of C-16 and C-22 double bonds can readily be accomplished under conditions which leave the C-5 double bond untouched.[18] Thus hydrogenation at atmospheric pressure (5% Pt/C, EtOH, or EtOAc) ceased cleanly with the absorption of 2 equiv to give the Δ^5-ester **4c** (78% yield on **3c**)[19], mp 110.5–112 °C; $[\alpha]_D$ −19.0°, NMR 5.52 (m, 1 H, C-6 H), 3.62 (s, 3 H, OMe), 1.06 (s, 3 H, C-19 Me), 0.90 (d, J = 6 Hz, 3 H, C-21 Me), and 0.65 ppm (s, 3 H, C-18 Me).

Note Added in Proof: Since this paper was submitted a similar report using our methodology for the Lewis acid catalyzed ene reaction has appeared.[20]

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(17) Woodward, R. B.; Sondheimer, F.; Taub, D.; Heusler, K.; McLamore, W. M. *J. Am. Chem. Soc.* **1952**, *74*, 4223.

(18) Hershberg, E. B.; Oliveto, E. P.; Gerold, C.; Johnson, L.; *J. Am. Chem. Soc.* **1951**, *73*, 5073.

(19) The structure has been fully secured by single-crystal X-ray analysis, for which we are grateful to Dr. J. F. Blount.

(20) Dauben, W. G.; Brookhart, T. *J. Am. Chem. Soc.* **1981**, *103*, 237.

Laser-Desorption Mass Spectrometry/Mass Spectrometry and the Mechanism of Desorption Ionization

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Two newer aspects of mass spectrometry, desorption ionization and mass spectrometry/mass spectrometry, are subjects of increasing interest for their utility and the chemistry they access. The desorption methods, including field desorption,[1] plasma desorption (fission fragment mass spectrometry),[2] secondary ion mass spectrometry,[3] electrohydrodynamic ionization,[4] and laser desorption[5] have had remarkable success in extending the coverage of mass spectrometry to involatile and thermally labile compounds. Mass spectrometry/mass spectrometry has allowed characteristic spectra to be taken for individual constituents in complex mixtures[6] and is also contributing to our knowledge of ion structures and chemistry.

We now report, for the first time, spectra obtained by combining laser desorption with mass spectrometry/mass spectrometry. Remarkable similarities in fragmentation behavior with secondary ion mass spectra (SIMS) are evident, and this provides evidence for mechanistic similarities[7] between SIMS and laser desorption (LD). Attachment of alkali metals to organic molecules (cationization) is a common feature of desorption ionization while numerous other metals, including Ag, Cu, Pt, Al, Fe, etc., have long been known to cationize organic molecules under conditions of ion bombardment.[8] We now show that this process also occurs during laser desorption of involatile compounds which further indicates the existence of underlying similarities between LD and SIMS.[9] The procedures used here are also noteworthy, because steady ion currents (several thousand ions per laser pulse) of cationized sucrose are obtained for relatively long periods (minutes).

Figure 1 shows the LD mass spectrum of sucrose supported on silver foil in the presence of ammonium chloride.[10] Similar spectra, excluding the NH_3-adduct ions, were obtained without ammonium chloride which was added to the sample because of its demonstrated effect in enhancing ionization in SIMS.[12] The laser-desorption spectrum shows cation (Ag^+) attachment to sucrose to yield m/z 451/449 as the dominant high-mass species.[13] The products of glycosidic cleavage with retention of the metal ion (m/z 289/287) and of this cleavage followed by dehydration (m/z 271/269) represent the most abundant fragment ions, although some dehydration of the cationized molecule is also observed. All four ions $(Ag + S)^+$, $(Ag + S{-}H_2O)^+$, $(Ag + G)^+$, and $(Ag + G{-}H_2O)^+$ (S = sucrose, G = glucose) occur in similar relative abundances in the SIMS spectrum (Figure 2) of sucrose supported on silver.[12] Differences of note between the spectra are the ammonia-solvated ions [including $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ seen at lower mass] which occur in the LD spectrum and the inorganic cluster ions (Ag_3^+, Ag_3Cl^+, $Ag_3Cl_2^+$) and the sodium cationized molecule which are observed in SIMS. A preliminary interpretation is that laser desorption at these power densities causes thermal generation of NH_3. It is also apparent that the internal energy of the cationized molecule, $(Ag + S)^+$ is largely independent of the method of ionization.[14]

Figure 3 shows the mass-analyzed ion kinetic energy (MIKE) spectrum or MS/MS spectrum (MS/MS = mass spectrometry/mass spectrometry) for one of the isotopic forms of silver

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(1) (a) Beckey, H. D. "Principles of Field Ionization and Field Desorption Mass Spectrometry"; Pergamon: London, 1977. (b) Schulten, H. R. *Int. J. Mass. Spectrom. Ion Phys.* **1979**, *32*, 97.

(2) (a) MacFarlane, R. D.; Torgeson, D. F. *Science (Washington, DC)* **1976**, *191*, 920. (b) Schueler, B.; Krueger, F. R. *Org. Mass Spectrom.* **1980**, *15*, 295.

(3) (a) Day, R. J.; Unger, S. E.; Cooks, R. G. *Anal. Chem.* **1980**, *52*, 557A. (b) Benninghoven, A.; Sichterman, W. *Org. Mass Spectrom.* **1977**, *12*, 545. (c) Colton, R. J. *J. Vac. Sci. Technol.*, in press.

(4) (a) Stimpson, B. P.; Evans, C. A., Jr. *Biomed. Mass Spectrom.* **1978**, *5*, 52. (b) Lai, S. T. F.; Chan, K. W.; Cook, K. D. *Macromolecules* **1980**, *13*, 953.

(5) (a) Conzemius, R. J.; Capellen, J. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 197. (b) Posthumus, M. A.; Kistemaker, P. G.; Meuzelaar, H. L. C.; Ten Noever de Braw, M. C. *Anal. Chem.* **1978**, *50*, 985. (c) Kaufman, R.; Hillenkamp, F. *Ind. Res./Dev.*, **1979**, *21*, 145. (d) Stoll, R.; Röllgen, F. W. *Org. Mass Spectrom.* **1979**, *14*, 642.

(6) (a) Kruger, T. L.; Litton, J. F.; Kondrat, R. W.; Cooks, R. G. *Anal. Chem.* **1976**, *48*, 2113A. (b) Kondrat, R. W.; Cooks, R. G. *Anal. Chem.* **1978**, *50*, 81A. (c) Yost, R. A.; Enke, C. G. *Anal. Chem.* **1979**, *51*, 1251A. (d) Hunt, D. F.; Shabanowitz, J; Giordani, A. B. *Anal. Chem.* **1980**, *52*, 386. (e) McLafferty, F. W. *Acc. Chem. Res.* **1980**, *13*, 33.

(7) Evidence for such similarities is increasing, compare: Daves, G. D., Jr. *Acc. Chem. Res.* **1979**, *12*, 359. Benninghoven, A., Ed. "Proceedings of Ion Formation From Organic Solids Workshop"; University of Münster: Münster, Germany, Sept 30, 1980; to be published by Springer-Verlag.

(8) (a) Grade, H.; Winograd, N.; Cooks, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 7725. (b) Day, R. J.; Unger, S. E.; Cooks, R. G. *Anal. Chem.* **1980**, *52*, 353.

(9) It is noteworthy that ICR experiments show the attachment of metal ions (including Ag^+) to gas-phase organic molecules on laser irradiation of the metal, see: Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

(10) The laser used was a Quanta-Ray DCR-1A (Mountainview, CA) 1.06 μ with a 10-Hz repetition rate set to deliver ~0.1 J/pulse with a power density at the sample of the order of 10^8 W/cm^2. The laser beam was focused to a 2-mm spot size which intercepted (at 90°) a cylindrical silver foil extension to the standard mass spectrometer solids probe. The mass spectrometer used was a reversed geometry (MIKES) instrument[11] equipped with a chemical ionization source (CI) which was modified to allow the laser beam to pass through the source cavity. All ions observed were a direct result of the laser irradiation since the ionizing filament was left off during these experiments. Mass spectra were recorded by using an analogue electrometer (Kiethley model 640, Cleveland, Oh). This electrometer has a very long inherent time constant (ca 0.5 s) which effectively smoothed the pulsed character of the mass spectra. Mass spectra were acquired by pulsing the laser continuously at 10 Hz and slowly scanning the magnet at ca. 1 amu/s.

(11) Beynon, J. H.; Cooks, R. G.; Amy, J. W.; Baitinger, W. E.; Ridley, T. Y. *Anal. Chem.* **1973**, *45*, 1023A.

(12) Liu, L. K.; Busch, K. L.; Cooks, R. G. *Anal. Chem.*, in press.

(13) Approximately 10^4 ions per pulse compared to $\approx 5 \times 10^5$ ions per pulse for Ag^+ which, with $(Ag + NH_3)^+$ and $(Ag + 2NH_3)^+$, is the dominant lower mass ion.

(14) Compare also: Busch, K. L.; Unger, S. E.; Cooks, R. G. In "Proceedings of Ion Formation From Organic Solids Workshop"; Benninghoven, A., Ed.; Unveristy of Münster: Münster, Germany; to be published by Springer-Verlag.

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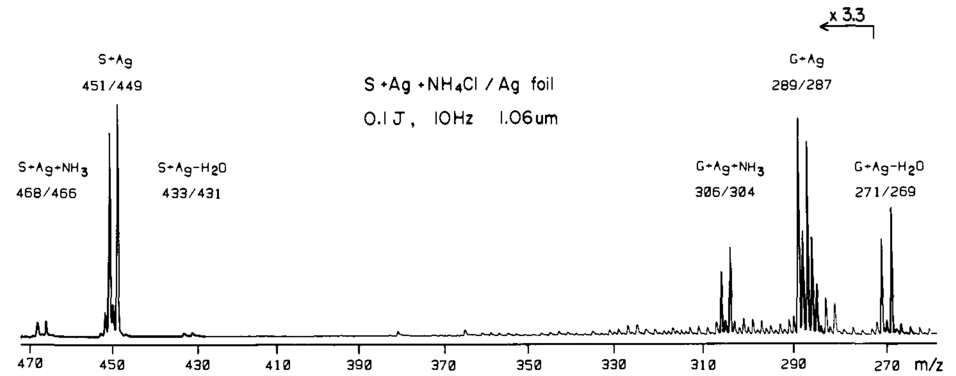

Figure 1. Laser-desorption mass spectrum of sucrose (S), admixed with NH_4Cl and silver powder and supported on silver foil (analog output of a single scan).

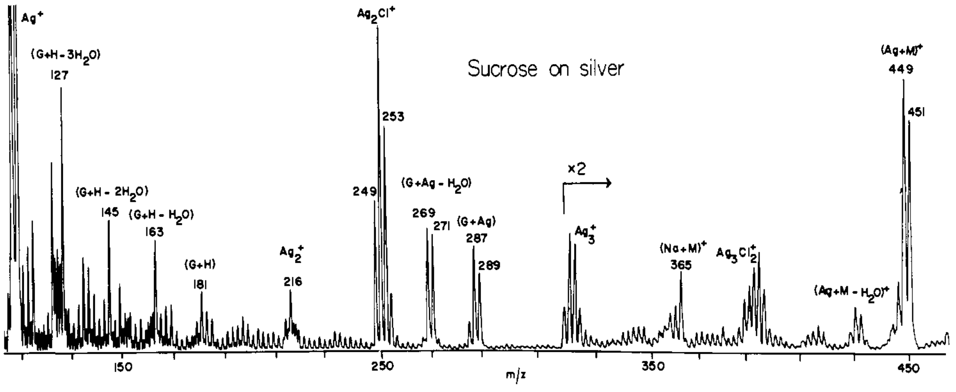

Figure 2. Secondary ion mass spectrum of sucrose, admixed with NH_4Cl and supported on silver foil.

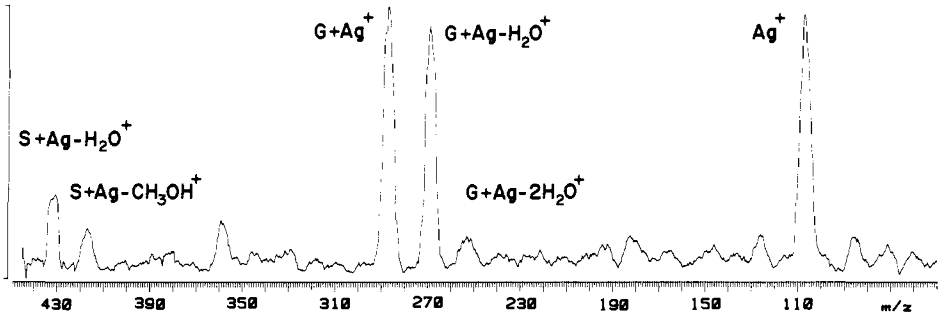

Figure 3. MS/MS spectrum of the $^{107}Ag^+$ adduct of sucrose generated by laser desorption.

cationized molecule, viz. $(^{107}Ag + S)^+$. The spectrum[15] displays the same ions (i) previously postulated to arise as fragments from the cationized molecule in the SIMS spectrum[12] and (ii) seen in the LD mass spectrum (Figure 1). These data provide new evidence which supports the hypothesis that fragments in the mass spectrum arise by unimolecular dissociation of the internally excited silver adduct formed during the SIMS or LD ionization process. This we take as significant further evidence that the cationized molecule undergoes normal unimolecular dissociation in SIMS and so serves as the precursor of lower mass fragment ions. This postulate was previously advanced by comparisons of MIKE spectra of protonated molecules and organic anions with the corresponding positive and negative ion SIMS spectra.[8,16]

A feature of this work is the fact that ion currents were reasonably strong and persisted for many minutes. This contrasts with some earlier observations of rapid loss of signal in laser desorption, which led some to expect that unusual measures might need to be taken to make LD compatible with slow scanning (sector) mass spectrometers.[17] On the other hand, Schmidt and colleagues[18] have shown that pulsed laser irradiation, in combination with surface preparation by mechanical scratching, provides long-lasting ion signals.[19] Ion ejection in our experiments occurred for some 300 μs[20] following a 10-ns laser pulse, with a source pressure of 0.010 torr (presumably due to thermal generation of NH_3 as no CI reagent gas was used).

This communication has emphasized the information provided by the new LDMS/MS combination on the desorption phenomenon. Of even more significance, may be marriage of the analytical capability of mass spectrometry/mass spectrometry with

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(15) MS/MS spectra were obtained by using a pulse-counting detector (Princeton Applied Research Model 1121/1109, Princeton NJ), which is interfaced to a HP2100 computer system used to control the mass spectrometer. The laser was pulsed at 10 Hz for the duration of the data acquisition period, which for Figure 3 was approximately 30 min. During the acquisition period the electric sector voltage was repetitively scanned under computer control, and the resulting MS/MS spectra were ensemble averaged by the computer. The MS/MS spectrum was sampled at 0.5-amu intervals, at a rate of 100 Hz (10-ms counting periods). There was no synchronization of laser pulsing with the 0.5-amu sample intervals. The accumulated spectrum (Figure 3) was further smoothed before plotting by using a single pass with a 5-point moving average smooth.

(16) Unger, S. E.; Day, R. J.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Phys.*, in press.

(17) Cotter, R. J. *Anal. Chem.* **1980**, *52*, 1767.

(18) Heresch, F.; Schmid, E. R.; Huber, J. F., *Anal. Chem.* **1980**, *52*, 1803.

(19) Such scratching of the smooth metal surface, while not always necessary, has long been used as part of sample preparation in molecular SIMS.

(20) This time increased with the source pressure, reaching 1.5 ms at 0.5 torr of isobutane.

the convenient and powerful procedure of laser desorption.

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Formate Ion as a Monodentate Ligand. Synthesis, Structure, and Decarboxylation of (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH

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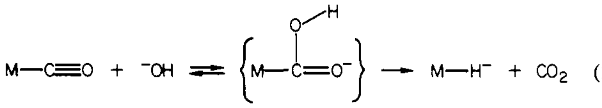
There has been considerable current interest in the homogeneous catalysis of the water–gas shift reaction (eq 1) by transition-metal

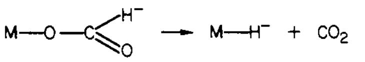
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

carbonyl complexes.[1] Several of the catalytically active systems involve mono- or multinuclear metal carbonyls in alkaline solutions. A common mechanistic feature in all such processes consists of the nucleophilic addition of hydroxide ion at the carbon center of the metal-bound carbon monoxide ligand with subsequent formation of a metal hydride species and CO_2 (eq 2). It is of



$$M{-}C{\equiv}O + {}^{-}OH \rightleftharpoons \left\{M{-}\overset{\overset{\displaystyle O{-}H}{|}}{C}{=}O^{-}\right\} \longrightarrow M{-}H^{-} + CO_2 \qquad (2)$$

importance to appraise the role of metal formate species in these reactions because of the ubiquitous nature of the formate ion in these alkaline solutions ($CO + {}^{-}OH \rightleftharpoons HCO_2^{-}$) and the known ability of metal formates to undergo decarboxylation to metal hydrides and CO_2 (eq 3).[2] Hence there are potentially two



$$M{-}O{-}C\overset{H^{-}}{\underset{O}{\lessgtr}} \longrightarrow M{-}H^{-} + CO_2 \qquad (3)$$

intermediates,[3] a metallocarboxylic acid and a metalloformate, capable of affording H_2 and CO_2 during base catalysis of the water–gas shift reaction. We have recently begun rather extensive reactivity studies on metal carbonyl species possessing the M–COOH and M–O_2CH functionalities and herein report some preliminary observations with (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH. This is a judicious species to investigate, since the metallocarboxylic acid analogue, (η^5-C_5H_5)Fe(CO)$_2$COOH, has briefly been described by Crice, Kao, and Pettit.[4]

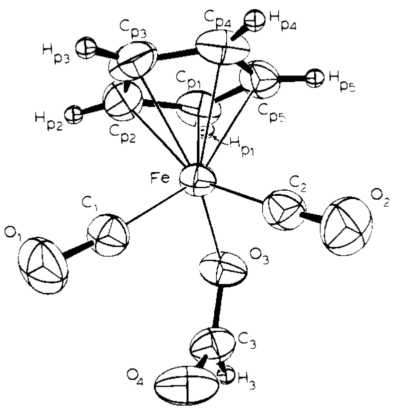


Figure 1. A perspective drawing of (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH. Some bond lengths are as follows: Fe–O(3), 1.957 (2); Fe–C(1), 1.781 (3); Fe–C(2), 1.784 (3); O(1)–C(1), 1.135 (3); O(2)–C(2), 1.133 (4); O(3)–C(3), 1.277 (3); O(4)–C(3), 1.208 (4); C(3)–H(3), 1.03 (3); Fe–Cp(av), 2.096 (3) Å. The distal Fe–O(4) distance is 3.172 (2) Å. All hydrogen atoms were located and refined.

The synthesis of (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH was achieved by stirring (η^5-C_5H_5)Fe(CO)$_2$(THF)$^{+}$[5] with an aqueous solution of NaO$_2$CH for 2.5 h at room temperature under nitrogen. Upon removal of water the residue was extracted with methylene chloride, filtered through Celite, and concentrated under vacuum. Addition of hexane with cooling afforded red crystals of the desired product.[6] The ν(CO) spectrum in heptane exhibited two bands of comparable intensity at 2055 and 2016 cm^{-1}. The infrared spectrum in the $\nu(CO_2)$ region is indicative of monodentate metal formate species, consisting of a strong antisymmetric $\nu(CO_2)$ vibration at 1620 cm^{-1} and a somewhat weaker symmetrical $\nu(CO_2)$ at 1293 cm^{-1}.[7] The detailed geometry of the complex has been established by X-ray crystallography.[8] The structural results are shown in Figure 1. The complex has approximate C_s symmetry with the mirror plane containing the atoms of the formate moiety and the C_{p_1} carbon atom of the cyclopentadienyl ligand and bisecting the OC–Fe–CO angle. The monodentate formate ligand is oriented in the solid state so as to place its uncoordinated oxygen atom [O(4)] in the proximity of the metal center which concomitantly maximizes the Fe–H(3) nonbonding distance. This observation may be of importance when considering intimate mechanistic aspects of the decarboxylation process (vide infra). Similar orientations for the acetate and trifluoroacetate groups are seen in low-valent metal carbonyl derivatives possessing these moieties.[9]

When (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH is placed in a ^{13}CO-saturated heptane solution, a facile intermolecular CO exchange process is noted (eq 4). Infrared spectral traces in the ν(CO) region

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH + n\,^{13}CO \rightleftharpoons (\eta^5\text{-}C_5H_5)Fe(CO)_{2-n}(^{13}CO)_nO_2CH + nCO \qquad (4)$$

observed during the course of this ligand exchange reaction are depicted in Figure 2. As seen in Figure 2, upon replacement of the ^{13}CO atmosphere with ^{12}CO, bands due to the all-^{12}CO (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH reappear with an attendant decrease in bands assignable to the ^{13}CO-enriched species. Hence, metal–

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(1) (a) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 252. (b) Cheng, C. H.; Hendriksen, D. E.; Eisenberg, R. *Ibid.* **1977**, *99*, 2791. (c) Kang, H.; Mauldin, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *Ibid.* **1977**, *99*, 8323. (d) King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D. *Ibid.* **1978**, *100*, 2925. (e) Darensbourg, D. J.; Darensbourg, M. Y.; Burch, R. R., Jr.; Froelich, J. A.; Incorvia, M. J. *Adv. Chem. Ser.* **1979**, *No. 173*, 106. (f) Frazier, C. C.; Hanes, R.; King, A. D.; King, R. B. *Ibid.* **1979**, *No. 173*, 94. (g) Pettit, R.; Cann, K.; Cole, T.; Maudlin, C. H.; Slegeir, W. *Ibid.* **1979**, *No. 173*, 121. (h) Singleton, T. C.; Park, L. J.; Price, J. C.; Forster, D. *Prepr. Div. Pet. Chem., Am. Chem. Soc.* **1979**, *24*, 329. (i) Laine, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 6451. (j) Baker, E. C.; Hendriksen, D. E.; Eisenberg, R. *Ibid.* **1980**, *102*, 1020. (k) King, A. D.; King, R. B.; Yang, D. B. *Ibid.* **1980**, *102*, 1028. (l) Ungermann, C.; Landis, V.; Moya, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Rinker, R. G.; Ford, P. C. *Ibid.* **1979**, *101*, 5922.

(2) See, e.g., the review by: Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79.

(3) Additionally, bidentate formate species are known to undergo this decarboxylation process. See, e.g., the review by: Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev.* **1978**, *47*, 334.

(4) Crice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

(5) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153.

(6) An alternative preparation of the complex has been previously reported by: Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

(7) In unidentate complexes the separation between the two $\nu(CO_2)$ vibrations is larger than that in the free ion [where $\Delta\nu(CO_2)$ = 200 cm^{-1}], whereas the opposite trend is seen in bidentate complexes. See, e.g.: Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1977.

(8) Single crystals of (η^5-C_5H_5)Fe(CO)$_2$O$_2$CH were grown from CH$_2$Cl$_2$/hexane. They belong to the space group $P2_1/n$ with a = 6.799 (2), b = 12.325 (4), c = 10.440 (3) Å; β = 106.84 (2)°; Z = 4. R = 2.9% for 1782 reflections with $I > 3\sigma(I)$. Crystallographic analysis was carried out by Dr. Cynthia S. Day at Crystalytics Co., Lincoln, NE.

(9) (a) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398. (b) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.*, in press.

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