If the Hm(RNC)$_2$ and 1-MeImHmCNR and MbCNR all give excited-state five-coordinated species which have rather similar spectra, then we conclude that these excited states involve porphyrin $\pi \rightarrow \pi^*$ transitions which have little contribution from the metal. In this way any excited-state five-coordinated heme would have this same long wavelength absorption.

The rates of decay of the excited state (k^*) are more dependent upon structure. The chelated protoheme obtained upon photolysis of the CO or isocyanide complexes relaxes with a half-life of about 2 ps compared to 8.5 ps for t-BuNCHm*. The αChNCHm* appears to relax even faster than does excited-state chelated protoheme*. Excited-state myoglobin (Mb*), obtained from photolyses of MbCO or MbCNR, also relaxes to ground-state Mb, a rate that is similar to that of chelated protoheme*.

These variations of excited-state lifetime with the nature of the fifth ligand suggest caution in interpreting photolyses of LHmCO complexes etc., in which L varies, for example, in cytochrome P450–CO. However, in almost all cases the bleached Soret band in LHm* does not return appreciably during the decay to the ground state. This makes the Soret change a somewhat better indication of geminate return than is the five-coordinated absorption if the latter absorbs in the region of 440–450 nm.

It is not clear why the excited-state heme–isocyanide complex relaxes more slowly than does the excited-state heme–imidazole complex. It has been suggested that the heme–CO[19] and heme–CS[20] complexes, isoelectronic with RNC–heme, are low spin and perhaps planar, whereas the heme-base species is high spin and domed.[20] It therefore seems logical that the excited electronic states are also different. Thus RNC–Hm* might be a triplet state which returns slowly to a singlet ground state. But the electronic basis for these long lived excited states is not clear, and some theoretical work on these complexes is in order.

Finally, these studies confirm the generally accepted proposals that picosecond photolysis of the complex BHmL breaks an L–Hm bond, that return occurs in the cage in competition with diffusion, and that *we can confidently separate excited-state relaxation from geminate return*. This finding should provide a means of studying these excited states.

All kinetics reported here are accurately exponential whether the reaction is excited-state decay, geminate recombination/diffusion, or pseudo-first-order reactions. We see no evidence for the nonexponential decay in these solvents, a matter considered in detail elsewhere.[18]

Acknowledgment. We are grateful to the National Institutes of Health (Grant HL 13581 [Traylor]) and to the National Science Foundation (Grant CHE-9114613 [Magde]) for support.

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[19] Wayland, B. B.; Mehne, L. F.; Swartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2379–2383. Wayland reported the spin state of the five-coordinated Fe(TPP)CO was a singlet. We have made the analogous five-coordinated PHDME-CO and determined that the Soret maximum occurs at 400 nm. Because of the similarities in crystal-field strength of CO and isocyanide and the Soret positions, we have postulated that the five-coordinated PHDME-CNR ground state is a singlet. OEPFe-CS is a singlet.[14]

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Communications to the Editor

The Use of Self-Assembled Monolayers and a Selective Etch To Generate Patterned Gold Features[1]

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The combination of aqueous, alkaline cyanide ion (1 M KOH, 0.1 M KCN) and dioxygen rapidly etches Au(0) (eq 1).[2-4] Self-assembled monolayers (SAMs) of long-chain alkanethiolates

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4[Au(CN)_2]^- + 4OH^- \qquad (1)$$

on the surface of the gold block this etching. Using a number of techniques—micromachining, microwriting, electron-beam lithography, ion-beam lithography—it is possible to form patterns of SAMs on the Au surface. By combining these techniques for forming patterns with selective etching using the CN$^-$/O$_2$ solution, high-resolution patterns of gold on silicon can be fabricated with dimensions as small as 1 μm.[5]

One procedure used a pen to write patterns of hexadecanethiolate[6] as monolayers on Au substrates. The pen, filled with hexadecanethiol, was clamped to a X-Y micrometer, and the gold sample was moved across the tip of the pen at 100–1000 μm/s.[7] This system allowed the formation of 1–100 μm features. Only the drop of thiol (i.e., not the tip of the pen) was in contact with the gold surface. Etching resulted in complete removal of the underivatized Au and underlying Ti.[8,9]

Figure 1 shows a representative line. The regions of the Au surface protected by the SAM exhibited little pitting (fewer than 5 pits, approximately 1 μm in diameter, per mm^2): the density of pitting did not increase for exposures of an additional 12 h. The monolayer was not removed: profilometry confirmed that the thickness of the protected Au was the same before and after immersion in the etching solution. The hydrophobicity of the protected surface (measured by the contact angle of water) did not change. Two-point conductivity measurements indicated that lines having widths of 10 μm were electrically conducting: there were no breaks in the gold over distances of 1–2 cm. Adjacent, unconnected lines spaced apart by 1–2 mm were electrically

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[1] This research was supported in part by the Office of Naval Research and the Defense Advanced Research Projects Agency.

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[6] Hexadecanethiol is the longest chain alkanethiol that is liquid at room temperature and was the best for writing lines. The thiolate monolayer should be autophobic. Autophobic alkanethiol "ink" allowed smooth formation of continuous lines without leaving excess thiol on a line and without loss of definition through reactive spreading. We used a Staedtler pen.

[7] The gold film (2000 Å in thickness) was prepared by electron beam evaporation onto a titanium-primed (100 Å Ti) silicon wafer.

[8] The etch solution consisted of 1 M KOH and 0.1 M KCN in distilled water. The solution container was open to the ambient air and stirred vigorously. Alternatively, the solution was saturated with dioxygen using a coarse frit. For samples of Au used within 1 day of preparation, we observed no significant difference in resolution or rate of etching using either etch solutions that were saturated with oxygen or those that were not. For such fresh samples, etching was complete in 10–15 min for thin (500 Å) Au films and in 30–45 min for thicker (2000 Å) films. When samples were used several days after preparation, the rate of etching, when dioxygen was not bubbled through the solution, was slower by factors of 5 to 10 than when it was. We assume the slowed etching reflected adsorption of adventitious organic impurities on the surface. After removal of the sample from the etch solution, it was rinsed with distilled water and ethanol and dried in a stream of nitrogen. It was not necessary to control parameters such as temperature and stirring rate rigorously.

[9] The Au and Ti in the regions not protected by the SAM dissolved completely, as determined by energy dispersive X-ray spectroscopy (EDX).

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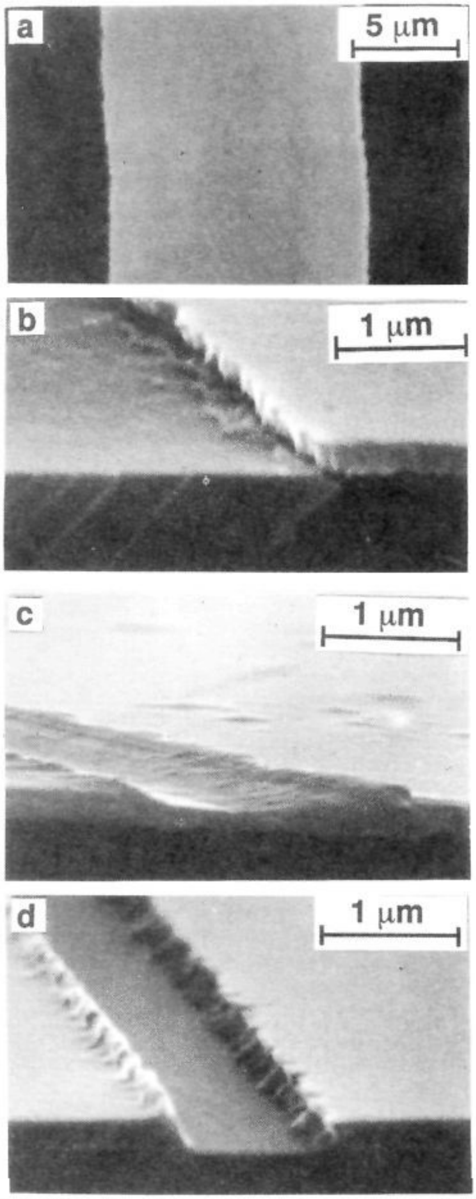

Figure 1. (a) Scanning electron micrograph of a protected Au line (the central stripe; ~12 μm wide) formed by etching. Note the lack of pitting on the protected region. Such protected lines could be extended for centimeters. (b) Profile of a protected line (obtained by fracturing the silicon wafer perpendicular to the line) showing the resolution of the edge after exposure to the CN^-/O_2 etch. (c) Fractured profile of a micromachined trench before etching. (d) Side profile of a trench after etching.

isolated from each other, with resistances between them greater than 1 MΩ.

We were also able to micromachine lines reproducibly in the monolayer, with very high spatial resolution, and subsequently to etch away the gold in the machined regions (Figure 1).[9,10] As with the protected Au line, the edges of the trench exhibited excellent sharpness.

SAMs—14–20 Å, ordered, organic layers[8,11]—can thus protect a surface from corrosion. This thin organic resist material, in combination with patterning and selective etching, provides a convenient method for forming structures of gold on silicon, with feature sizes as small as 1 μm. Because this procedure does not require photolithographic equipment, it is particularly suitable for use in chemical laboratories and for applications such as rapid prototyping of microelectrode arrays and other relatively simple structures.

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(10) The width of the trench was dependent upon the sharpness of the mechanical probe and the pressure used in the micromachining process. We routinely formed trenches of width 0.5–2 μm. Abbott, N. L.; Folkers, J. P.; Whitesides, G. M. *Science* **1992**, *257*, 1380.

(11) SAMs formed from alkanethiols with longer chains also exhibited excellent protection. Shorter chain thiols including perfluorinated systems provided limited protection from the etching.

Spectroscopic and Theoretical Description of the Electronic Structure of the $S = {}^3/_2$ Nitrosyl Complex of Non-Heme Iron Enzymes

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Non-heme iron centers are present in the catalytic active sites of a large number of enzymes which are involved in the binding and activation of dioxygen.[1] A member of this class, soybean lipoxygenase (SBL), catalyzes the reaction of 1,4-unsaturated lipids with dioxygen to form a hydroperoxide product.[2] Nitrosyl complexes of enzymes serve as reversible analogues of possible dioxygen intermediates involved in catalysis. SBL-NO and other non-heme ferrous enzyme nitrosyl complexes (formulated as $\{FeNO\}^7$)[3] exhibit an unusual $S = {}^3/_2$ EPR signal,[4] which is also observed in $\{FeNO\}^7$ model complexes.[5] A wide range of bonding descriptions have appeared[6] for these complexes, which include $[Fe^+d^7(S = {}^3/_2)\text{-}NO^+(S = 0)]$, $[Fe^{2+}d^6(S = 2)\text{-}NO^0(S = {}^1/_2)]$ antiferromagnetically coupled, $[Fe^{3+}d^5(S = {}^1/_2)\text{-}NO^-(S = 1)]$ ferromagnetically coupled, and $[Fe^{3+}d^5(S = {}^3/_2)\text{-}NO^-(S = 0)]$. In order for the NO derivative of these enzymes to be used as a probe of electron distribution related to dioxygen reactivity, a clear understanding of the electronic structure and associated spectral features of the $S = {}^3/_2$ $\{FeNO\}^7$ unit is required. Spectroscopic techniques and theoretical methods have been used to study SBL-NO and two $S = {}^3/_2$ ground-state model complexes,[7] $FeL(NO)(N_3)_2$, where L = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane and FeEDTA-NO. These studies have produced a new bonding

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