this evidence combined with the bands arising from the phytyl group, the C_{11} ester methyl, and the C_{10} proton suggest that the pigment is a chlorophyll derivative.

The five sharp bands between 235 and 190 cps cannot be assigned unambiguously, but each is clearly equivalent and corresponds to one of the five low-field methyl singlets expected from the compound 2-desvinyl-2-acetylchlorophyll a.

In conclusion, the major green oxidation product of bacteriochlorophyll is 2-desvinyl-2-acetylchlorophyll a, the structure proposed for the compound by Holt and Jacobs.[5] The biological importance of this pigment as a logical biosynthetic precursor for bacteriochlorophyll remains doubtful, since acetone extracts of *R. rubrum* bacteria when chromatographed in the dark show no sign of any green pigment;[19] perhaps the concentration

is too low for detection by this method (less than $\sim 1\%$ of the concentration of bacteriochlorophyll). Furthermore, it is unlikely that this pigment is the same as the one reported by Gould, *et al.*,[7] for although the absorption spectra are similar they are not identical, and the visible spectrum of the magnesium-free derivative and the nmr spectrum in acetone[20] are clearly different from those described above. The chlorophyll-like pigment of Gould, *et al.*, is probably one of the lesser pigments detected both in the photo- and chemical oxidations of bacteriochlorophyll.

(19) M. Byrn, M. Calvin, and J. Lindsay Smith, *J. Am. Chem. Soc.*, 88, 3178 (1966).

(20) E. S. Gould, unpublished observations.

Communications to the Editor

Stereochemically Nonrigid Organometallic Compounds. II. 1,3,5,7-Tetramethylcyclooctatetraenemolybdenum Tricarbonyl

Sir:

There is a class of organometallic compounds of the transition elements—perhaps a very large class—in which one or more internal rearrangement processes, carrying the molecule from one to another of two or more equivalent configurations, may occur with an activation energy of such a magnitude that the temperature dependence of the rate may be observed. In some cases the rate at room temperature is such that nuclei which are, presumably, not instantaneously in identical environments appear to be equivalent on the time scale of an nmr measurement; sometimes,[1,2] low-temperature measurements are capable of revealing the probable instantaneous configuration (*i.e.*, the structure of lowest free energy) due to the appearance of a well-resolved, nonaveraged spectrum. In one case[2] so far, it has even been possible, by careful examination and interpretation of the behavior of the nmr spectrum at temperatures between the low- and high-temperature limiting spectra, to determine in some detail the path by which the rearrangement process occurs. In other cases, *e.g.*, $(C_5H_5)_2Hg$[3] and $C_8H_8Fe(CO)_3$,[4,5] even at the lowest accessible temperatures ($\sim -160°$) complete

(1) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, 88, 709 (1966).

(2) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *ibid.*, 88, 4371 (1966).

(3) G. G. Dvoriantseva, K. F. Turchin, R. B. Materikova, U. N. Sheinker, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 166, 868 (1966).

(4) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.* (Amsterdam), 4, 313 (1965).

(5) F. A. Cotton, A. Davison, and J. W. Faller, to be published; F. A. L. Anet and S. Winstein, private communication.

development of a "static" spectrum including fine structure is not observed. There are still other cases[6,7] in which time-averaged spectra have been reported at room temperature, but low-temperature data are as yet lacking, at least in detail.

One example of the latter type was recently reported by Winstein, *et al.*,[8] who observed that $C_8H_8Mo(CO)_3$ exhibits only a single resonance at room temperature, whereas structure can be resolved at $-30°$.

In order to determine the influence of attaching heavy groups in place of protons to the rings in these systems, with the particular hope of reducing to a more convenient range the rates of some of the faster and hence not readily investigated systems, we have studied, *inter alia*, the effect of replacing C_8H_8 by 1,3,5,7-tetramethylcyclooctatetraene in some molecules.[9]

We report here our results on the analog of the molybdenum complex, *viz.*, $(CH_3)_4C_8H_4Mo(CO)_3$.[10]

(6) J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Am. Chem. Soc.*, 86, 3589 (1964).

(7) While the systems specifically mentioned here all contain cyclic unsaturated organic groups, what are possibly intramolecular environment averaging processes also occur in some noncyclic systems, notably allyl complexes.

(8) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, 87, 3267 (1965).

(9) The synthesis of 1,3,5,7-tetramethylcyclooctatetraene was accomplished by the method of P. de Mayo and R. W. Yip, *Proc. Chem. Soc.* (London), 84 (1964). We are grateful to Professor de Mayo for providing much information beyond that given in the published note.

(10) Air-sensitive red crystals of 1,3,5,7-$(CH_3)_4C_8H_4Mo(CO)_3$, melting at 90–93° dec, were prepared by refluxing equal weights of tetramethylcyclooctatetraene and diglyme-molybdenum tricarbonyl in hexane for 16 hr. *Anal.* Calcd for $C_{15}H_{16}MoO_3$: C, 52.95; H, 4.73. Found: C, 51.99; H, 4.89. The infrared spectrum in cyclohexane showed three strong carbonyl stretching frequencies at 1987, 1930, and 1903 cm^{-1} (± 3 cm^{-1}).

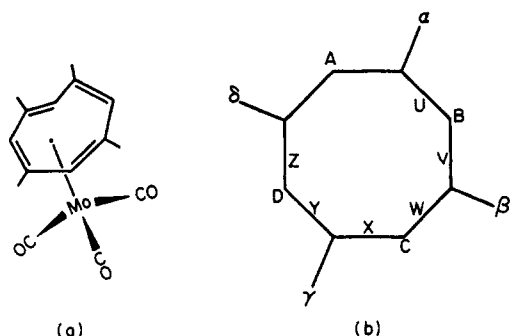(11) An X-ray crystallographic study has been undertaken to clarify the structural details.

Figure 1. (a) The probable instantaneous molecular configuration. (b) A purely topological diagram (*i.e.*, no bond angles, bond orders, or other structural details implied) of $(CH_3)_4C_8H_4Mo(CO)_3$. $\alpha, \beta, \gamma, \delta$ are the methyl groups. A, B, C, D are the vinyl (ring) protons. U, V, W, X, Y, Z are points at which a perpendicular to the mean ring plane could be erected to coincide with the threefold axis of the $Mo(CO)_3$ group.

Figure 2. The temperature variation of the proton nmr spectrum of $1,3,5,7\text{-}(CH_3)_4C_8H_4Mo(CO)_3$. Temperatures quoted correspond approximately to those for spectra measured on $DCCl_3$ solutions, using a Varian A-60 spectrometer.

The most reasonable assumption[11] for the most favorable or instantaneous molecular configuration would be that shown in Figure 1a; hence the limiting, low-temperature spectrum should consist of four nonequivalent methyl proton resonances and four nonequivalent ring proton resonances. As Figure 2a shows, a spectrum of this type is observed at $-30°$ in $DCCl_3$.[12]

As the temperature is raised, the spectrum undergoes many changes; the behavior is far more complicated than mere collapse of the ring and methyl protons each to a single line. What does happen can be summarized as follows. (1) Two of the vinyl peaks (2,4) and all of the methyl peaks broaden and collapse; the other two vinyl peaks (1,3) show little if any change while this is occurring. (2) In the vinyl region a broad peak begins to appear at a frequency which is the average of those of peaks 2 and 4; simultaneously, a doublet arises in the methyl region, one component at the mean frequency of peaks 5 and 6, the other at the mean frequency of peaks 7 and 8. (3) At still higher temperatures vinyl peaks 1 and 3 broaden and collapse; at the highest temperatures accessible[13] a very broad peak just begins to appear at the mean frequency of 1 and 3. (4) The peak due to averaging of 2 and 4, however, *continues to become sharper* as peaks 1 and 3 are collapsing. (5) As peaks 1 and 3 are collapsing, the methyl doublet begins to broaden and collapse but does not become an unequivocally single peak before decomposition becomes too severe to permit reliable observation.

We propose the following explanation of these facts, using Figure 1b as a purely topological guide. Assume the molybdenum atom to be initially at V. As the temperature rises a V $\rightarrow$ U $\rightarrow$ V oscillatory motion (phase 1) commences and accelerates. This averages A with C, α with β, and δ with γ, *viz.*, Scheme I. This explains observations 1 and 2. As the temperature

rises further a transannular shift (U $\rightarrow$ Y $\rightarrow$ U; V $\rightarrow$ Z $\rightarrow$ V) sets in (phase 2), leading to the averaging indicated in Scheme II. This explains results 3, 4, and 5, especially 4.

The possibility of a cyclic eccentric rotation, U $\rightarrow$ V $\rightarrow$ W $\rightarrow$ X $\cdots$ $\rightarrow$ U, which would give Scheme III,
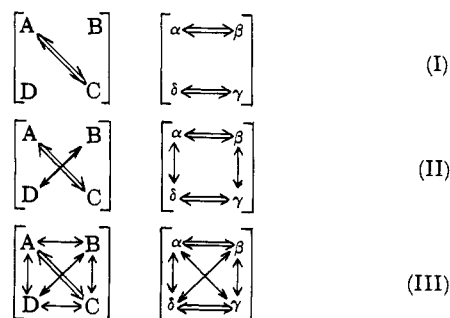
as the second phase, is ruled out within the temperature range of observation by result 4.[14,15]

(14) In $C_8H_8Mo(CO)_3$ the reported single peak at high temperature is consistent with cyclic, eccentric rotation (and also with other possible mechanisms leading to complete averaging). Since in this case there would be no reason why V $\rightarrow$ W should not occur if U $\rightarrow$ V occurs, this is entirely reasonable. It then becomes impossible to say whether the transannular or rocking motion plays a role in the $C_8H_8Mo(CO)_3$ case or not since its effects will be obscured by those of the eccentric rotation. The exact dynamical reason why a V $\rightarrow$ W is appreciably less easy than a U $\rightarrow$ V or even a Y $\rightarrow$ Z type shift in $1,3,5,7\text{-}(CH_3)_4C_8\text{-}H_4Mo(CO)_3$ still requires investigation.

F. A. Cotton, J. W. Faller,[16] A. Musco[17]

*Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts   02139*

---

(12) The results are qualitatively the same in several solvents, although, of course, slight differences in chemical shifts and small changes in the temperature dependence of line widths are found; full details will be given in a later publication. However, there can be no doubt the phenomena observed are characteristic of the solute molecule itself, with solvent effects being of no essential importance.

(13) $(CH_3)_4C_8H_4Mo(CO)_3$ is not very stable thermally; the rate of decomposition becomes appreciable at $\sim 50°$ and great at temperatures $\geq 80°$. However, allowing for the irreversible production of decomposition products, all the temperature-induced changes in the spectrum are reversible with temperature.
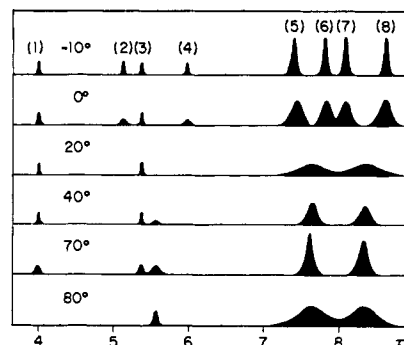
Stereochemically Nonrigid Organometallic Compounds. III. Concerning the Structure of Cyclooctatetraeneiron Tricarbonyl in Solution

Sir:

Since the discovery of cyclooctatetraeneiron tricarbonyl[1–3] and the reports that its proton resonance

(1) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, 82, 366 (1960).
(2) M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959).
(3) K. Nakamura, *Bull. Chem. Soc. Japan*, 32, 880 (1959).