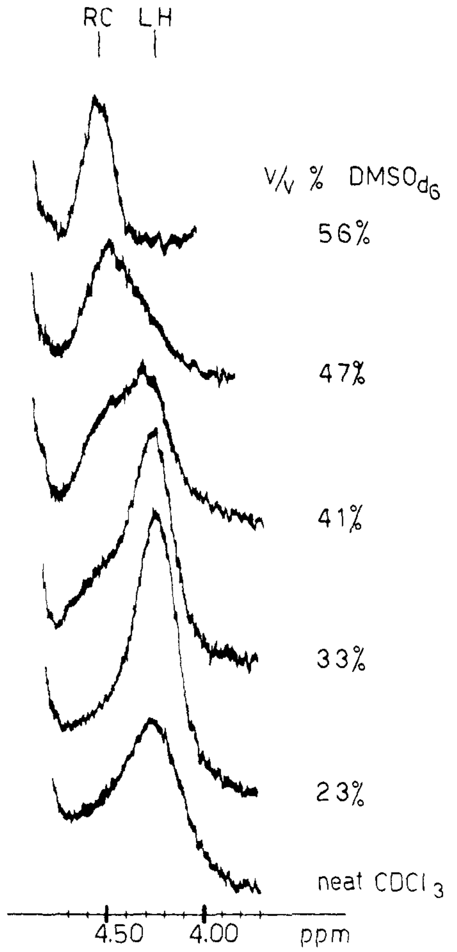


Figure 1. 100-MHz spectra, α-C*H* region, of poly-β-benzyl-L-aspartate in $CDCl_3$–Me_2SO-d_6; RC = random coil, LH = left-handed helix.

weight polypeptide samples the helix–coil transition is manifested in the nmr by the characteristic double-peak α-C*H* and amide N*H* resonances. If the two components of the main-chain doublets are well separated then in the case of the α-CH the up-field resonance may be assigned to helix and the low field to coil on the basis of constancy of total area[4] and a good correlation of peak areas with b_0.[7] The shift difference between the peaks $\Delta_{H/C}$(α-C*H*) is solvent dependent[8] and therefore represents the sum of a solvation effect (which might or might not be a result of protonation) and an intrinsic conformational effect.

Poly-β-benzyl-L-aspartate (PBLA) is random coil in dimethyl sulfoxide (Me_2SO)[9] and addition of chloroform induces transition to the left-handed (LH) helical form. The transition midpoint lies at about 42% Me_2SO-d_6. Figure 1 shows the PBLA α-C*H* spectrum at 100 MHz which is seen to exhibit the characteristic "double-peak" phenomenon. The LH helix shift is 4.30 ppm (with respect to internal TMS) as previously reported[10] and the coil shift in 56% Me_2SO-d_6 (and in pure Me_2SO-d_6) is 4.64 ppm. When TFA is used as the random coil inducing solvent, the coil shift in $CDCl_3$–5% TFA is 4.80 ppm.[8] This difference of 0.16 ppm in the coil shifts illustrates the importance of solvation in the α-C*H* helix–coil shift difference $\Delta_{H/C}$(α-CH).

Now Me_2SO-d_6, which in this experiment simply replaces TFA as the coil-inducing solvent, is not acidic and has no exchangeable protons. In the presence of fairly strong acids it even acts as a weak Lewis base. There can therefore be no protonation at all of the amide groups by Me_2SO-d_6 and it follows that protonation is not essential either for inducing the helix to coil transition or for the observation of different and characteristic helix and coil shifts for the main chain protons in the spectra of polypeptides.

PBLA is an atypical polypeptide in that it forms LH helices in chloroform. We have obtained similar results to the above using right-handed poly-γ-benzyl-L-glutamate (PBLG) samples of several molecular weights and also a number of PBLG–PBLA copolymers. The conclusions therefore appear general for this solvent system. An account of the complete series of studies will appear elsewhere.

Acknowledgment. E. M. Bradbury and C. Crane-Robinson are grateful to the CNR of Italy for fellowships during the tenure of which this work was carried out.

E. M. Bradbury,* C. Crane-Robinson
Biophysics Laboratories, Physics Department
Portsmouth Polytechnic, Portsmouth PO1 2DZ, England

L. Paolillo, P. Temussi
Laboratorio per la Chimica e Fisica di Molecole
di Interesse Biologico del C.N.R.
Arco Felice, Naples, Italy

Received October 21, 1972

---

(7) E. M. Bradbury, C. Crane-Robinson, H. Goldman, and H. W. E. Rattle, *Nature (London)*, **217**, 812 (1968).

(8) E. M. Bradbury, B. G. Carpenter, C. Crane-Robinson, and H. W. E. Rattle, *ibid.*, **220**, 69 (1968).

(9) E. M. Bradbury, C. Crane-Robinson, V. Giancotti, and R. M. Stephens, *Polymer*, **13**, 33 (1972).

(10) E. M. Bradbury, B. G. Carpenter, C. Crane-Robinson, and H. Goldman, *Macromolecules*, **4**, 557 (1971).

Characterization and X-Ray Structure of $(Me_3SiOC)_4Fe_2(CO)_6$

Sir:

An unusual product assigned the dimeric formula $[(Me_3Si)_2Fe(CO)_4]_2$ has been obtained from the reaction of Me_3SiI with $Na_2Fe(CO)_4$ in tetrahydrofuran.[1,2] An interesting structure based on an Fe_2C_2 tetrahedron was proposed,[1,2] and it appeared that the reaction provided a further example of the sometimes unexpected course of reactions between organosilicon halides and metal carbonyl anions.

An anomalous feature of the reported $(Me_3Si)_4Fe_2(CO)_8$ compound was the observation in its mass spectrum of peaks due to $[(Me_3Si)_4Fe_2(CO)_9]^+$ and $[(Me_3Si)_4Fe_2(CO)_{10}]^+$ in greater abundance than those of the presumed molecular ion. The earlier assignment[2] of these peaks as (P + CO) and (P + 2CO) seemed improbable,[3] and we considered it more likely that the

---

(1) M. A. Nasta and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **93**, 2813 (1971).

(2) M. A. Nasta and A. G. MacDiarmid, *ibid.*, **94**, 2449 (1972).

(3) The only other report known to us of a "(P + 2CO)" peak in a metal carbonyl molecule is by D. S. Fields and M. J. Newlands, *J. Organometal. Chem.*, **27**, 213 (1971), for the compound $C_6H_5(OC)_2FeSnCl_2C_6H_5$. This report is incorrect. The mass spectrum of a sample of this compound prepared several years ago in our laboratory (by Dr. J. K. Hoyano) showed the parent peak at *m/e* 444 with higher peaks at 460, 480, 508, and 536, none corresponding to (P + CO) or (P + 2CO). We attribute these peaks to impurities or to thermal decomposition during measurement.

correct molecular formula was $(Me_3Si)_4Fe_2(CO)_{10}$.[4] The crystal structure of the molecule reported here verifies that ten CO groups are indeed present and thus vindicates the useful principle that the peak of largest *m/e* in the mass spectrum of a metal carbonyl derivative normally gives the *minimum* number of carbonyl groups present.[5,6]

A sample of the compound in question was prepared by the procedure of Nasta and MacDiarmid,[2] except that Me_3SiBr was used instead of Me_3SiI. The infrared and mass spectra of the yellow product were in excellent agreement with those reported.[1,2] A crystal suitable for crystallographic study was obtained by sublimation in an evacuated sealed tube.

The compound crystallizes in the triclinic system with lattice parameters a = 11.535 (6), b = 12.288 (6), and c = 12.543 (6) Å; α = 72.01 (3), β = 87.31 (4), and γ = 88.08 (4)°; and an observed density of 1.32 g ml^{-1} which favors two formula units of $(Me_3Si)_4Fe_2(CO)_{10}$ per unit cell (ρ_{calcd} 1.34 g ml^{-1}) rather than $(Me_3Si)_4Fe_2(CO)_8$ (ρ_{calcd} 1.23 g ml^{-1}). The space group $P\bar{1}$ was indicated by the statistical distribution of $|E|$'s and was assumed for subsequent calculations. The structure has been solved with conventional heavy-atom techniques using 1486 statistically reliable reflections which were measured on an automated Picker diffractometer using Mo Kα X radiation. The structure was refined to a conventional R value of 0.085. The rather high R value, at the present stage of refinement, reflects (1) difficulty with crystal decomposition and (2) inadequacy of the thermal models for the peripheral atoms.

The molecular structure, which is shown in Figure 1,[7] confirms the reformulation as $Fe_2Si_4C_{22}H_{36}O_{10}$ and is entirely consistent with all spectroscopic data. The molecule contains a substituted butadiene fragment bonded to one $Fe(CO)_3$ group with two σ bonds to form an iron-containing heterocyclic diene. This five-membered ring is π bonded to a second $Fe(CO)_3$ group and an iron–iron bond (2.50 Å) completes the linkage between two nonequivalent $Fe(CO)_3$ groups. Each carbon atom of the FeC_4 ring has a trimethylsiloxy substituent and appears to have been derived from a carbonyl group. That all four trimethylsilyl groups are attached to oxygen is unexpected, in that only two are cleaved by anhydrous HCl.[1,2] The compound is an analog of $(CO)_6Fe_2C_4(OH)_2(CH_3)_2$ whose synthesis[8] and structure[9] have been reported, but in this case only two of the carbon atoms of the FeC_4 ring are derived from carbonyl groups. The mechanism of the overall reaction is not clear but poses an interesting question as to whether the silicon is directly attacked by carbonyl oxygen or migrates there after initial formation of an iron–silicon bond.

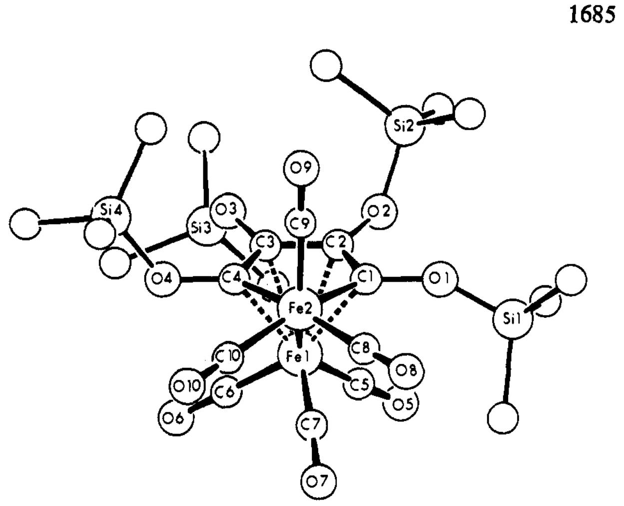


Figure 1. The molecular structure of $(Me_3SiOC)_4Fe_2(CO)_6$.[7] Selected bond lengths (Å) are Fe1–Fe2 = 2.500 (3); average Fe1–CO = 1.72 (2); average Fe2–CO = 1.83 (2); average Fe1–C1,C4 = 2.13 (2); average Fe1–C2,C3 = 2.19 (2); average Fe2–C1,C4 = 1.92 (2); average C(1–4)–O(1–4) = 1.39 (3); average O(1–4)–Si(1–4) = 1.66 (2); average Si(1–4)–CH_3 = 1.86 (2). Selected bond angles are C1–O1–Si1 = 146 (1); C2–O2–Si2 = 124 (1)°; C3–O3–Si3 = 138 (1)°; C4–O4–Si4 = 127 (1)°.

The geometry of the $Fe(CO)_3C_4Fe(CO)_3$ portion of the molecule shows excellent agreement with that reported by Hock and Mills,[9] and the more interesting details of the structure concern the siloxy side chains. These substituent groups are arranged in a manner that minimizes intramolecular repulsions, with each C_{ring}–O–Si plane approximately perpendicular to the FeC_4 plane (deviations 3, 3, 17, and 3°), and with silicon atoms alternately up and down with respect to the FeC_4 plane. With this particular arrangement the variations in the geometry of the siloxy side chains reflect intermolecular forces. The large range of C_{ring}–O–Si angles (124–146°) as a result of these rather weak forces is in accord with the concept of a "soft" angle at oxygen as suggested by spectroscopic[10] and structural studies.[11] This result strongly suggests that solid-state structures of siloxy derivatives are of negligible utility in attempts to correlate the angles at oxygen with such effects as d_π–p_π bonding. Such attempts should be based on gas-[12] or liquid-phase studies.

The original report of the Me_3SiI–$Na_2Fe(CO)_4$ reaction[1] was accompanied by the suggestion that complexes $(OC)_4Fe(MR_3)_2$ and $(OC)_4Fe(H)SiR_3$ (M = Si, Ge, Sn, Pb; R = organic group or halogen) prepared in this laboratory[13] and elsewhere may have been incorrectly formulated as monomeric and octahedral. We strongly reject this suggestion insofar as our own results are concerned on the basis of mass spectrometric results and X-ray crystallographic results,[14] including the structure of $(OC)_4Fe(H)SiPh_3$.[15]

(4) The reported analytical results,[1,2] while favoring the $(CO)_8$ formulation, are not inconsistent with ten carbonyl groups.

(5) Cases are known where the mass spectrum shows *fewer* than the full number of carbonyl groups in the molecule, *e.g.*, $RSn[Co(CO)_4]_3$.[6]

(6) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 2222 (1966).

(7) Atom coordinates for $(Me_3SiOC)_4Fe_2(CO)_6$ 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-73-1684. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(8) R. Clarkson, E. R. H. Jones, P. C. Wailes, and M. C. Whiting, *J. Amer. Chem. Soc.*, **78**, 6206 (1956).

(9) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961).

(10) J. R. Aronson, R. C. Lord, and D. W. Robinson, *J. Chem. Phys.*, **33**, 1004 (1960).

(11) W. L. Roth and D. Harker, *Acta Crystallogr.*, **1**, 34 (1948).

(12) W. Airey, C. Glidewell, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, **8**, 413 (1971), and references there cited.

(13) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967); R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 1208 (1968); W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969); *Inorg. Chem.*, **10**, 4 (1971).

(14) R. Ball and M. J. Bennett, *ibid.*, **11**, 1806 (1972).

(15) M. J. Bennett and K. Simpson, to be submitted for publication.

Acknowledgment. We thank Dr. A. S. Foust for preliminary photographic X-ray work, the Killam Fund for a postdoctoral fellowship to R. P. S., and the National Research Council of Canada for financial support.

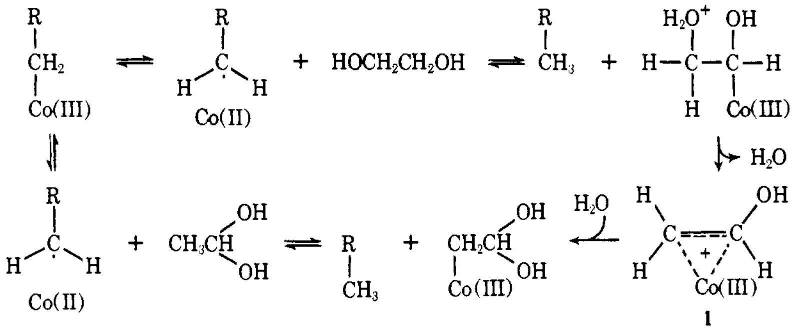
M. J. Bennett, W. A. G. Graham,* R. A. Smith, R. P. Stewart, Jr.
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada
Received November 30, 1972

A Direct Method for Cobalt–Carbon Bond Formation in Cobalt(III)-Containing Cobalamins and Cobaloximes. Further Support for Cobalt(III) π Complexes in Coenzyme B_{12} Dependent Rearrangements

Sir:

The mechanism of action of coenzyme B_{12} dependent enzymes has been shown to involve a net substrate rearrangement in which a hydrogen exchanges places with an alkyl, acyl, or electronegative group on an adjacent carbon atom.[1-5] Recent observations suggest that an early step in the enzymatic reaction is the homolytic cleavage of the cobalt–carbon bond of the coenzyme,[2,6,7] and detailed information concerning the routes and stereochemistry of the hydrogen migration is known.[1,8-10] However, little is known about the mode of migration of the other group.[1-4,11-14]

Scheme I. Proposed Mechanism for the Rearrangements Controlled by B_{12} Dependent Enzymes

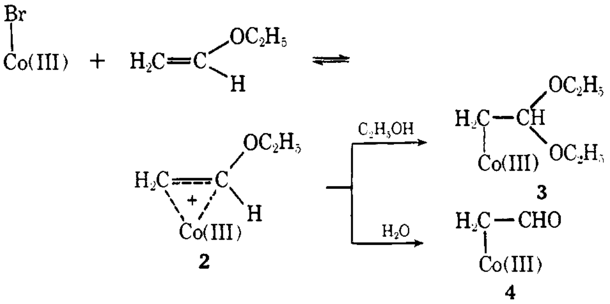


We recently reported evidence for σ ⇄ π rearrangements in cobaloximes[15] and suggested a role for Co(III) π complexes in these enzymatically controlled rearrangements (Scheme I). The dioldehydrase reaction (ethylene glycol → acetaldehyde) has been chosen as a typical example. $R–CH_2–Co(III)$ represents the enzyme–coenzyme complex where the methylene group is that of the 5′-deoxyadenosine moiety.

The principal intermediate in this reaction sequence is the π-complex **1**. Our observations on the solvolysis of 2-acetoxyethyl-*2*-^{13}*C*-(pyridine)cobaloxime[15] support the intermediacy of such a π complex, but in order to better characterize such species it was desirable to prepare Co(III) π complexes directly from Co(III) complexes and olefins.

We have been unable, so far, to observe any interaction between ethylene and Co(III)-containing cobalamins or cobaloximes. This, however, is not too surprising since transition metal π complexes are, in general, most stable when the metal is in a low oxidation state and when the olefin is electron deficient.[16] The π complex sought would contain cobalt in its highest normal oxidation state. This suggested that electron-rich olefins should be used, and indeed the π complex proposed in the enzymatic system (Scheme I) contains such an electron-rich olefin (in this case enol acetaldehyde).

If reaction between a Co(III) cobaloxime and an electron-rich olefin, such as ethyl vinyl ether, were to give the π-complex **2**, then we anticipated that an ambient nucleophile would attack at the oxygen-bearing carbon atom of the complex to give a neutral species. When a methylene dichloride solution of bromo(pyridine)cobaloxime was treated with ethyl vinyl ether in the presence of triethylamine and ethanol, complete alkylation at the cobalt occurred to give a mixture of the acetal **3** and the aldehyde **4**.



These observations are consistent with the quenching of a π complex either by ethanol, to give the acetal, which is stable under the reaction conditions, or by water, to give a hemiacetal which then collapses to the

---

(1) M. K. Essenberg, P. A. Frey, and R. H. Abeles, *J. Amer. Chem. Soc.*, **93**, 1242 (1971).

(2) S. A. Cockle, H. A. O. Hill, R. J. P. Williams, S. P. Davies, and M. A. Foster, *ibid.*, **94**, 275 (1972).

(3) T. J. Carty, B. M. Babior, and R. H. Abeles, *J. Biol. Chem.*, **246**, 6313 (1971).

(4) W. W. Miller and J. H. Richards, *J. Amer. Chem. Soc.*, **91**, 1498 (1969).

(5) R. L. Switzer, B. G. Baltimore, and H. A. Barker, *J. Biol. Chem.*, **244**, 5263 (1969).

(6) B. M. Babior, T. H. Moss, and D. C. Gould, *ibid.*, **247**, 4389 (1972).

(7) T. H. Finlay, J. Valinsky, K. Sato, and R. H. Abeles, *ibid.*, **247**, 4197 (1972).

(8) P. A. Frey, M. K. Essenberg, and R. H. Abeles, *ibid.*, **242**, 5369 (1967).

(9) R. G. Eager, B. G. Baltimore, M. M. Herbst, H. A. Barker, and J. H. Richards, *Biochemistry*, **11**, 253 (1972).

(10) M. Sprecher, M. J. Clark, and D. B. Sprinson, *J. Biol. Chem.*, **241**, 872 (1966).

(11) B. Babior, *ibid.*, **245**, 6125 (1970).

(12) J. Rétey, A. Umani-Ronchi, J. Seibl, and D. Arigoni, *Experientia*, **22**, 502 (1966).

(13) J. N. Lowe and L. L. Ingraham, *J. Amer. Chem. Soc.*, **93**, 3801 (1971).

(14) P. Dowd and C. S. Nakagawa, *Proc. Nat. Acad. Sci. U. S.*, **69**, 1173 (1972).

(15) R. B. Silverman, D. Dolphin, and B. M. Babior, *J. Amer. Chem. Soc.*, **94**, 4028 (1972).

(16) M. Herberhold, "Metal π-Complexes," Vol. II, Part 1, Elsevier, New York, N. Y., 1972.