plateau from 6–9 or 10 oxygens, or the plateau may reflect experimental uncertainty in a downward decline from 6–13 oxygens. In the latter case, least-squares fits of the lines should confirm the approximate linearity.[12] The calculated slopes, intercepts, and correlation factors suggest a straight-line relationship and that the plateaus are artifacts. It seems reasonable, however, to presume that side-chain oxygen atoms positioned in a range of distances from the ring might be useful for secondary binding but, beyond a certain point, be inaccessible.

There are at least two obvious explanations for the eventual decline in binding constants. One is that as the number of oxygens in the side arm increases, hydrogen bonding by the medium decreases its flexibility (a ponderal effect) and thereby its effectiveness in binding. Another possibility is coiling of the side arm limiting access by the cation. This might be due to a hydrophobic effect (i.e., a lipophilic–lipophilic interaction) or water-bridged hydrogen bonds between ring and sidearm. Further work is in progress to clarify this observation.

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Supplementary Material Available: Measurement of binding constants for **1–17** and preparation of lariat ethers (4 pages). Ordering information is given on any current masthead page.

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(12) The slopes, intercepts, and correlation factors (r) calculated for the 15-membered and 18-membered nitrogen lariats are as follows: slopes −0.16, −0.15; intercepts 5.50, 5.48; $r = -0.975, -0.938$. The slopes are calculated from the peak toward the higher values of n, rendering the intercepts meaningless except for comparative purposes.

Soret-Excited Resonance Raman Spectrum of (Carbon monoxy)leghemoglobin: Assignment of $\nu_{\text{Fe–CO}}$

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Many resonance Raman spectra in the low-frequency region (<700 cm^{-1}) have been reported recently for hemeproteins.[1-12] The intensities of Raman bands in this region have been enhanced by laser excitation into or near the Soret absorption band[1-10] or into charge-transfer absorptions.[11,12] Bands have been assigned to Fe–L(axial) stretching vibrations either by inference or by direct isotopic substitution in the ligands. For example, vibrations due to Fe–OH$^-$, Fe–N$_3^-$, and Fe–F$^-$ in derivatives of ferric myoglobin have been observed by Asher et al.[11,12] using laser excitation in the range 600–630 nm. Desbois et al.[1] have assigned similar bands in the resonance Raman spectra of the same myoglobin derivatives by using excitation (441.6 nm) near the Soret absorption band. In the ferrous form of oxygen binding hemeproteins, bands have been assigned to $\nu_{\text{Fe–O}_2}$ in oxyhemoglobin[2] (HbO$_2$), oxymyoglobin[1,3] (MbO$_2$), and oxyleghemoglobin[4] (LbO$_2$) and to Fe–N$_\epsilon$ (proximal histidine) in deoxyhemoglobin,[2,5,6] deoxymyoglobin,[1,7] and deoxyleghemoglobin.[4] To date, only one report of a resonance Raman spectrum, in the low-frequency region, of a carbon monoxide complex of a hemeprotein has appeared.[8] No attempt was made to assign $\nu_{\text{Fe–CO}}$ in that work. We report here excellent spectra of soybean CO-leghemoglobin. From isotopic substitution (^{12}C^{16}O → ^{13}C^{18}O) we are able to assign, for the first time, $\nu_{\text{Fe–}^{12}\text{C}^{16}\text{O}}$ (505 cm^{-1}). Our results also suggest that the excitation wavelength which most favors photodissociation of bound carbon monoxide is distinct from that which gives rise to the resonance enhancement of the $\nu_{\text{Fe–CO}}$ Raman band.

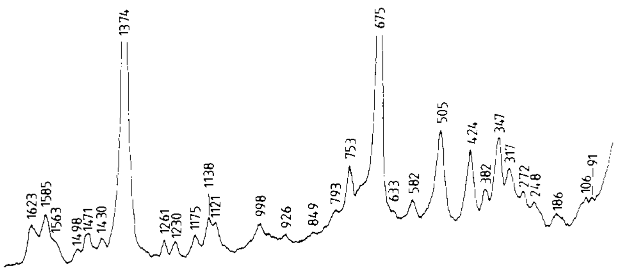

Figure 1. Single scan resonance Raman spectrum of CO-leghemoglobin (50 μM). Laser excitation 413.1 nm; 45 mW at sample; 1-cm^{-1} s^{-1} scan; 1-s time constant; 7.5-cm^{-1} resolution. Ferric soybean Lb, purified as in ref 15, was introduced into a sample spinning cell sealed with a septum, flushed with argon, and a twofold excess of dithionite was added to give deoxyleghemoglobin. The CO complexes were formed by injection of ^{12}C^{16}O (Matheson Gas Products) or ^{13}C^{18}O (Prochem, B.O.C. Limited; 92% ^{13}C, 98.5% ^{18}O) such that the samples were under a 1:1 mixture of carbon monoxide and argon at atmospheric pressure. All samples were in 10 mM phosphate buffer (pH 7.0) containing 0.1 mM EDTA.

The resonance Raman spectrum[13] (50–1700 cm^{-1}) of soybean CO-leghemoglobin obtained with 413.1-nm laser excitation is shown in Figure 1. An obvious feature of the spectrum is the strong polarized band at 505 cm^{-1} which has not appeared in other Soret-excited resonance Raman spectra of myoglobin,[1,3] hemoglobin,[2,5,6] or leghemoglobin[4] derivatives. Figure 2 shows the resonance Raman spectra of Lb^{12}C^{16}O and Lb^{13}C^{18}O excited with 441.6- and 457.9-nm laser irradiation. The only band that shifts significantly ($\Delta\nu = 13$ cm^{-1}) upon isotopic substitution is the band at 505 cm^{-1}. The frequency shift calculated from a change in the reduced mass, upon substitution of ^{13}C^{18}O, for an isolated Fe–CO stretch is 16.5 cm^{-1}. We attribute the 505-cm^{-1} band to the Fe–CO vibration. The difference between the calculated and observed shift upon isotopic substitution may reflect a constraint on the CO mobility or nonlinearity of the Fe–C–O moiety. A similar band has been observed by Rimai et al.[8] in the resonance Raman spectrum of HbCO at 506 cm^{-1}. From the position, intensity, and polarization of this band we assign it to $\nu_{\text{Fe–CO}}$.

Other features of the spectra are also of interest. First, the absence of any band near 220 cm^{-1} is noted. Desbois et al.[1] observed bands in this region for the fully ligated ferrous low-spin derivatives of MbO$_2$ and MbNO. Tsubaki et al.,[3] on the other hand, did not observe such a band for a variety of oxymyoglobins and suggested that the bands observed by Desbois and co-workers arose from a photodissociated deoxymyoglobin component. Our spectra support such a view.

In the present Raman studies of LbCO, spectra were obtained with excitation at different wavelengths. The quality of the spectra varied markedly and provided some insight into the excitation wavelength dependence of photodissociation. The spectrum in Figure 1 was obtained with 45 mW from a tightly focused laser beam (413.1 nm). To obtain spectra without significant photodissociation using 457.9- and 441.6-nm excitation (Figure 2) it was necessary to defocus the laser beam as well as to use lower powers. The plasma lines in the spectra are an unfortunate

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(13) Raman spectra were obtained by using the apparatus described in ref 4. Experimental conditions are described in the figure captions. The spectrometer was calibrated with carbon tetrachloride and individual spectra were checked against plasma lines. All peaks are accurate to ±1 cm^{-1}.

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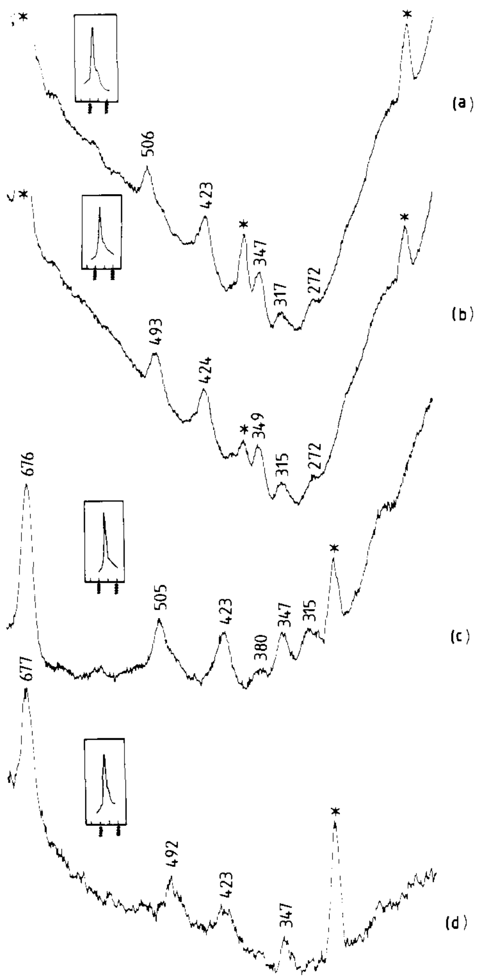

Figure 2. Resonance Raman spectra of CO-leghemoglobin (0.3 mM). (a) $Lb^{12}C^{16}O$—457.9 nm; (b) $Lb^{13}C^{18}O$—457.9 nm; (c) $Lb^{12}C^{16}O$—441.6 nm; (d) $Lb^{13}C^{18}O$—441.6 nm. Typical conditions were 15 (457.9 nm) and 10 mW (441.6 nm) at sample; 0.2-cm^{-1} s^{-1} scan; 5-s time constant; 12-cm^{-1} resolution; 4 scans accumulated. Insets show 1300-cm^{-1} region which was used to monitor extent of photodissociation. A He–Cd laser was used to provide irradiation at 441.6 nm. Asterisk denotes plasma line.

consequence of this defocusing. In Raman spectra of LbCO and MbCO reported earlier using 488.0- and 514.5-nm excitation it was also necessary to defocus the incident beam and to use low laser power (12 mW).[14] It is thus apparent that photodissociation is reduced as excitation is moved into the Soret absorption band. Spectra recorded in this laboratory show that the intensity of the Fe–CO stretch is strong with 413.1-nm irradiation and absent with 514.5-nm irradiation. Thus we conclude that the absorption band which is responsible for resonance enhancement of the ν_{Fe-CO} Raman band is distinct from that which is most favorable for photodissociation.

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Registry No. CO, 630-08-0; Fe, 7439-89-6.

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Lewis Acid Assisted Reaction of *N*-Formylimidazole with a Transition-Metal Complex. Formyl Group Transfer

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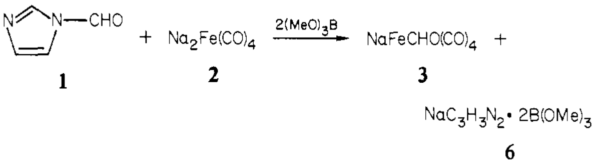
A very common route for syntheses of acyl transition-metal compounds has involved attack of transition-metal nucleophiles on acyl halides. This method has apparently not been used for formyl group transfer reactions because of the thermal instability[1] and/or difficulty of synthesis and handling[2] of formyl halides. To our knowledge, the only example of the synthesis of a stable formylmetal complex via a nucleophilic displacement reaction on an organic X–CHO substrate involved the use of acetic formic anhydride.[3] With few exceptions,[3,4] most preparations of mononuclear formylmetal complexes have utilized hydride attack on carbonyl ligands bound to the metal.[5,6]

In 1962, Staab and Polenski reported the facile synthesis of *N*-formylimidazole (**1**) by treatment of carbonyldiimidazole with formic acid.[7] A search of the subsequent literature has revealed that little chemistry of **1** has been explored although the reactivities of a variety of alkyl and aryl *N*-acylimidazoles toward non-transition-metal nucleophiles have been examined.[8] We describe herein what we believe to be the first study of the reactivities of *N*-acylimidazoles toward a transition-metal nucleophile. In preliminary studies, we have examined the reactivity of **1** toward $Na_2Fe(CO)_4$ (**2**), since the expected product of a nucleophilic displacement, $NaFeCHO(CO)_4$ (**3**), has been characterized and shown to be kinetically stable in solution.[3]

We have found that certain Lewis acids promote the reaction of **1** with **2** to produce formyliron complex **3** in high yields. When mixtures of **1** and triethylboron or trimethoxyboron were treated with **2** in HMPA and THF (1:2 molar ratio = 1) at 25–27 °C, the immediate formation of product mixtures which contained **3** and Lewis acid–imidazole anion adducts were observed (reaction 1).[9] The highest yields of **3**, and a near quantitative overall



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