(>98%) crude alcohol **7** which was converted to the corresponding trimethylsilyl ether **8** by treatment with trimethylsilyl chloride–triethylamine for 8 hr at 25° in tetrahydrofuran (90% yield). Epoxidation of **8** with 1 equiv of *m*-chloroperbenzoic acid in methylene chloride at 0° containing sodium bicarbonate as an acid acceptor gave in 80% yield a mixture of **9** and **10** with the desired isomer **9** predominating by 9:1 as determined by nmr signals due to oxirane methyl at 1.21 and 1.24, respectively. The stereoselectivity of the epoxidation process was anticipated on the basis that the most stable conformation of the six-carbon side chain in **8** is as shown (see ref 4a) and the strong steric shielding at one face of the trisubstituted double bond by the silyloxy and bromine ring substituents. Attempted hydrolysis of the silyl ether linkage under the usual conditions in protic solvents (potassium carbonate in methanol; ammonium chloride in tetrahydrofuran–water; ammonium chloride in methanol–water) led to rapid attack on the epoxide ring by the liberated primary hydroxyl group, presumably giving products containing a tetrahydrofuran or tetrahydropyran ring. However, hydrolysis under aprotic conditions (anhydrous tetrabutylammonium fluoride in tetrahydrofuran), followed by cyclization with sodium methoxide, gave a 9:1 mixture of **11** and **12** in high yield (nmr signals due to oxirane methyl at δ 1.29 and 1.35, respectively).[13] Hydroxylation with osmium tetroxide in pyridine gave in 81% yield a 9:1 mixture of **13** and **14**. Chromatographic separation gave pure **13**, mp 103.5–105° (31% from **5**)[11] [found for **13**: ir max ($CHCl_3$) 2.8, 5.72, 9.3 μ; nmr peaks at δ 1.26 (3 H, CH_3), 3.72 (3 H, OCH_3), and 4.1 (2 H, m, H_A and H_B)].[14]

Conversion of diol **13** to the monomethyl ether **15** was accomplished in 47% yield (65% based on recovered starting material) by treatment with 1.3 equiv of sodium *tert*-amylate in tetrahydrofuran followed by addition of excess methyl iodide. Reaction of **15** with excess methyllithium in tetrahydrofuran at −78° gave the dihydroxy diepoxide **16** (*ca.* 75% yield) [found for **16**: ir max ($CHCl_3$) 2.95 and 9.1 μ; nmr peaks at δ 1.27 (3 H, CH_3), 1.30 (6 H, CH_3) 3.52 (3 H, OCH_3), 3.63 (1 H, d of d, J_{AC} = 11 Hz, J_{AB} = 2 Hz, H_A), and 4.4 (1 H, br, H_B)], which was acetylated to afford the monoacetate **17** (95% yield) by treatment with pyridine–acetic anhydride for 24 hr at 50° [found for **17**: ir max ($CHCl_3$) 2.9, 5.72, 8.05 μ; nmr peaks at δ 1.28 (9 H, CH_3), 2.07 (3 H, CH_3), 3.40 (3 H, OCH_3), 3.58 (1 H, d of d, J_{AC} = 11 Hz, J_{AB} = 2 Hz, H_A), 5.55 (1 H, br, H_B)]. Dehydration of the alcohol **17** was effected by mesylation with mesyl chloride–triethylamine in tetrahydrofuran for 30 min at −15°[15] followed by elimination promoted by the addition of 1 equiv of tetrabutylammonium bromide in tetrahydrofuran (stirring for 3 hr at 25°) to give fumagillyl acetate as the major product and the isomer **18** as a minor product (ratio 3:1, respectively). The position selectivity in the elimination of **17** appears to be considerably less than reported[16] for a similar case (selectivity 9:1) under the same conditions. Saponification of this mixture of acetates with anhydrous potassium carbonate in methanol gave (±)-fumagillol (**2**) and its isomer **19** as a mixture which was inseparable by tlc. Separation was achieved by high-pressure liquid chromatography using a Waters Associates ALC-202 instrument (using silica gel with 4:1 methylene chloride–acetonitrile as solvent), giving pure (±)-fumagillol, mp 111–113°, identical with natural fumagillol by tlc, ir, nmr, and mass spectral comparison. This was converted to (±)-fumagillin (identical with natural material by tlc and infrared comparison) as described above.[17]

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(13) The use of fluoride ion in this process was suggested by the high value of the Si–F bond energy (*ca.* 135 kcal/mol); see also, C. S. Kraihanzel and J. E. Poist, *J. Organometal. Chem.*, **8**, 239 (1967).

(14) In the nmr spectrum of **13** (and also compounds **15–17** and **1**) the half band widths of the four peaks due to the CH_2 of the spirooxirane ring were approximately the same as expected for equatorial orientation of that CH_2 [see L. J. T. Andrews, J. M. Coxon, and M. P. Hartshorn, *J. Org. Chem.*, **34**, 1126 (1969)].

(15) R. K. Crossland and K. L. Servis, *ibid.*, **35**, 3195 (1970).

(16) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 4735 (1971).

(17) This research was assisted financially by the National Institutes of Health and the National Science Foundation.

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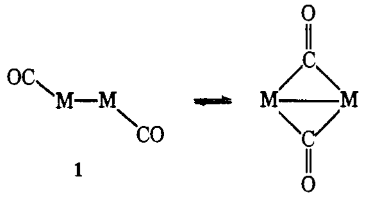
Temperature-Dependent Carbon-13 Nuclear Magnetic Resonance Spectra of the h^5-Cyclopentadienyliron Dicarbonyl Dimer, an Application of a Shiftless Relaxation Reagent

Sir:

Applications of Fourier transform (FT)[1] methods to obtain carbon-13 nmr (cmr) spectra of metal carbonyls have as yet remained largely unexploited.[2] The reason underlying this state of affairs is that metal-bonded carbonyls have long T_1 relaxation times. Consequently, small flip angles and long pauses between successive pulses in the FT experiment are required to obtain a free induction decay. If small amounts of kinetically inert, paramagnetic metal complexes with a totally symmetric ground state such as tris(acetylacetonato)-chromium(III) are added to solutions of metal carbonyls, T_1 relaxation times are drastically reduced, absolutely no contact chemical shift is detected within ±0.1 ppm, and little line broadening is observed for $Cr(acac)_3$ concentrations less that 0.10 *M*.

The utility of this shiftless relaxation reagent is demonstrated by cmr studies of $[(h^5\text{-}C_5H_5)Fe(CO)_2]$ (I) and $Fe_3(CO)_{12}$ (II). These studies prove that at least the first of these molecules undergoes bridged–nonbridged structure interconversions of the kind **1** ⇄ **2** and is therefore a member of a newly found important class of stereochemically nonrigid molecules as suggested by Cotton and coworkers.[3]



1 **2**

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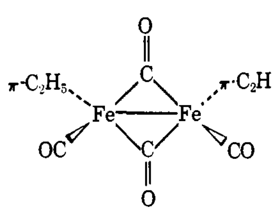
(1) R. E. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **37**, 93 (1966).

(2) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971). A few chemical shifts are reported therein, but no experimental details are given.

(3) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970).

Two different isomeric forms (**3** and **4**) of I in the solid state have been defined by X-ray crystal-structure determinations.[4,5] The trans form **4** crystallizes at ambient laboratory temperatures while the cis form **3** may be obtained only by precipitation from polar solvents like CH_2Cl_2 at *ca.* $-80°$. Investigations of both solution and solid-state Raman and infrared (ir) spectra[6–11] together with dipole moment[12] measurements first predicted the presence of **4** and **5** in solution but similar measurements for a number of analogous [(π-dienyl)Fe$(CO)_2$] compounds led Manning[13] to hypothesize the presence in solution of the nonbridged structure **3**. A recent variable-temperature proton nmr (pmr) investigation of I in solution detected one signal due to the rapid equilibration of two h^5-C_5H_5 resonances above $-40°$ which broadened and separated at $-70°$ into two resonances not necessarily of equal intensity[3] depending on solvent polarity, with, presumably, the cis downfield resonance being favored as CH_2Cl_2 was added to the CS_2 toluene solvent used for pmr studies. We now report cmr spectra which evidence *both cis–trans and intramolecular bridging–terminal carbonyl interconversions.*



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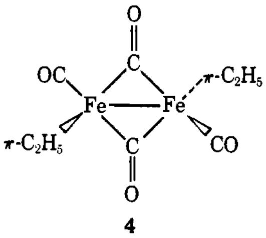

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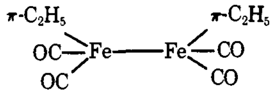

5

All cmr spectra of 75% CH_2Cl_2–25% 1,2-dibromotetrafluoroethane (for ^{19}F lock) solutions 0.2 *M* in **1** with 2% (v/v) CS_2 (chemical-shift reference) and 0.1 *M* [$Cr(acac)_3$] added were measured using a Bruker HFX-10 nmr system, the details of which have been presented elsewhere.[14] Varying dimer or $Cr(acac)_3$ concentration did not affect chemical shifts or temperature dependence of the spectra.[1]

At ambient probe temperatures, for the dimer, one broad carbonyl resonance is observed at 50.2 ppm downfield from CS_2 and one more intense cyclopentadiene resonance is detected at 106.7 ppm upfield. As the temperature is raised, both signals become quite sharp. However, as the temperature is lowered, the carbonyl and cyclopentadiene resonances behave differently. The cyclopentadiene signal behaves quite like the proton h^5-C_5H_5 resonance observed by Cotton, *et al.*[3] We take this as being further evidence of the cis ↔ trans equilibrium.

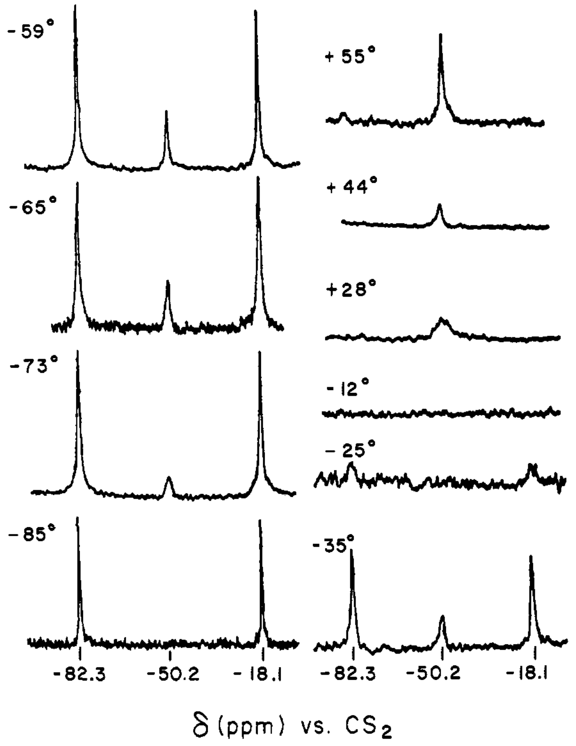

Figure 1. Temperature-dependent ^{13}C nmr spectra of the carbonyls in $[h^5$-$C_5H_5Fe(CO)_2]_2$.

The temperature variation of the carbonyl resonances is illustrated in Figure 1. Below $-90°$, two discrete resonances are detected, the one at -18.1 ppm within 0.1 ppm of the $Fe(CO)_5$ chemical shift, the other at -82.3 ppm, a separation of 1450 Hz. When solution temperature is raised to $-73°$ a broad resonance is observed precisely midway between the two low-temperature forms. This resonance sharpens to maximum height at $-59°$. Concurrently, the two low-temperature signals broaden only a little. Between -59 and $-25°$ all three resonances broaden severely. At $-12°$, no signals are seen, but as temperature is raised further, one signal is detected at -50.2 ppm precisely midway between the two low-temperature limit signals.

An interpretation which is fully consistent with the pmr and cmr observation can be given as follows. (a) Both cis–trans interconversion and intramolecular exchange are occurring above *ca.* $-35°$. This interconversion at 55° averages both the CO and C_5H_5 signals. (b) The cis and trans forms both interconvert bridging and terminal carbonyls but with different activation energies. At the low-temperature limit, no interconversion occurs, but the present resolution (± 0.6 ppm) precludes resolution of separate signals. As the temperature is raised, the trans form (less favored in CH_2Cl_2) undergoes intramolecular interconversion but the cis form remains intact. The averaging of bridging (δ -83.2) and terminal (δ -18.2) cmr signals gives rise to a new resonance at -50.2 ppm which is broad at first detection ($-73°$), but becomes sharp at $-59°$. At $-35°$ the cis form may begin intramolecular conversion

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(4) O. S. Mills, *Acta Crystallogr.*, **11**, 620 (1968).

(5) R. F. Bryan, P. T. Greene, D. S. Field, and M. J. Newlands, *Chem. Commun.*, 1477 (1969).

(6) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(7) F. A. Cotton, A. D. Liehr, and G. Wilkinson, *ibid.*, **1**, 175 (1955).

(8) F. A. Cotton, H. Stammreich, and G. Wilkinson, *ibid.*, **9**, 3 (1959).

(9) K. Noack, *ibid.*, **25**, 1383 (1963).

(10) R. D. Fisher, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967); K. Noack, *ibid.*, **7**, 151 (1957).

(11) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).

(12) E. Weiss, H. Hubel, and R. Merenyi, *Chem. Ber.*, **95**, 1155 (1962).

(13) A. R. Manning, *J. Chem. Soc. A*, 1319 (1968); A. R. Manning and P. A. McArdle, *ibid.*, *A*, 1498 (1969).

(14) O. A. Gansow, A. R. Burke, and J. Killough, *J. Amer. Chem. Soc.*, **93**, 4297 (1971).

or may simply begin to participate in the cis–trans equilibration which dominates the cmr and pmr spectra at temperatures above −25°. The large 1450-Hz spectral range over which the resonances are spread causes no signals to be seen at −12°.

We find no other cmr signals which might correspond to the intermediate **5**. A recent cmr study[15] of over 20 $(h^5\text{-}C_5H_5)Fe(CO)_2X$ derivatives, where X represents a wide variety of substituents, showed that all CO resonances lie within 7.2 ppm of $Fe(CO)_5$, thus assuring that the signal at −50.2 ppm is not from **5**.

Studies of $Fe_3(CO)_{12}$ by cmr have been limited by solubility to a −10 to 50° temperature range. Only one sharp resonance is measured at −20.1 ppm *vs.* CS_2, whereas the crystal structure[16] has both bridging and terminal carbonyls, indicating that this molecule is either a triangle of iron atoms with each iron being bonded to four carbonyls or a fluxional molecule undergoing some sort of bridging-terminal CO interconversion of the type discussed above. Our research group has also obtained spectra at −110° for $Fe(CO)_5$, $[(C_6H_5)_3P]Fe(CO)_4$, and (norbornadiene)$Fe(CO)_3$. No structural interconversion was observed.

We are presently undertaking solvent dependent cmr studies of **1** as well as preparing the ^{13}C enriched dimer and $Fe_3(CO)_{12}$.

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[15] O. A. Gansow, D. A. Schexnayder, and B. Y. Kimura, *J. Amer. Chem. Soc.*, in press.

[16] C. H. Wei and L. F. Dahl, *ibid.*, **91**, 1351 (1969).

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Structure of Uranium Borohydride by Single-Crystal X-Ray Diffraction

Sir:

In conjunction with optical, vibrational, and magnetic resonance studies of metal tetrahydroborate complexes currently in progress in our laboratories, the need for detailed structural information about $M(BH_4)_4$ compounds (M = Zr, Hf, Th, U)[1] became apparent. Although X-ray diffraction results are available for $Zr(BH_4)_4$ at −160°, the exact positions of the bridging hydrogen atoms were not elucidated.[2] Thus neutron diffraction work appeared necessary to resolve this point and a program to study $M(BH_4)_4$ molecules using this technique was set up.[3] To prepare for these studies, the single-crystal X-ray structure of uranium borohydride was determined. The results are sufficiently interesting that, although lacking information about the hydrogen atom positions and subject to refinement following the neutron investigation, preliminary communication seems warranted.

Uranium borohydride, $U(BH_4)_4$, was synthesized from uranium tetrafluoride and aluminum borohydride according to the method of Schlessinger and Brown.[4] Dark green crystals suitable for X-ray diffraction were grown by vacuum sublimation and sealed in capillaries under nitrogen. An irregular plate of approximate dimensions 0.07 × 0.20 × 0.25 mm was used for data collection. Precession photographs revealed the Laue symmetry to be tetragonal, $4/mmm$, with the extinctions $h00$, $h \neq 2n$, and $00l$, $l \neq 4n$, consistent with the enantiomorphic pair of space groups $P4_12_12$ (No. 92) and $P4_32_12$ (No. 96).[5] The unit cell parameters are $a = 7.49 \pm 0.01$ Å and $c = 13.24 \pm 0.01$ Å, and assuming four formula weights per unit cell the calculated density of 2.66 g cm^{-3} seems reasonable.[6] A total of 560 independent *hkl* reflections[9] was collected by diffractometer using Mo Kα radiation at 20°. The data were corrected for background, Lorentz, polarization, and absorption ($\mu = 207.9$ cm^{-1}) effects. The structure was initially solved for the positions of the uranium and one boron atom from a three-dimensional Patterson map in space group $P4_12_12$.[9] The uranium atom occupies special position (4a) of site symmetry 2. A difference Fourier synthesis clearly revealed the position of the other crystallographically independent boron atom. Least-squares refinement of the atomic coordinates, anisotropic uranium atom thermal parameters, and isotropic boron thermal parameters converged at a value of 0.040 for the discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ based on 493 data points for which $I_{obsd} > 3\sigma(I_{obsd})$ and 14 variable parameters. The results are summarized in Table I and Figures 1 and 2.[11]

From Figure 1 it is readily apparent that the structure of uranium borohydride is polymeric, consisting of interlocking helical chains in which individual units are related by a fourfold screw axis. There are six tetrahydroborate groups associated with each uranium atom,

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[1] For a recent review of this class of compounds, see B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, **11**, 99 (1970).

[2] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967).

[3] Neutron diffraction studies are being carried out at the Brookhaven National Laboratories in collaboration with W. C. Hamilton and S. J. LaPlaca on uranium borohydride, and with the additional collaboration of W. J. Kennelly and T. J. Marks on hafnium borohydride.

[4] H. I. Schlessinger and H. C. Brown, *J. Amer. Chem. Soc.*, **75**, 219 (1953).

[5] "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, pp 182, 186.

[6] The unit cell of uranium borohydride has been previously investigated by Zachariasen[7] and apparently mistakenly reported to be orthorhombic.[8] The original crystal class and unit cell parameters[7] are consistent with the present results. We thank Dr. Zachariasen for pointing out ref 7 to us.

[7] W. H. Zachariasen, Manhattan Project, Chicago Metallurigal Laboratory, CP 3774, July 1–Dec 1, 1946, p 17.

[8] H. R. Hoekstra and J. J. Katz, U. S. Atomic Energy Commission, AECD 1894, March 1948.

[9] Because of anomalous dispersion effects,[10] $F(hkl) \neq F(khl)$, and both forms of data were included in all calculations reported here. Trial refinements in both space groups (inverting the coordinates through the origin) indicated No. 96 to be the correct one, the final weighted and unweighted residuals being 0.050 and 0.041, respectively, in $P4_12_12$, compared to 0.048 and 0.040 in $P4_32_12$. All results reported here are for refinement in $P4_32_12$, in which the agreement between observed and calculated values of $|F(hkl)| - |F(khl)|$ after the final refinement was superior.

[10] J. A. Ibers, *Acta Crystallogr.*, **22**, 604 (1967), and references cited therein.

[11] A list of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-2552. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.