C(12). Examination of a space-filling model of **8** reveals that the intermediate manganese(V) oxo species can readily abstract the C(12) α- and β-hydrogens. It is of interest to note that the reagent with the shorter, more rigid tether **2** leads to hydrogen atom abstraction at the site furthest removed from the 3α-position on the steroid. Surprisingly, the more flexible reagent **8**, which in principle can hydroxylate at C(12), C(14), and/or C(17), only induces hydrogen atom abstraction at C(12) and C(14), only a few atoms removed from the point of attachment.

In summary, intramolecular hydrogen atom abstraction via reactive oxomanganese(V) species such as **2** and **8** leads to direct hydroxylation of steroids. It should be pointed out that attempts to effect such transformation employing the corresponding iron(III) porphyrin analogues gave rise to significantly lower yields of hydroxylated steroids.[12] The major limitation of steroid hydroxylation via oxometalloporphinates, in particular with the iron(III) porphyrin, is the facile oxidative degradation of the porphyrin. Further studies are underway to (1) determine the scope of this metalloporphyrin-based oxygen transfer process for the hydroxylation of steroids and (2) design porphyrin ligands that are not prone to oxidative degradation.

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(12) Unpublished results of Dr. Randolph Belter, Indiana University.

Base-Free Silylene Complexes $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2Ru{=}Si(SR)_2]BPh_4$ (R = Et, *p*-MeC_6H_4)

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Transition-metal silylene complexes ($L_nM{=}SiR_2$) have attracted attention as intriguing synthetic targets for many years. This interest relates to their proposed roles in various catalytic cycles, but also derives from the rich reaction chemistry associated with closely related carbene complexes ($L_nM{=}CR_2$).[1] Recently the first well-characterized examples of silylene complexes as donor adducts ($L_nMSiR_2{\leftarrow}B$) have been reported by groups in the U.S.,[2] Germany,[3] and Japan.[4] Our route is based on electron-rich transition-metal fragments for stabilization of the silylene silicon, and removal of a group bound to silicon.[2] The complex Cp*-$(PMe_3)_2RuSiPh_2OTf$ (Cp* = η^5-C_5Me_5) possesses a weakly bound triflate group as characterized by its behavior in solution, the molecular structure, and a downfield ^{29}Si NMR shift of 112.39 ppm. The triflate group is readily displaced by acetonitrile to give $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]^+$. Dynamic NMR studies have shown that, in dichloromethane, this complex dissociates acetonitrile to produce the base-free silylene $[Cp^*(PMe_3)_2Ru{=}SiPh_2]^+$.[2b]

Calculations[5] and experimental work by Lambert and coworkers[6] indicate that thiolate groups have a stabilizing influence on silylenium ions (SiR_3^+). These results prompted us to investigate the use of thiolate groups in stabilizing cationic silylene complexes, which would also contain a three-coordinate silicon center. Here we report results of these studies, which have allowed isolation of the first base-free silylene complexes.

The tris(thiolato)silyl complexes **1** and **2** were prepared in good yields by an established procedure from $Cp^*(PMe_3)_2RuCH_2SiMe_3$ and the appropriate silane $HSi(SR)_3$.[2b] Starting from these new silyl complexes, triflate derivatives **3**–**5** have been obtained by exchange reactions with Me_3SiOTf (eq 1).[7] As expected, the

$$Cp^*(PMe_3)_2RuSi(SR)_3 \xrightarrow[-Me_3SiSR]{Me_3SiOTf} Cp^*(PMe_3)_2RuSi(SR)_2OTf \xrightarrow[-Me_3SiSR]{Me_3SiOTf} Cp^*(PMe_3)_2RuSiSR(OTf)_2 \quad (1)$$

1, R = *p*-tol; 2, R = Et — 3, R = *p*-tol; 4, R = Et — 5, R = *p*-tol

X-ray crystal structures of **3** and **5** established the presence of covalent, but long, Si–O(triflate) bonds.[8] Spectroscopic data are also consistent with covalent structures in the solid state and in dichloromethane solution. The ^{29}Si NMR shifts for **3**–**5** (δ 77.14, 86.05, and 37.10, respectively) are upfield from the shift for $Cp^*(PMe_3)_2RuSiPh_2OTf$, but are not unusual.[1] For **3**, infrared $\nu(SO_3)$ vibrational modes for covalently bound triflate were observed for the solid state (1367 cm^{-1}, Nujol mull) and in dichloromethane solution (1362 cm^{-1}).[9]

As for $Cp^*(PMe_3)_2RuSiPh_2OTf$, the triflate groups of **3** and **4** are chemically labile. In acetonitrile solution, triflate is displaced to produce $[Cp^*(PMe_3)_2RuSi(SR)_2NCMe]^+OTf^-$ complexes, as indicated by $\nu(SO_3)$ infrared bands that reveal the presence of only ionic triflate (**3**, 1269 cm^{-1}; **4**, 1268 cm^{-1}). For **4**, the inequivalent methylene protons of the SEt groups exchange rapidly, appearing as a single resonance (q, δ 2.88) in dichloromethane-d_2 down to −70 °C. In the less polar solvent toluene-d_8, the process that exchanges these protons is slowed considerably, resulting in an observed coalescence temperature of 21 °C (ΔG^*_{294K} = 14.9 ± 0.3 kcal mol^{-1}). These results are most consistent with an exchange mechanism consisting of dissociation of triflate anion to form $Cp^*(PMe_3)_2Ru{=}Si(SEt)_2^+$, and return of triflate anion to the opposite face of the silylene ligand.[10] Since it then appeared that the base-free silylene complexes $[Cp^*(PMe_3)_2Ru{=}Si(SR)_2]BPh_4$ (**6**, R = *p*-tol; **7**, R = Et) might be reasonably stable, attempts were made to isolate them.

Compounds **3** and **4** react with $NaBPh_4$ in dichloromethane to produce a precipitate of NaOTf. Workup of the solution and crystallization from dichloromethane–diethyl ether allow isolation of compounds **6** and **7** (eq 2). Elemental analyses and NMR

$$Cp^*(PMe_3)_2RuSi(SR)_2OTf \xrightarrow[-NaOTf]{+NaBPh_4} \left[Cp^*(PMe_3)_2Ru{=}Si\begin{matrix}SR\\SR\end{matrix}\right]^+ BPh_4 \quad (2)$$

6, R = *p*-tol; 7, R = Et

spectra show that these yellow, crystalline materials do not contain solvent. Correlations between ^{13}C and ^{29}Si NMR shift data[11] suggest that a silylene complex would exhibit a low-field ^{29}Si NMR shift, since ^{13}C NMR shifts for terminal carbene ligands are generally in the range 240–370 ppm.[12] For example, the ^{13}C

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(1) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415 and references therein.

(2) (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673.

(3) (a) Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669. (b) Zybill, C.; Wilkinson, D. L.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 583. (c) Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368. (d) Zybill, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203.

(4) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415.

(5) Apeloig, Y.; Godleski, S. A.; Heacock, D. J.; McKelvey, J. M. *Tetrahedron Lett.* **1981**, *22*, 3297.

(6) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201.

(7) Full characterization data and syntheses for new compounds are provided in the supplementary material.

(8) Grumbine, S. D.; Straus, D. A.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L., manuscript in preparation.

(9) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(10) A similar process has been identified for $Cp(NO)(Ph_3P)$-$ReGePh_2OTf$: Lee, K. E.; Gladysz, J. A. *Polyhedron* **1988**, *7*, 2209.

(11) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

0002-7863/90/1512-7801$02.50/0

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.

(12) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.
(13) Matachek, J. R.; Angelici, R. J. *Inorg. Chem.* **1986**, *25*, 2877.
(14) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (c) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804. (d) Kiel, W. A.; Buhro, W. E.; Gladysz, J. A. *Organometallics* **1984**, *3*, 879. (e) Bly, R. S.; Wu, R.; Bly, R. K. *Organometallics* **1990**, *9*, 936.

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.

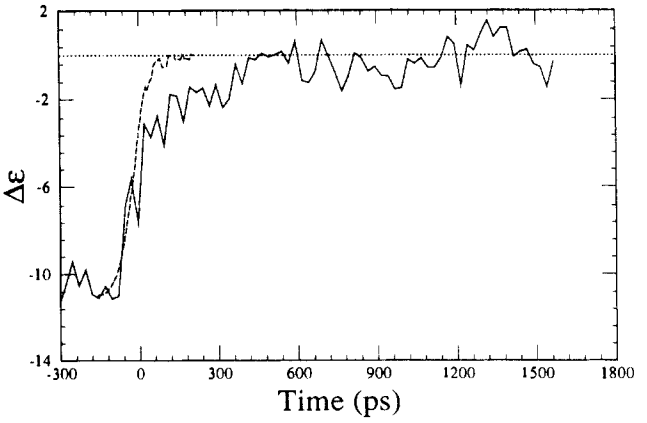

Figure 1. Transient circular dichroism kinetics of Mb probed at 355 nm following the photodissociation of CO (solid line). The dashed line is the normalized transient absorption signal recorded at this wavelength. The transient CD data reveal two processes. The dotted line is the equilibrium CD value 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

(1) For a recent review see: Hochstrasser, R. M.; Johnson, C. K. In *Ultrashort Light Pulses*; Kaiser, W., Ed.; Springer: New York, 1988; pp 357–417.
(2) (a) Anfinrud, P. A.; Han, C.; Hochstrasser, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 8397. (b) Moore, J. N.; Hansen, P. A.; Hochstrasser, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 5062.
(3) Petrich, J. W.; Martin, J. L.; Houde, D.; Poyart, C.; Orszag, A. *Biochemistry* **1987**, *29*, 7914.
(4) (a) Martin, J. L.; Migus, A.; Poyart, C.; Lecarpentier, Y.; Astier, R.; Antonetti, A. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 173. (b) Jongeward, K. A.; Magde, D.; Taube, D. J.; Marsters, J. C.; Traylor, T. G.; Sharma, V. S. *J. Am. Chem. Soc.* **1988**, *100*, 7690 and references within.
(5) (a) Phillips, S. E. V. *J. Mol. Biol.* **1980**, *142*, 531. (b) Baldwin, J.; Chothia, C. *J. Mol. Biol.* **1979**, *129*, 192. (c) Fermi, G.; Perutz, M. F. *Atlas of Molecular Structures in Biology 2. Haemoglobin and Myoglobin*, Clarendon Press: 1981.
(6) (a) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry*, Freeman and Co: New York, 1980. (b) Creighton, T. E. *Proteins: Structures and Molecular Properties*, Freeman and Co: New York, 1984.
(7) Xie, X.; Simon, J. D. *Rev. Sci. Instrumen.* **1989**, *60*, 2614.
(8) Xie, X.; Simon, J. D. *J. Opt. Soc. Amer. B.* **1990**, *7*, 1673.
(9) Milder, S. J.; Bjorling, S. C.; Kuntz, I. D.; Kliger, D. S. *Biophys. J.* **1988**, *53*, 659.

0002-7863/90/1512-7802$02.50/0