

9.0 to 11.2%. Careful inspection of the difference map at $R = 9.0\%$ shows that the only peaks present are those attributed to H atoms and that there are no other solvent molecules in the lattice. Each end of the two solvent molecules has two van der Waals' contacts (3.1–3.7 Å) with atoms in the host molecules.

Discussion

The alkali metal ion complex of antamanide is most stable in a lipophilic environment.² The nature of the folding of the residues of the complex is understandable in terms of the above observation. The cup in which the Li^+ resides is rimmed with the hydrogen atoms from four pyrrolidine rings, the isopropyl moiety of Val₁ and the tolyl moiety of Phe₆. In addition, the hole in the top of the complex is plugged by a CH_3CN solvent molecule and the CH_3 group of that molecule completes the hydrophobic surface. The lower half of the molecule is surrounded by phenyl groups, thus continuing the hydrophobic surface. Of the six NH groups available for hydrogen bonding, two participate in intramolecular bonds in the interior of the molecule, two make hydrogen bonds with the Br^- ions, while the remaining two NH groups, N(5) and N(10), are so effectively shielded by the hydrophobic side groups that they do not participate in hydrogen bonding. Thus the almost completely hydrophobic surface of the globular complex should facilitate its movement through the lipid layers of cell membranes.

A comparison of the conformation of the Li^+ -antamanide complex with the K^+ -nonactin complex¹⁸ and the K^+ -valinomycin complex¹⁹ (preliminary results) shows several differences. In both K^+ complexes, the K^+ occupies the center of the complex and is symmetrically surrounded by six or eight O atoms with $\text{K}\cdots\text{O}$ distances ranging from 2.7 to 2.8 Å. Furthermore, the nonactin ring folds into a figure resembling

(18) B. T. Kilbourn, J. D. Dunitz, L. A. R. Pioda, and W. Simon, *J. Mol. Biol.*, **30**, 559 (1967).

(19) M. Pinkerton, L. K. Steinrauf, and P. Dawkins, *Biochem. Biophys. Res. Commun.*, **35**, 512 (1969).

the seams of a tennis ball with very nearly $\bar{4}$ symmetry and completely encases the K^+ . The valinomycin, containing both D and L residues, forms a thick doughnut shaped ring around the K^+ and has nearly $\bar{3}$ symmetry. The Li^+ -antamanide, on the other hand, has much less symmetry, only an approximate twofold axis, and much bulkier side groups. Moreover, the Li^+ resides in a relatively shallow cup with all ligands from the ion to the antamanide moiety on one side of the Li^+ . The other side of the Li^+ is strongly coordinated to a solvent molecule.

Curiously, there is another cavity in the molecule located below the Li^+ which remains empty. The lower cavity is lined with six carbonyl O atoms, O(1), O(3), O(6), and O(8) which coordinate with the Li^+ in the upper cavity and O(4) and O(9) in addition. The intramolecular O(4) \cdots O(9) distance is 3.76 Å, O(9) \cdots O(8) is 3.88 Å, and all other O \cdots O approaches involving O(4) or O(9) are larger. The question arises as to why the Li^+ ion is attracted to the upper open cavity rather than the lower cavity.

The spectroscopic data of Faulstich, *et al.*,⁴ show that uncomplexed antamanide in polar solvents in the presence of H_2O has a conformation similar to that of the Na^+ complex. If uncomplexed antamanide is already folded into a conformation close to that described here for the Li^+ complex, then it is plausible that the upper open cavity is much more accessible to the Li^+ ion than the lower cavity which is surrounded by the bulky hydrophobic side groups of Phe₅, Phe₉, and Phe₁₀ as well as the CH_3 of Ala₄.

Acknowledgment. I wish to express my appreciation to Drs. Th. Wieland, H. Faulstich, and W. Burgermeister of the Max Planck Institute für Medizinische Forschung, Heidelberg, for providing the crystals and to Dr. B. Witkop of the National Institutes of Health for helpful discussions. This project was supported in part by the Office of Naval Research Project Order P04-0095 and in part by the NIAMD of the National Institutes of Health.

Communications to the Editor

Intramolecular Rearrangement in Olefin-Tetracarbonyliron Complexes. Importance of Olefin Rotation on the Barrier for Rearrangement

Sir:

Although the fluxional nature of five-coordinated transition metal complexes is receiving a great deal of attention,¹ the study of the rearrangement in $\text{Fe}(\text{CO})_5$ and its derivatives, a potentially large class of fluxional molecules, is being frustrated, except in a few cases,² by

(1) (a) P. Meakin and J. P. Jesson, *J. Amer. Chem. Soc.*, **95**, 7272 (1973); (b) J. R. Shapley and J. A. Osborn, *Accounts Chem. Res.*, **6**, 305 (1972).

(2) J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970); (b) J. D. Warren, M. A. Busch, and R. J. Clark, *ibid.*, **11**, 452 (1972); (c) L. Kruczynski and J. Takats, *J. Amer. Chem. Soc.*, **96**, 932 (1974).

the apparently low activation barriers involved.³ In our quest to find an $\text{L}\cdot\text{Fe}(\text{CO})_4$ system amenable to a variable temperature nmr study, the explanation offered by Muetterties, *et al.*,⁵ to account for the contrasting fluxional behavior between amino- and thiophosphoranes and other XPF_4 type molecules seemed particularly relevant and exciting. By comparing the free energy of activation due to P–N bond rotation to that due to the rearrangement barrier (permutation of

(3) (a) The ^{13}C nmr spectrum of $\text{Fe}(\text{CO})_5$ is a single sharp line down to ca. -170° .^{1a} (b) The intramolecular rearrangement in $\text{Fe}[(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]\text{Fe}(\text{CO})_5$ is still rapid at -80° .⁴

(4) M. Akhtar, P. D. Ellis, A. G. MacDiarmid, and J. D. Odom, *Inorg. Chem.*, **11**, 2917 (1972).

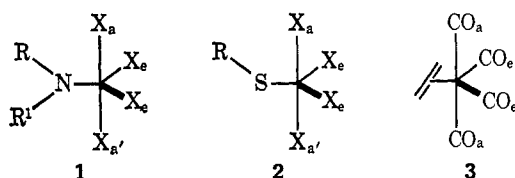
(5) E. L. Muetterties, P. Meakin, and R. Hoffman, *J. Amer. Chem. Soc.*, **94**, 5674 (1972).

Table I^{a,b}

	<i>T</i> , °K	δ(CO)	δ(C=C)	δ(CO ₂)	δ(CH ₂)	δ(CH ₃)	<i>E</i> _a , kcal/mol
Diethyl fumarate	303		134.0	164.9	61.5	14.3	
(Diethyl fumarate)-Fe(CO) ₄	293	205.8	44.9	174.4	61.3	14.7	14.3 ± 0.4
	243	{206.6 (2), 204.8 (2)}	44.0	174.3	61.1	14.4	
Diethyl maleate	303		130.3	165.4	61.3	14.2	
(Diethyl maleate)-Fe(CO) ₄	303	206.3	46.6	172.4	61.5	14.3	14.1 ± 0.4
	243	{207.2 (2), 206.8 (1), 204.2 (1)}	45.8	172.4	61.3	13.8	
Ethyl acrylate	303		{103.2, 129.4} ^c	166.1	60.7	14.4	
(Ethyl acrylate)-Fe(CO) ₄	283	208.8	{34.5, 44.8} ^c	175.2	61.0	14.7	11.1 ± 0.3
	193	{209.8 (1), 208.9 (1), 208.2 (1), 207.4 (1)}	{33.5, 43.1} ^c	174.9	60.6	14.1	

^a Chemical shift measured with respect to ¹³CD₂Cl₂ and adjusted to TMS = 0 by δ(CD₂Cl₂) + 54.1 ppm = δ TMS. ^b The complexes were prepared according to E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdock, *Helv. Chim. Acta*, **46**, 288 (1963). ^c First entry methylene carbon; second corresponds to the carbon bearing the ester function.

fluorine atom positions), they concluded that "the resistance to P-N bond rotation makes a major contribution to the Berry rearrangement barrier in R₂NPF₄ molecules." The structural similarity between amino-(1) and thiophosphorane (2) and (olefin)-Fe(CO)₄ type complexes (3), coupled with the well-established



phenomenon of olefin rotation⁶ and associated rotational barrier of 9–15 kcal/mol indicated that this class of molecules should indeed have activation barriers for rearrangement high enough to render them eminently suitable for variable temperature nmr investigation.

The variable temperature ¹³C nmr spectra, in the carbonyl region, of (diethyl maleate)- and (diethyl fumarate)-Fe(CO)₄ are shown in Figure 1a and 1b. The low temperature limiting spectra are entirely consistent with the assumption of an instantaneous structure in solution as depicted by 3, *i.e.*, a trigonal bipyramid with olefin lying in the equatorial plane. Single-crystal X-ray structure determination on tetracarbonyl(fumaric acid)iron,⁷ tetracarbonyl(acrylonitrile)iron,⁸ and 1,5-cyclooctadienebis(tetracarbonyliron)⁹ has in fact established this geometry for the solid state. Moreover solution ir studies carried out on related (halogenoolefin)-Fe(CO)₄ complexes¹⁰ are also entirely consistent with structure 3. For such a structure we would expect, as observed in Figure 1a, three lines (relative intensity 2:1:1) for equatorial and non-

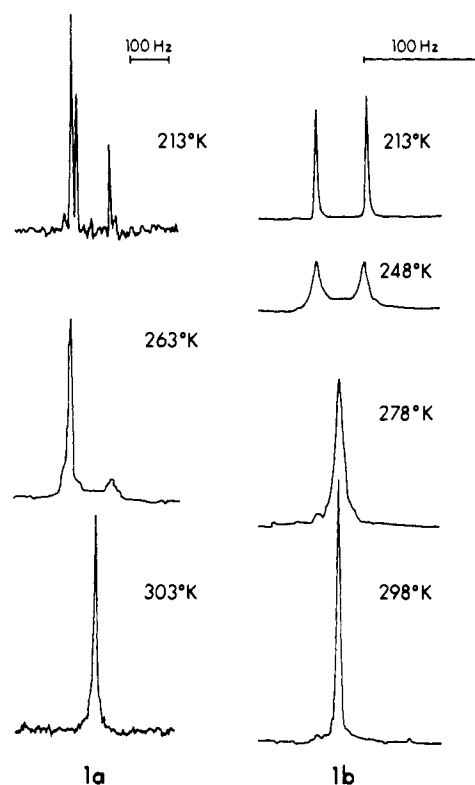


Figure 1. Variable temperature ¹³C nmr spectra of (diethyl maleate)-Fe(CO)₄ (1a) and (diethyl fumarate)-Fe(CO)₄ (1b) in the carbonyl region.

equivalent axial carbonyl groups in the case of the maleate¹¹ and two lines of equal intensity, Figure 1b, for the fumarate. Table I also lists data for tetracarbonyl-(ethyl acrylate)iron, an illustrative example of an asymmetric (olefin)-Fe(CO)₄ complex; again the anticipated four-line spectrum is obtained at low temperature. The high temperature limiting singlet spectrum indicates averaging of the carbonyl groups positions. The associated activation energies (carbonyl group permutations) and pertinent nmr data are listed in Table I.

The spectral behavior, which is reversible with tem-

(11) Slight temperature dependence of the chemical shifts causes the appearance of a two-line spectrum at intermediate temperatures; see, for example, Figure 1a at 263°K.

(6) (a) R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 2519 (1969); (b) B. F. G. Johnson and J. A. Segal, *J. Chem. Soc., Chem. Commun.*, 1312 (1972); (c) J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. Dalton Trans.*, 1776 (1972).

(7) C. Perdone and A. Singer, *Inorg. Chem.*, **7**, 2614 (1968).

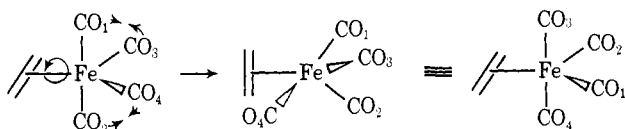
(8) A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).

(9) C. Kruger, *J. Organometal. Chem.*, **22**, 697 (1970).

(10) F.-W. Grevels and E. Koerner von Gustorf, *Justus Liebigs Ann. Chem.*, 1821 (1973).

perature, independent of solvent, and unaffected by added free olefin, unequivocally rules out simple olefin rotation as being solely responsible for the averaging of the carbonyl groups, since such a process would not exchange axial carbonyl groups with equatorial ones as demanded by the observed single line at high temperatures. Unfortunately, due to the simplicity of the spectrum, the nmr line shape changes contain no mechanistic information. As a result analysis of the axial-equatorial carbonyl group exchange in terms of "basic permutational sets"¹² with the present data is not feasible. We would only like to point out that a synchronous olefin rotation and Berry rearrangement of the carbonyl groups (Scheme I), which by the way are

Scheme I



inseparable, provides a simple pathway for the exchange process.¹³ The process is also attractive since it offers a ready rationale for the observed dramatic increase in the activation barrier upon the replacement of one CO group by an olefin moiety.^{3a} Should the above process be operative it also suggests a very close correspondence between the strength of the metal-olefin bond, or more precisely its π component,^{15,16} and the obtained energies of activation based on carbonyl group exchange.¹⁷ Our observation that the rate of rearrangement decreases in the series styrene⁻¹⁸ > (ethyl acrylate)- > benzalacetone- > (diethyl maleate)- ~ (diethyl fumarate)- > trifluoroethylene-Fe(CO)₄¹⁹ is a clear indication of this.

Studies are in progress to establish more convincingly the correlation between Fe-olefin bond strength and activation barriers for carbonyl group exchange.

Acknowledgment. We thank the University of Alberta and the National Research Council of Canada for financial support of this research.

(12) P. Meakin, E. Muetterties, and J. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

(13) We note that Whitesides and Mitchell¹⁴ have established that the rearrangement in (CH₃)₂NPF₄ is consistent with the Berry mechanism.

(14) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).

(15) The σ component of the metal-olefin bond by virtue of its cylindrical symmetry contributes little to the barrier for olefin rotation. The π interaction between metal d orbitals and π^* olefin orbitals is, however, different for the olefin in the equatorial plane and perpendicular to it. The barrier to olefin rotation will therefore primarily reflect the differences in the π interactions between these two forms.

(16) We thank a referee for bringing this point to our attention.

(17) In fact, the activation energies obtained are not a true measure of the barriers to olefin rotation, since if we assume, as we have done, the Berry rearrangement in these complexes then the geometry of the transition state is close to a square pyramid with the olefin occupying the apical position. The barrier to olefin rotation in this state is greatly reduced compared to that in the ground state because of the fourfold character of the barrier.

(18) Limiting spectrum at 148°K, four carbonyl resonances in the ratio 1:1:1:1.

(19) Limiting spectrum at 283°K, three carbonyl resonances in the ratio 2:1:1 (¹⁹F decoupled), and single broad resonance at 338°K.

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Received February 21, 1974

Preparation and Structure of η^1 -Pentachlorocyclopentadienylpentacarbonylmanganese(I), (η^1 -C₅Cl₅)(CO)₅Mn

Sir:

In this communication the preparation and structure of the first σ -bonded pentachlorocyclopentadienyl-transition metal complex are described. The preparation of pentachlorocyclopentadienyl-metal complexes has proved a somewhat difficult task in the past. Decachloroferrocene and decachlororuthenocene were obtained by repetitive metalation exchange-halogenation reactions.^{1,2} Bis- and monopentachlorocyclopentadienyl (C₅Cl₅⁻) complexes of mercury have been prepared with 1,2,3,4,5-pentachlorocyclopentadiene or thermally unstable TIC₅Cl₅.^{3,4} We recently reported the convenient synthesis of halogen substituted η^5 -cyclopentadienylrhodium complexes *via* the insertion reactions of diazocyclopentadienes into halogen-bridged dirhodium species.⁵ Extension of this reaction has resulted in the first C₅Cl₅⁻ derivatives of manganese.⁶

Two yellow crystalline products, (η^1 -C₅Cl₅)(CO)₅Mn (I) and (η^5 -C₅Cl₅)(CO)₃Mn (II) are obtained from the reaction of manganese pentacarbonyl chloride and 2,3,4,5-tetrachlorodiazocyclopentadiene in pentane at room temperature. They are conveniently separated by fractional crystallization from the filtered reaction mixture.⁷ Four carbonyl stretching bands are observed in the solution (cyclohexane) infrared spectrum of the less soluble compound I. These occur at 2128 (m), 2077 (w), 2044 (vs), and 2011 (s) cm⁻¹ and are assigned to the A₁⁽²⁾, B₁, E, and A₁⁽¹⁾ modes, respectively.⁸ Excluding bands due to the carbonyl groups, the remainder of the spectrum (4000-400 cm⁻¹; Nujol mull) is virtually identical with that reported for Hg(C₅Cl₅)₂,^{3,4} indicating that the pentachlorocyclopentadienyl ligand is σ -bonded. This has been confirmed by the preliminary results of an X-ray structural analysis which are reported at this time.

Crystals of (η^1 -C₅Cl₅)(CO)₅Mn are monoclinic: space group *P*2₁/*n*, a special setting of *P*2₁/*c* (no. 14, *C*_{2h}⁵); *a* = 13.701 (2), *b* = 8.758 (1), *c* = 13.329 (1) Å; β = 107.78° (1); *Z* = 4. Data collection (Nb-filtered Mo K α radiation, Syntex P₁ Autodiffractometer) yielded 1560 symmetry independent reflections having $2\theta_{MOK\alpha} < 43.0^\circ$ (0.5 limiting Cu K α spheres) and *I* > 2 σ (*I*). Direct methods were used to locate the manganese and three chlorine atoms. The remaining atoms were located using standard difference-Fourier techniques. Unit-weighted full-matrix least-squares refinement, employing anisotropic thermal parameters for all atoms,

(1) F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **92**, 3239 (1970).

(2) F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **95**, 870 (1973).

(3) G. Wulfsberg and R. West, *J. Amer. Chem. Soc.*, **93**, 4085 (1971).

(4) G. Wulfsberg, R. West, and V. N. Mallikarjuna Rao, *J. Amer. Chem. Soc.*, **95**, 8658 (1973).

(5) V. W. Day, B. R. Stults, K. J. Reimer, and A. Shaver, *J. Amer. Chem. Soc.*, **96**, 1227 (1974).

(6) While this work was in progress, a possible C₅Cl₅⁻ complex of palladium was briefly mentioned by N. Yoshimura, S.-I. Murahashi, and I. Moritani, *J. Organometal. Chem.*, **52**, C58 (1973).

(7) A standard reaction of 24-hr duration, employing 0.45 g of each reactant in 20 ml of pentane, yields 0.32 g of I and 0.29 g of II. Satisfactory analysis has been obtained for both compounds.

(8) Theory predicts three infrared bands for local C_{1v} symmetry but the infrared-forbidden B₁ mode is sometimes observed: L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, **12**, 53 (1969), and references therein.