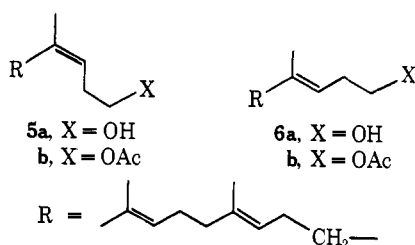


Figure 1.

1.16 relative to that for *trans,trans*-farnesol, suggesting a formation of a homolog of farnesol. Glpc-mass spectrometric analysis of the material derived from non-labeled **3** with **2b** also showed a peak at a retention volume reasonable for a homofarnesol (1.35 relative to that for *trans,trans*-farnesol on a 1-m column of Silicon OV-1 1% at 150°) and the mass spectrum for this peak exhibited a parent ion at m/e 236 ($C_{16}H_{28}O$) with an intensity of 1.9% relative to the base peak at 69. Peaks were also observed at 218 ($M - 18$), 205 ($M - 31$), 193 ($M - 43$), 167 ($M - 69$), 137 ($C_{10}H_{17}$) with relative intensities of 0.4, 0.4, 1.6, 2.0, and 5.8, respectively.

For a further identification, *cis*- (**5a**) and *trans*-homofarnesol (**6a**) were chemically synthesized essentially according to the method of Lucius¹¹ as modified by Watanabe,¹² and the enzymatically derived material was compared with the authentic specimens by glpc-mass spectrometry. Both the retention time and the mass spectrum of this material were completely identical with *cis* isomer **5a** in various conditions with Silicon OV-1. Since a better glpc separation was observed with the acetates (**5b** and **6b**) on Carbowax 20M, the product of



the enzymatic reaction was converted into the acetate. The glpc-mass spectrometry of the acetate also clearly revealed the identity with the *cis* isomer (**5b**) and denied the presence of the *trans* isomer (**6b**). Thus, the formation of **4** from **2b** and **3** was proved. The yield was *ca.* 50% based on **3**.

The exclusive formation of the *cis* isomer (**4**) catalyzed by the prenyltransferase which is responsible for the synthesis of the *trans* isomer of farnesyl pyrophosphate can be explained by assuming that the binding site for **1a** contains an M site and P site which must be filled up simultaneously with the methyl group

(11) G. Lucius, *Chem. Ber.*, **93**, 2263 (1960).

(12) M. Watanabe, Master of Science Thesis, Tohoku University, Sendai, Japan, 1969.

and pyrophosphate moiety of the **1a** molecule, respectively, to hold C-4 and *pro-R* H of C-2 at the fixed position. In the case of the homolog (**2b**) possessing an extra methylene, both of the methyl and pyrophosphate groups can fit exactly in M site and P site when the methylene chain is lifted to take such a conformation that the *cis* condensation is indispensable (Figure 1).

We have observed an abnormal reaction with the other homolog (**1b**) catalyzed by isopentenyl pyrophosphate isomerase and proposed a mechanism involving two essential sites for the methyl and pyrophosphate moieties.¹³ It is noteworthy that in the prenyltransferase reaction **1b** acts as a substrate normally and that **2b** acts abnormally in the stereochemical relation concerning the double bond formation. The reason for the normal reaction of **1b** may be as follows. The binding of the methyl and the pyrophosphate group with a conformation leading to the *cis* product results in the shift of the reacting points (C-4 and C-2) to a wrong position, whereas the binding with a conformation leading to the *trans* product can hold, though with a little distortion, these reacting points within the right position. In other words, M site may have a capacity for accommodating up to an ethyl group.

It is also of interest that the reactivity of **2b** with dimethylallyl pyrophosphate was almost negligible as compared with that of geranyl pyrophosphate (**3**). This marked difference will add support to our proposal⁶ that there are involved in the prenyltransferase two separate sites for the reaction of dimethylallyl pyrophosphate with **1a** and the reaction of **3** with **1a**.

(13) T. Koyama, K. Ogura, and S. Seto, *J. Biol. Chem.*, **248**, 8043 (1973).

Kyozo Ogura,* Akio Saito, Shuichi Seto
Chemical Research Institute of Non-Aqueous Solutions
Tohoku University
Sendai, Japan

Received March 1, 1974

Rapid Intramolecular Rearrangements in Pentacoordinate Transition Metal Compounds. V. The Coupling of Olefin Rotation and Berry Pseudorotation in Tetracarbonyliron-Olefin Complexes¹

Sir:

Variable temperature ¹³C nmr studies on metal carbonyl complexes are proving to be a valuable probe into structural and dynamic behavior in solution. However, for $Fe(CO)_5$ ² and several of its derivatives (e.g., (norbornadiene) $Fe(CO)_3$,^{2c} $[(CH_3)_2PCH_2CH_2P(CH_3)_2]Fe(CO)_3$,^{2d} $[(C_6H_5)_2PCH_2P(C_6H_5)_2]Fe(CO)_3$,³ $R_3PFe(CO)_4$,^{2e,4} $(\eta^4\text{-cyclooctatetraene})Fe(CO)_3$,⁵ and (diene) $Fe(CO)_3$ ⁶) the activation energy for intramolecu-

(1) First presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973.

(2) (a) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958); (b) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); (c) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972); (d) M. Akhtar, P. D. Ellis, A. G. MacDiarmid, and J. D. Odom, *Inorg. Chem.*, **11**, 2917 (1972).

(3) F. A. Cotton, K. I. Hardcastle, and G. A. Rusholme, *J. Coord. Chem.*, **2**, 217 (1973).

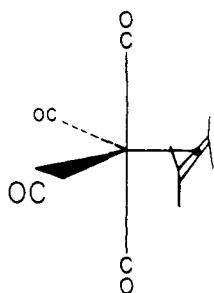
(4) (a) C. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969); (b) B. E. Mann, *J. Chem. Soc., Chem. Commun.*, 1173 (1971).

(5) G. Rigatti, G. Boccalon, A. Cecon, and G. Ciaconetti, *J. Chem. Soc., Chem. Commun.*, 1165 (1972).

(6) L. Kruczynski and J. Takats, *J. Amer. Chem. Soc.*, **96**, 932 (1974).

lar rearrangement about iron is so low that ^{13}C limiting spectra are either unobserved or achieved only at very low temperatures. These observations may be interpreted using an idealized approach we have recently presented.⁷ Thus, if ligand site exchange is occurring by a Berry process⁸ then rearrangement of these complexes involves no gross violation of positional, steric, or strain rules⁹ and a low barrier might be expected. The parallels with phosphorus(V) chemistry are thus evident and suggest an experiment in which carbonyl equilibration at iron may be readily observed.

For XPF_4 molecules where noncylindrical π -bonding between X and P is said to occur (e.g., X = NR_2 , SR), the barrier to fluorine site exchange about P is significantly increased by coupling of the Berry process with rotation about the P-X bond.¹⁰ In analogy, therefore, we have investigated the carbonyl ligand site exchange in complexes of the type $\text{Fe}(\text{CO})_4(\text{olefin})$. X-Ray structural determinations of $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHCN})$ ¹¹ and $(-)\text{Fe}(\text{CO})_4(\text{fumaric acid})$ ¹² show the olefin to occupy an equatorial site in a TBP structure with the olefinic carbon atoms essentially lying in the equatorial plane.



The complexes $\text{Fe}(\text{CO})_4(\text{olefin})$ (olefin = $\text{CH}_2=\text{CH}(\text{COOCH}_3)$ (**1**), *cis*- $\text{CH}(\text{COOCH}_3)=\text{CH}(\text{COOCH}_3)$ (**2**), *trans*- $\text{CH}(\text{COOCH}_3)=\text{CH}(\text{COOCH}_3)$ (**3**), *trans*- $\text{CH}(\text{COOC}_2\text{H}_5)=\text{CH}(\text{COOC}_2\text{H}_5)$ (**4**), $\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)$ (**5**), and $\text{Cl}_2\text{C}=\text{CF}_2$ (**6**)) were prepared by standard routes.¹³ ^{13}C nmr spectra (100 MHz, FT mode, ^1H noise decoupled) in CD_2Cl_2 solution¹⁴ of the carbonyl ligands of **1**, **3**, **4**, and **5** at 25° each show a sharp singlet; **2** exhibits a somewhat broad singlet whereas **6** shows two approximately equal but broad resonances. Coordinated olefinic carbon resonances are observed at *ca.* 80–100

(7) J. R. Shapley and J. A. Osborn, *Accounts Chem. Res.*, **6**, 305 (1973).

(8) The physical process describing the Berry mechanism is strictly applicable only to molecules of D_{3h} or C_{2v} symmetry. For a brief discussion of the constraints upon its application to molecules of lower symmetry see ref 7.

(9) Interestingly, limiting spectra for the complexes (diene) $\text{Fe}(\text{CO})_3$ have been observed for 1,3- but not 1,4- or 1,5-diene complexes.⁹ Strain effects may be operative here also.

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

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

(12) C. Pedone and A. Sirign, *Inorg. Chem.*, **7**, 2614 (1968).

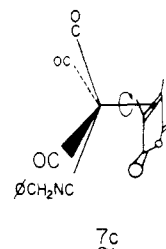
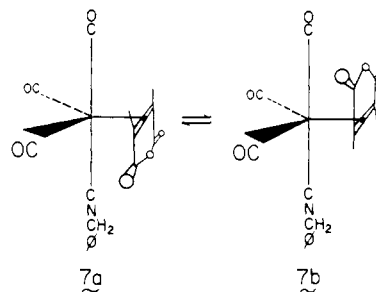
(13) (a) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963); (b) R. Fields, M. M. Germain, R. N. Haszeldine, and P. W. Wiggins, *J. Chem. Soc. A*, 1969 (1970); (c) E. Koerner von Gustorf, M. C. Henry, and C. Di Pietro, *Z. Naturforsch. B*, **21**, 42 (1966).

(14) Solutions were from *ca.* 0.5 to 1.5 M in $\text{Fe}(\text{CO})_4(\text{olefin})$ and 0.04 to 0.06 M in $\text{Cr}(\text{acac})_3$.¹⁵ Typical sample parameters were: acquisition time 0.5–1.5 sec, pulse delay 0–1.5 sec, pulse width ~ 36 μsec , total 300–1000 pulses.

(15) See O. A. Gansow, A. R. Burke, and G. N. La Mar, *J. Chem. Soc., Chem. Commun.*, 456 (1972); O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2250 (1972); S. Barcza and N. Engstrom, *ibid.*, **94**, 1762 (1972).

ppm upfield of the free olefin. On lowering the temperature **1**, **2**, **3**, and **4** exhibit broadening and collapse of the carbonyl resonances, and a limiting spectrum consistent with expected ground state structure results. Hence **1** shows four carbonyl resonances (relative intensities 1:1:1:1), **2** shows three (2:1:1), and **3** and **4** show two resonances (2:2). No change in the olefinic ^{13}C resonances (with or without free olefin present) was observed during this process. However, observations on **1** and **2** show *olefin rotation not to occur independently of the carbonyl equilibration*.¹⁶ Hence, olefin rotation in the TBP ground state structure does not appear to be a facile process.¹⁷ For **3** and **4**, the barrier to exchange can be estimated¹⁸ as $\sim 13.0 (\pm 0.3)$ kcal mol⁻¹ (at -10°) which is, however, comparable to values found for olefin rotation in Rh(I) and Pt(II) complexes.¹⁹ In contrast, **5** yields a single sharp ^{13}C carbonyl resonance down to -80° , implying a much lower rearrangement barrier. **6**, however, exhibits a limiting spectrum even at ambient temperatures and a lower limit for rearrangements can be estimated as > 15.0 kcal mol⁻¹. *The barrier to carbonyl site exchange increases with increasing π -acceptor ability of the olefin as $5 < 1 < 2 \sim 3 \sim 4 < 6$.*

These observations are in accord with a process involving coupling of the olefin rotation with a Berry pseudorotation about iron. However, intramolecular exchange of the equatorial bound olefin with an axially bound carbonyl would also be consistent with these data. Accordingly, we have prepared a series of isocyanide substituted complexes²⁰ of the type, $\text{Fe}(\text{CO})_{4-n}(\text{C}_6\text{H}_5\text{-CH}_2\text{NC})_n(\text{maleic anhydride})$ (**7**, **8**, and **9**) (where $n = 1, 2$, and 3, respectively).



Solution infrared and ^1H and ^{13}C nmr studies on **7**

(16) For example, in **1** olefin rotation alone would produce a two-line ^{13}C spectrum for the carbonyl ligands.

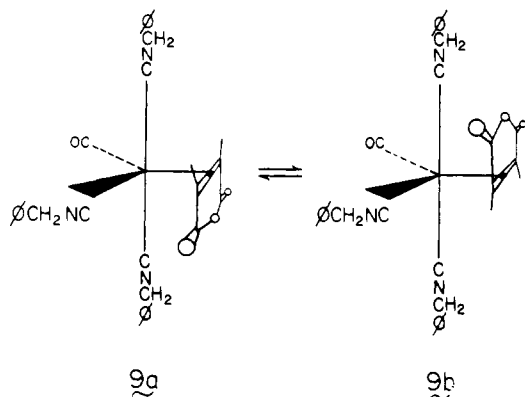
(17) Note, however, olefin rotation in $\text{Os}(\text{CO})(\text{NO})(\text{C}_2\text{H}_4)(\text{PPh}_3)_2^+$, B. F. G. Johnson and J. A. Segal, *J. Chem. Soc., Chem. Commun.*, 1312 (1972).

(18) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

(19) R. Cramer and G. S. Reddy, *Inorg. Chem.*, **12**, 346 (1973); J. Ashley-Smith, Z. Douek, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 128 (1974), and references therein.

(20) The complexes were isolated by thin-layer chromatography from the reaction of $\text{Fe}(\text{CO})_4(\text{maleic anhydride})$ and $\text{C}_6\text{H}_5\text{CH}_2\text{NC}$ (in the appropriate ratios) in toluene at $90\text{--}95^\circ$.

establish that two isomers **7a** and **7b** equilibrate in solution. At -30° , the ^{13}C spectrum of the carbonyl ligands consists of two unequal sets of resonances, each set having two signals in 2:1 ratio. As the temperature is raised, all resonances collapse and at 25° , a single 2:1 pattern emerges. Similarly the variable temperature ^1H spectrum shows the appropriate changes in both the olefinic and benzylic resonances. The equilibration **7a** \rightleftharpoons **7b** is thus not accompanied by interchange of the olefin with an axial carbonyl ligand since this could necessarily cause axial-equatorial carbonyl site equilibration.²¹ Exchange of the olefin with the axial isocyanide ligand can also be ruled out by studies on **9**. Isomers **9a** and **9b** are seen to interconvert at 0° , but again no equilibration of axial and equatorial isocyanide ligands is observed during this process. It is noteworthy that this latter process can be observed at higher temperatures ($>60^\circ$) in this case.



The observations on **7**, **8**, and **9** could be simply explained by rotation about the metal-olefin bond without accompanying motion about the metal center. However, we have seen that this cannot be so with the closely analogous $\text{Fe}(\text{CO})_4(\text{olefin})$ complexes **1** and **2**. Hence, a preferable description for the observed behavior (including **7**, **8**, and **9**) involves a concerted process involving the coupling of the olefin rotation with Berry pseudorotation about iron. In **7**, **8**, and **9**, the accompanying motion about the metal cannot be observed in the nmr experiment. However, a nonconcerted mechanism is an attractive alternative, in which the square pyramidal **7c** is not a transition state but an intermediate of sufficient lifetime during which rate determining olefin rotation can occur. Olefin rotation in such an intermediate would be expected to be of lower energy than in the ground TBP states **7a** and **7b**.

Acknowledgments. This work has been supported by the Alfred P. Sloan and Henry and Camille Dreyfus Foundations in the form of fellowships (J. A. O.) and by the National Science Foundation in the form of a generous grant (GP 32317) for the XL-100 MHz nmr spectrometer.

(21) Note that although the preference⁷ for the equatorial site is olefin $>$ CO $>$ RNC (a) the interchange between carbonyl and isocyanide ligands in $\text{Fe}(\text{CO})_4(\text{C}_6\text{H}_5\text{CH}_2\text{NC})$ is very fast at -80° in CD_2Cl_2 and (b) use of a bulkier isocyanide, e.g., *t*-BuNC may cause the stability sequence above to be altered.

S. T. Wilson, N. J. Coville
J. R. Shapely, J. A. Osborn*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received April 1, 1974

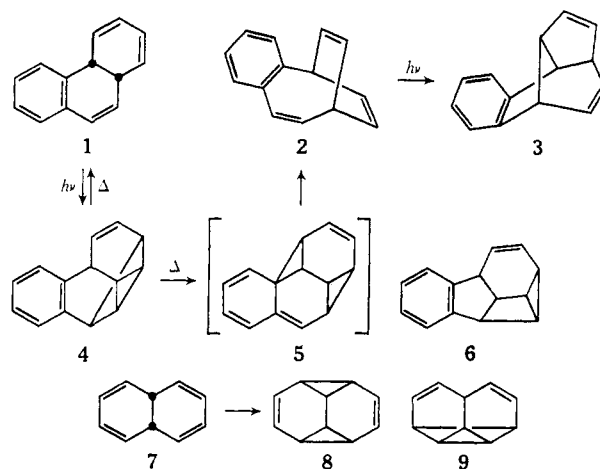
Isolation and Thermolysis of 4,5-Benzotetracyclo[4.4.0.0^{2,10}.0^{3,9}]deca-4,7-diene, a New $(\text{CH})_{10}$ Derivative

Sir:

It has been reported that photolysis of **1** results in an apparent 1,3-carbon shift to afford an isomer **2** which rearranges to **3** when irradiated under similar conditions.¹ We have reexamined this reaction and find that **2** is not formed photochemically. The major photoproduct is **4**, a substance having a hitherto unknown $(\text{CH})_{10}$ skeleton.

We have used nmr spectroscopy to follow photolysis of **1** at room temperature in ether or acetone solution (Pyrex filter). The nmr signals due to starting material disappear, and a new substance, **4**, appears together with a small amount of phenanthrene as the only other significant product.² Neither **2** nor **3** can be detected by nmr in the final photolysis mixture.

After purification by chromatography, **4** is obtained as a colorless oil, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 273 (ϵ 800) and 266 nm (ϵ 870), *m/e* 180. The nmr spectrum (CDCl_3) contains four aromatic protons, δ 6.7–7.1 (m), H_7 at δ 6.22 (d of d with partly resolved fine coupling, $J_{7,8} = 8$ Hz, $J_{6,7} = 7$ Hz), H_8 at δ 5.40 ppm (d of d, $J_{7,8} = 8$ Hz, $J_{8,9} = 7$ Hz), H_6 at δ 3.70 (br t, $J_{6,7} = J_{1,6} = 7$ Hz), H_3 and H_9 at δ 3.2–3.5 (m), and cyclopropyl protons H_1 , H_2 , and H_{10} at δ 1.46–1.90 ppm (m). Of the possible benzo $(\text{CH})_{10}$ structures,⁴ only **4** and **6** are consistent with the chemical shifts in the spectrum. A final decision in favor of **4** is based on extensive spin decoupling experiments which show that neither vinyl proton is coupled to cyclopropyl protons ($J < 1$ Hz).



The new hydrocarbon is thermally labile and rearranges to a 6:5 mixture of **1** and **2** in the temperature range 71 – 83° ($E_a = 29.2 \pm 0.6$ kcal/mol, $\log A = 14.2 \pm 0.4$). This finding provides an obvious explanation for the contrast between our results and those reported previously, since glpc analysis was used to monitor the

(1) L. A. Paquette, M. J. Kukla, and J. C. Stowell, *J. Amer. Chem. Soc.*, **94**, 4902 (1972).

(2) Phenanthrene is also formed from **1** by disproportionation,¹ but control experiments indicate that this is a much slower reaction than the photolytic process. According to nmr analysis, the relative yield of phenanthrene formed photolytically is ca. 15%. At least four unidentified minor products are also present by glpc, 5% relative yield. Two of these correspond by glpc retention time to 2,3- and 5,6-benzotetracyclo[5.3.0.0^{4,10}.0^{2,9}]deca-2,5,8-trienes.^{1,3}

(3) E. Vedejs, R. A. Shepherd, and R. P. Steiner, *J. Amer. Chem. Soc.*, **92**, 2158 (1970).

(4) A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).