCC: $33.50

SCHEME 1



Results and Discussion

The C−F activation reaction is initiated by irradiation of the tungsten carbonyl **3** with 355 nm light. This causes the dissociation of a CO ligand and formation of the C−F bond-activated product **4**. The progress of the reaction can be measured in the infrared spectrum by looking at the metal−CO stretches. Previous femtosecond infrared studies of the photodynamics of metal carbonyls[21] provide information on the early dynamics of similar reactions. In solution, $W(CO)_6$ absorbs a UV photon, leading to rapid dissociation of one of the CO ligands. This coordinatively unsaturated $W(CO)_5$ species forms a complex with a solvent molecule in the first few hundred femtoseconds following dissociation, and then undergoes vibrational cooling, which takes ~10 ps. Complexes of metal carbonyls with THF are known to be much more stable than complexes of alkanes or haloalkanes, with THF ligands displacing the weaker ligands on a microsecond time scale.[22] When kept in a dry, oxygen-free environment, we have measured the stability of $W(CO)_5$THF to be several hours. It is expected that the short-time dynamics of this reaction will be similar, with the initial dissociation of a CO ligand, followed by formation of a complex to stabilize the metal center.

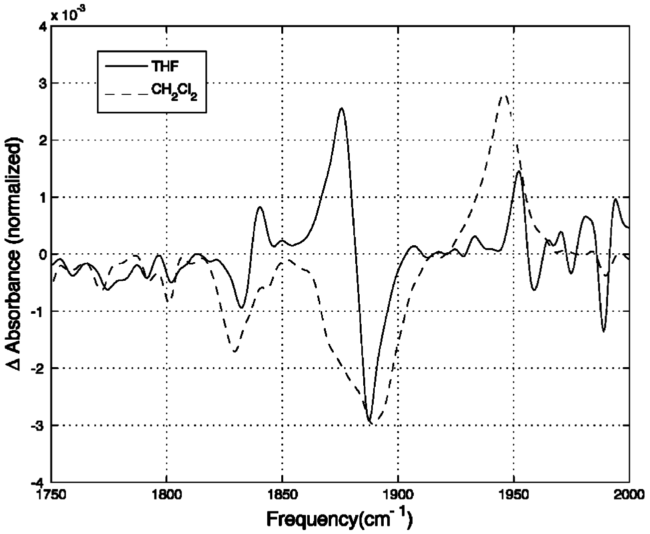


Figure 1. Difference spectra of the photochemical reaction of compound **3** following photolysis. In CH_2Cl_2 (dashed line) the reaction produces a C−F activated product, while in THF (solid) the reaction stops at the tungsten−THF solvent complex.

Figure 1 shows a static FTIR difference spectra after photolysis by a single 3 mJ UV laser pulse in both THF (solid line) and methylene chloride (dashed line) solvents. FTIR spectra of the original C−F activation product **2** by Richmond et al.[16]

TABLE 1: Results from DFT Calculations for Chemical Species Described in This Paper, Including Absolute Energies, and CO Vibrational Frequencies

molecule	calculated CO frequencies (cm^{-1})	calculated energy (Hartree)	energy difference (kcal/mol)[a]
parent molecule **3**	1974, 1875, 1862, 1852	−1059.252108	
intramolecular complex	1923, 1839, 1829	−1441.91786	0
THF solvent complex	1903, 1819, 1801	−1671.880473	−7.089831173
CH_2Cl_2 solvent complex-DMC	1903, 1796, 1790	−2401.569626	−3.082489817
CH_3CN solvent complex	1903, 1812, 1811	−1574.674603	−26.59552806
C−F activated product **4**	1991, 1937, 1870	−1441.9819	−40.19
C−F activated product **2**[16]	2004, 1952, 1879		

[a] Column 4 gives the difference in energy between the intermolecular solvent complex and the energy of the intramolecular complex plus the energy of the solvent ligand.

show CO stretches at 2020, 1937, and 1906 cm^{-1}, with the 1937 peak being the strongest. DFT calculations on this compound give predicted frequencies of 2004, 1952, and 1879 cm^{-1}. Calculations performed using a B3LYP DFT combined functional usually show frequencies that are 3−4% too high compared to experiment, but this does not appear to be the case in this system. The highest calculated frequency (2004 cm^{-1}) is actually lower than the measured frequency (2020 cm^{-1}). For compound **3**, both of the difference spectra show negative absorbances at 2011, 1878, and 1831 cm^{-1} resulting from bleaching of the parent molecule. When THF is used as a solvent, we observe new absorbances at 1876 and 1840 cm^{-1}, which represent a THF solvent complex. On the time scale of the difference spectra, we observe no formation of C−F activated product in THF, suggesting that either the intramolecular complex necessary for activation never forms, or that it forms, but the perfluorobenzene ring is displaced by the THF solvent ligand. This species is stable for several hours until it reacts thermally to form the C−F bond activated product. When CH_2Cl_2 is used as a solvent, we observe similar bleach peaks, but we observe a new absorbance peak at 1946 cm^{-1}, close to the previously measured 1937 cm^{-1}, and in reasonably good agreement with DFT calculations of the product CO stretches at 1991, 1937, and 1879 cm^{-1} shown in Table 1. This shows that we have formed the C−F activated product in methylene chloride solution.

Using nanosecond step-scan FTIR spectroscopy, we have measured the spectra of the intermediates formed during the first 200 μs following excitation in three different solvents. In each case, the spectrum does not evolve on the time scale from 100 ns to 200 μs, so only averaged spectra are shown. Figure 2 shows the transient spectrum in three different solvents: THF, CH_2Cl_2, and in CH_3CN. In the THF solvent, the nanosecond transient spectrum matches the static difference spectrum in Figure 1, showing that a complex is formed within the first 100 ns, and that it does not change over the time of the experiment. The transient spectrum in acetonitrile shows a similar spectral signature, with peaks at 1878 and 1831 cm^{-1}. In methylene chloride, the intermediate spectrum shows peaks at 1866 and 1821 cm^{-1}. The transient spectra show no formation of C−F bond activated product at 1947 cm^{-1} during the first 200 μs of the reaction. The transient spectrum in methylene chloride shows what may be a small peak at 1947 cm^{-1}, but it is small enough that it cannot be shown to be statistically significant. Calculated CO frequencies for the intramolecular and intermolecular complexes are shown in Table 1. For the intermolecular complex, they each have a CO stretch at 1903 cm^{-1} that corresponds to the symmetric stretch of the three CO ligands. The next CO stretch varies in frequency for each of the three solvents: 1842 in THF, 1830 in acetonitrile, and 1820 in methylene chloride. The relative frequencies agree well with the calculated frequencies of 1819 with THF, 1812 with acetonitrile, and 1796 with methylene chloride. The fact that the frequency of this CO stretch is solvent dependent suggests that this is a solvent complex, and not an intermolecular complex, which would be expected to have a similar spectrum in the different solvents. The calculated frequencies of the intramolecular complex are about 20 cm^{-1} higher in frequency than the solvent complexes, and there is no evidence of peaks in that region of the transient spectrum. Studies of a similar chemical system,[12] which undergoes activation of a pendant ligand, shows competition between intermolecular (with a solvent molecule) and intramolecular (with the pendant ligand) complex formation. In that system approximately 50% of the molecules formed an intramolecular complex, and the other 50% forming an intermolecular complex with a solvent molecule. On a time scale of 34 ns, the solvent ligand is displaced by the pendant ligand to form the intramolecular complex. In comparison, we only see formation of the intermolecular complex in this system.

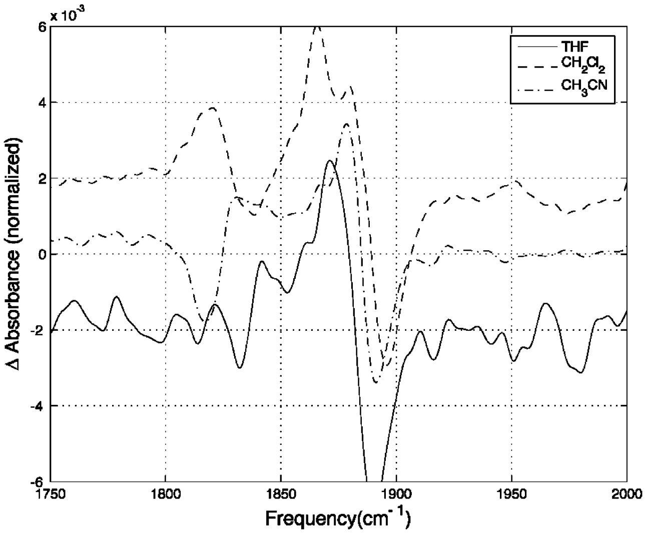


Figure 2. Nanosecond time-resolved spectra of the reaction intermediates in THF, methylene chloride, and acetonitrile. All intermediates show a peak at ~1903 cm^{-1}, corresponding to the symmetric CO stretch of a solvent complex, and peaks at 1819 (THF), 1812 (acetonitrile), and 1796 (methylene chloride), which correspond to the higher frequency asymmetric CO stretch.

The spectral shifts provide strong evidence that the short-time reaction intermediate in the C−F bond activation reaction is a solvent complex and not an intramolecular complex with the perfluorobenzene. This is surprising since the proximity of the pendant ligand would seem to favor formation of the intramolecular complex. DFT calculations of the structure of the compound **3** are shown in Figure 3. They show that the pendant ligand is oriented away from the metal atom, allowing solvent molecules easy access to the unsaturated metal center, but making formation of the intramolecular complex slow. If the kinetic product is the intermolecular complex, then in order

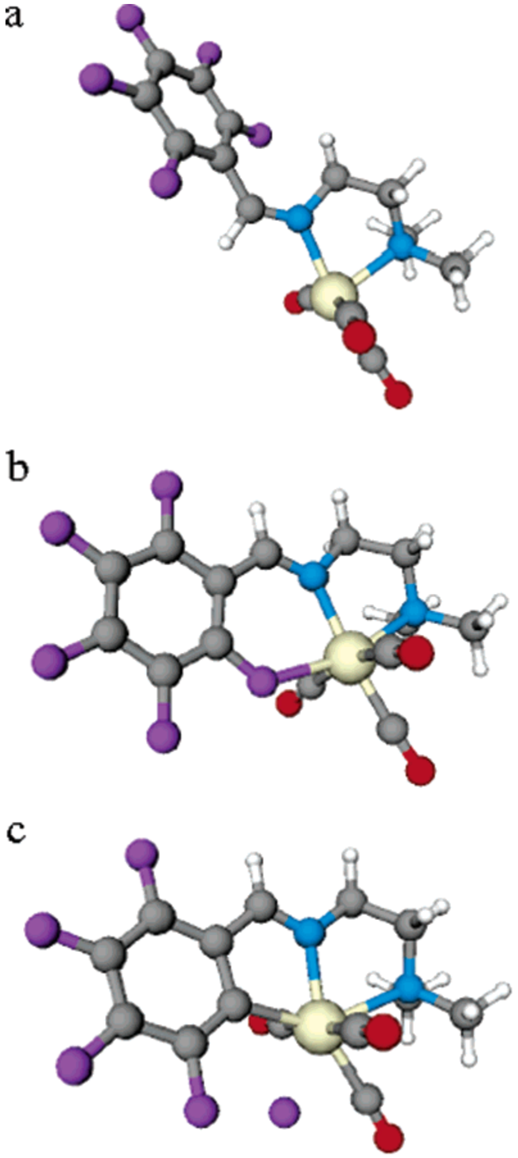


Figure 3. DFT-calculated 3-dimenstional structure from DFT calculations of (a) parent after losing CO ligand, (b) intermediate σ complex, and (c) final C−F activated complex.

for the final product to form, the pendant perfluorobenzene ligand must displace the solvent molecule and form a complex between the fluorine atom and the metal atom. This complex can then go on to form the final C−F activated product. The energy difference between the intra- and intermolecular systems can be approximated by calculating the difference between the energy of the intermolecular complex and the sum of the energies of the intramolecular complex and the solvent ligand. These energy values are shown in Table 1 in the energy difference column. This shows that all three intermolecular complexes are lower in energy than the intramolecular complexes, with the methylene chloride complex as the weakest, and acetonitrile the strongest. Reaction of this intramolecular complex to form the C−F activation product lowers the energy by 40 kcal/mol, providing the driving force for the final C−F activation step.

An interesting variation of this molecular system was also studied by Richmond and co-workers.[23] Compound **5** is almost identical to compound **1**, but with a single bond attaching the ring to the nitrogen rather than a double bond. Even though it is very similar in structure to the original compound it was found to have no C−F bond activation reactivity. This could be due to either the lack of formation of the intramolecular complexed intermediate, or to the raising of the energy of the final product, making it thermodynamically unstable. DFT calculations on the intramolecular complex show that changing this one double bond to a single bond changes the energy of the complex significantly. For the double bonded complex, the complex is 40 kcal/mol lower in energy than the naked tricarbonyl (i.e., the parent molecule with one CO ligand removed), but for the single bonded complex, the complex is 23 kcal/mol higher in energy. Thus there is no thermodynamic driving force for the pendant ligand to displace the solvent and form the intramolecular complex, so no reaction occurs.

Over the first 200 μs of the reaction, there is no decrease in the absorbance of the intermediate or any absorbance due to formation of product. Our current step scan electronics can measure only up to 200 μs. Rapid-scan FTIR allows for measurements of the spectrum on a millisecond time scale. Measurements of the reaction on the millisecond time scale show that the product is fully formed by 14 ms, the shortest time measurable with this technique. This is true even when the reaction mixture is cooled to 0 °C. While we have not been able to directly observe the C−F activation reaction, we can use this information to estimate an interval for the value of this time constant. If we assume that the reaction is at least three times longer than the 200 μs longest time from the step-scan measurement, and three times shorter than the 14 ms time from the rapid scan measurement, then the reaction must be occurring on a time scale of 0.6−5.0 milliseconds. Further, if we assume that the reaction follows standard Arrhenius behavior, then the reaction rate should be roughly 5 times faster at room temperature than at 0 °C. Thus we can assume that the reaction rate is between 0.6 and 1.0 ms.

The reactivity of compound **3** can be compared to a model compound **6**, $W(CO)_4$(tmeda), where tmeda is $(CH_3)_2NCH_2$-$CH_2N(CH_3)_2$. This has the same basic structure, but because it has no perfluorobenzene side chain it cannot form an intramolecular complex. After photolysis, the initial product has a CO vibration at 1970 cm^{-1}. On a time scale of 30 s, this frequency shifts to 1981 cm^{-1}. This 11 cm^{-1} shift is similar to the 14 cm^{-1} shift measured as the difference between σ and π complexes in a previous study of C−H bond activation.[8] This shift from a σ complex, where the metal is interacting with electrons on a fluorine atom, to a η^2 complex, where the metal is interacting with the bond between two carbon atoms on the ring, would change the geometry away from the transition geometry. Measurements of $W(CO)_6$ and $W(CO)_4$(tmeda) in C_6F_6 have shown that, while a solvent complex is formed after photolysis, the C−F bond activation reaction never occurs. The formation of an η^2 complex with benzene provides a possible explanation for this important difference between the metal center in the C−F activating complex **3** and the metal center in $W(CO)_4$(tmeda) or $W(CO)_6$. DFT calculations show that for the C−F activating compound **3**, the energy of the π complex is 7 kcal/mol higher in energy than the σ complex. For $W(CO)_6$ this is inverted, and the energy of the π complex is 10 kcal/mol lower in energy than the σ complex. If formation of the σ complex is necessary for the C−F reaction, then the pendant ligand facilitates the reaction by acting as scaffolding, holding the ring in the correct orientation for reaction, and eliminating formation of the η^2 complex.

Summary

We have investigated the photochemical C−F bond activation reaction of $W(CO)_4$ with a tethered perfluorobenzene ligand.

Following excitation and CO ligand loss, the coordinatively unsaturated metal complex forms a σ complex with a solvent molecule. Final reaction depends on displacement of the solvent molecule by the tethered ring and formation of a σ complex. This then reacts to form the final C−F activated product. This work suggests that the C−F bond process could be made more efficient if the molecule was altered to force the ring to be in closer proximity to the metal center.

Acknowledgment. The author gratefully acknowledges Dr. Thomas Richmond for synthesis and characterization of the metal complexes studied, and for assistance in interpreting the data, and the Ira and Marylou Fulton Supercomputer center for computational resources.

References and Notes

(1) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.

(2) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(3) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(4) Bengali, A. A.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 3879.

(5) Bergman, R. G. *Science* **1984**, *223*, 902.

(6) Asbury, J. B.; Ghosh, H. N.; Yeston, J. S.; Bergman, R. G.; Lian, T. Q. *Organometallics* **1998**, *17*, 3417.

(7) Asbury, J. B.; Hang, K.; Yeston, J. S.; Cordaro, J. G.; Bergman, R. G.; Lian, T. Q. *J. Am. Chem. Soc.* **2000**, *122*, 12870.

(8) Asplund, M. C.; Snee, P. T.; Yeston, J. S.; Wilkens, M. J.; Payne, C. K.; Yang, H.; Kotz, K. T.; Frei, H.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **2002**, *124*, 10605.

(9) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260.

(10) Yang, H.; Asplund, M. C.; Kotz, K. T.; Wilkens, M. J.; Frei, H.; Harris, C. B. *J. Am. Chem. Soc.* **1998**, *120*, 10154.

(11) Yang, H.; Snee, P. T.; Kotz, K. T.; Payne, C. K.; Frei, H.; Harris, C. B. *J. Am. Chem. Soc.* **1999**, *121*, 9227.

(12) Yeston, J. S.; To, T. T.; Burkey, T. J.; Heilweil, E. J. *J. Phys. Chem. B* **2004**, *108*, 4582.

(13) Jiao, T. J.; Pang, Z.; Burkey, T. J.; Johnston, R. F.; Heimer, T. A.; Kleiman, V. D.; Heilweil, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 4618.

(14) George, M. W.; Dougherty, T. P.; Heilweil, E. J. *J. Phys. Chem.* **1996**, *100*, 201.

(15) Dougherty, T. P.; Grubbs, W. T.; Heilweil, E. J. *J. Phys. Chem.* **1994**, *98*, 9396.

(16) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091.

(17) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373.

(18) Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221.

(19) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 888.

(20) Kendall, R. A.; Apra, E.; Bernholdt, D. E.; Bylaska, E. J.; Dupuis, M.; Fann, G. I.; Harrison, R. J.; Ju, J. L.; Nichols, J. A.; Nieplocha, J.; Straatsma, T. P.; Windus, T. L.; Wong, A. T. *Comput. Phys. Commun.* **2000**, *128*, 260.

(21) Lian, T.; Bromberg, S. E.; Yang, H.; Proulx, G.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **1996**, *118*, 3769.

(22) Schultz, R. H.; Krav-Ami, S. *J. Chem. Soc., Dalton Trans.* **1999**, 115.

(23) Buffin, B. P.; Poss, M. J.; Arif, A. M.; Richmond, T. G. *Inorg. Chem.* **1993**, *32*, 3805.