NMR shift for the carbene carbon in $[Cp(CO)_2Ru{=}C(SMe)_2]PF_6$ is δ 285.3.[13] Both **6** and **7** give rise to remarkably low field resonances in their ^{29}Si NMR spectra. At 23 °C, compound **6** exhibits a broad peak at δ 250.6, which sharpens to a well-defined triplet at −80 °C (δ 259.4, J_{SiP} = 34 Hz). For **7**, a broad peak at δ 264.4 was observed at −60 °C. Although the J_{SiP} coupling constants for **1–8** are all similar (34–39 Hz), this is not surprising, given the insensitivity of J_{CP} coupling constants for related alkyl and cationic carbene complexes to changes in hybridization at carbon.[14] For **6**, a solution molecular weight determination (isopiestic method, dichloromethane) gave a value of 990 (calcd 982 for the ion pair). This molecular weight measurement and the fact that the silicon of **6** is coupled to only two phosphorus nuclei rule out alternative structures with bridging silylene ligands. Attempts are underway to obtain X-ray quality crystals of **6**, **7**, and related derivatives.

Silylene complex **6** combines rapidly with acetonitrile to produce the donor adduct $\{Cp^*(PMe_3)_2RuSi[S(p\text{-tol})]_2NCMe\}^+BPh_4^-$ (**8**). The ^{29}Si NMR shift for **8** is δ 58.30 (t, J_{SiP} = 39 Hz), and single-crystal X-ray crystallography revealed structural features similar to those of the previously reported adduct $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]BPh_4$.[8] A related complex, $\{Cp^*(PMe_3)_2RuSi[S(p\text{-tol})]_2(pyr)\}^+BPh_4^-$ (**9**), was obtained by reaction of **3** with pyridine, followed by metathesis of the anion with $NaBPh_4$.

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Supplementary Material Available: Experimental procedures and characterization data for compounds **1–9** (5 pages). Ordering information is given on any current masthead page.

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Picosecond Time-Resolved Circular Dichroism Study of Protein Relaxation in Myoglobin Following Photodissociation of CO

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The photodissociation of (carbonmonoxy)myoglobin (MbCO) to form myoglobin (Mb) and free CO has been the subject of several recent time-resolved studies.[1] Transient infrared,[2] Raman,[3] and absorption[4] studies provide definitive evidence that photoinduced bond cleavage in heme proteins occurs within 350 fs of photolysis. However, examination of the crystal structure of MbCO and Mb suggests that relaxation of the tertiary structure of the protein is also expected following ligand loss.[5] In particular, in the local vicinity of the reaction site, dissociation causes the heme to dome, and the iron moves out of the porphyrin ring, causing the distal histidine to tilt and the F-helix to move.

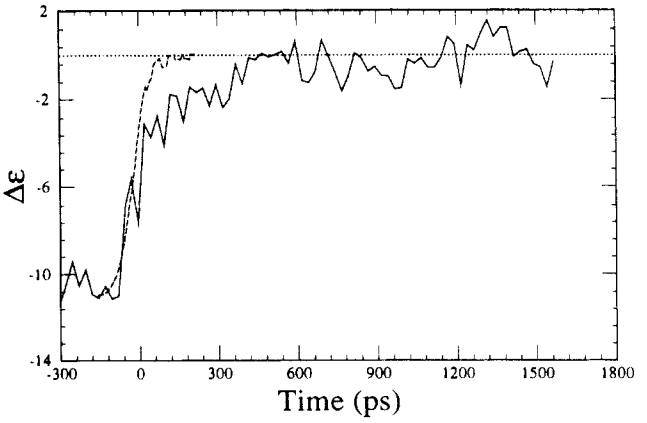

Figure 1. Transient circular dichroism kinetics of Mb probed at 355 nm following the photodissociation of CO (solid line). The dashed line is the normalized transient absorption signal recorded at this wavelength. The transient CD data reveal two processes. The dotted line is the equilibrium CD value for Mb. The instantaneous component (≈60% of the change in signal) is due to the electronic state change that occurs upon photodissociation. The longer time relaxation reflects conformational changes in the surrounding protein structure.

It is of great interest to determine the time scale(s) associated with the structural rearrangement of the surrounding protein. These motions are difficult to measure as most of the current transient spectroscopies used to probe protein dynamics are not sensitive to small changes in the tertiary structure. Steady-state circular dichroism (CD) spectroscopy has proven to be a powerful approach for studying protein structure.[6] Thus, one might expect that a time-resolved measurement of CD could provide new insights into dynamic structural rearrangements that occur in proteins following photoinitiated processes. We have developed a technique that allows the measurement of transient CD kinetics with picosecond resolution. The details of the experimental approach[7] and a theoretical analysis[8] of the signals obtained from this spectrometer have been previously discussed. In the present communication, we report a transient CD study of the N-band absorption of myoglobin following photodissociation of CO. This data provides important new insight into the relaxation dynamics of the protein following the photoinduced bond cleavage.

In Figure 1, the transient CD signal probed near the peak of the N-band absorption (λ = 355 nm) is plotted as a function of time following photolysis. The dashed line is a normalized transient absorption study on the same sample at the same wavelength, providing a measure of the instrument response. The CD signals observed prior to photolysis and at long times ($t >$ 1 ns) are consistent with the steady-state CD values of MbCO and Mb at 355 nm, respectively.[9] The important observation in Figure 1 is that the evolution of the CD signal is distinctly different from the transient absorption kinetics.

The CD kinetics exhibited in Figure 1 reveal two major components. Half of the observed signal change occurs within the instrument response. This is followed by a slower rise reflecting a relaxation process that is approximately 2 orders of magnitude

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slower than the dynamics of photoinduced bond cleavage. The instantaneous change in the CD signal following photolysis reflects the expected electronic state change of the heme group that accompanies dissociation.[10]

Several possible models can be invoked to account for the dynamic changes in the CD signal that is observed on the 100-ps time scale. Three molecular mechanisms that are consistent with the observed data include vibrational relaxation in the vicinity of the heme, a time-dependent splitting of the degeneracy of the heme transitions, and relaxation of the surrounding protein matrix. Recent picosecond Raman studies by Ondrias and co-workers[11] reveal that vibrational relaxation in the vicinity of the heme is complete within 30 ps, significantly faster than the relaxation process revealed by the CD data. This conclusion is also consistent with recent transient grating studies reported by Miller and co-workers.[12] In order to address the possibility of a time-dependent splitting in the degeneracy of the heme transitions, the following experiments were conducted: (1) picosecond linear dichroism studies on the Soret absorption bands, (2) transient picosecond magnetic circular dichroism of the Q-band absorption, and (3) detailed time-resolved absorption studies of the Q band. These studies, which will be reported in detail at a later date,[13] reveal no evidence for a time-dependent splitting of the degeneracy of the heme transitions and confirm that the spin state of the iron changes within 20 ps of photolysis.

From these observations we are able to conclude that transient CD kinetics provide information on the relaxation dynamics of the protein structure following photodissociation. Calculations reported by Hsu and Woody[14] suggest that the CD of the N band of Mb is primarily due to coupled oscillator interactions between the N_x and N_y transitions on the heme and the $\pi \rightarrow \pi^*$ transitions on the surrounding aromatic amino acids. These calculations also show that aromatic residues as far away as 12 Å from the heme can significantly contribute to the CD spectrum, suggesting that this new form of spectroscopy can be useful in probing the dynamics of protein structural changes that occur outside the immediate environment of the heme group.

One particular local molecular motion that could account for the evolution of the CD signal involves the tilting of the proximal histidine. This can be independently addressed by examining the near-infrared absorption band of Mb at 760 nm as this transition arises from a porphyrin to iron charge transfer and has been shown to be sensitive to the conformation of the proximal histidine with respect to the heme ring.[15] Detailed dynamical studies of this absorption band reveal no change in band shape or band position from 20 ps (the instrument response) to 10 ns following photodissociation.[13] This result suggests that the tilting of the proximal histidine, as well as other structural changes that contribute to the shape and maximum of this absorption band, is not responsible for the observed CD kinetics. Further studies on mutant proteins are planned in order to determine the origin of this relaxation process.

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Ab Initio Studies of the Electronic Structure of the Diuranium Molecule

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Although bonding between two transition-metal atoms is commonly observed, no discrete molecules showing direct actinide–actinide bonding have been isolated. Efforts to synthesize uranium analogues of metal–metal-bonded Mo and W clusters have failed; the propensity for forming U–ligand bonds is apparently much greater than that for forming U–U bonds.[1,2]

The simplest systems in which one could find direct actinide–actinide bonds are the ligand-free actinide diatomics, such as U_2, which has 12 valence electrons that could participate in the formation of U–U bonds. U_2 has been detected in the gas phase,[3] and significant $f\sigma$, $f\pi$, $f\delta$, and $f\phi$ diatomic interactions were predicted by our approximate nonrelativistic molecular orbital calculations at short bond lengths.[4] These theoretical studies provided no information on the bond length, binding energy, or detailed electronic structure of U_2. In addition, the inclusion of relativistic effects is essential for the proper description of heavy-metal systems. We therefore have undertaken the first ab initio study, including correlation and relativistic effects, of the bonding in an actinide diatomic molecule, U_2. The results reported here are decidedly different from those reported earlier[4] and indicate that the U_2 potential surface is quite complex, with two groups of states exhibiting energy minima at two different bond lengths.

SCF, CAS-SCF, and single-reference CI (SRCI) calculations have been performed on a Cray Y-MP (60 CPU h) using the COLUMBUS programs.[5] A relativistic core potential[6] replaced the 156 core electrons (1s–5d), while the 28 semicore (6sp) and valence (5f, 6d, 7s) electrons were described by a (5s6p5d4f) → [3s4p3d2f] Gaussian basis.[7] Relativistic effects give 7s, 6d, and 5f AOs of similar energy and spatial extent. The resultant MOs are closely spaced in energy, allowing many open-shell configurations. As with Cr_2,[8] both long-bond-length (LBL) and short-bond-length (SBL) energy minima are found.

In the SBL states of U_2, the 12 valence electrons occupy MOs formed from 5f, 6d, and 7s AOs, yielding low-spin states such as ^5A_g and $^3B_{1g}$ (D_{2h} symmetry). In the CAS-SCF approach, the lowest valence σ_g and π_u MOs were filled, and the remaining six electrons were distributed among two σ_g, one π_u, two δ_g, and one ϕ_u active MOs. The CAS-SCF calculations involved up to 1749 configuration functions (cf), and the ^5A_g SRCI expansion contained 75 329 cf. For the LBL states, six electrons occupy essentially atomic f orbitals. All possible states with six electrons in the $7s\sigma_g$, $7s\sigma_u^*$, $6d\sigma_g$, $6d\pi_u$, and $6d\delta_g$ MOs were investigated by CAS-SCF (up to 700 cf) and SRCI (up to 313 770 cf). SCF, CAS-SCF, and SRCI energies were evaluated at a range of bond lengths. The energies of the separated atoms were calculated by using a supermolecule of two U atoms at 200 au, ^9A_u state, to avoid size-consistency errors.

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