# $(\eta^3: \eta^1$ALLYLCARBONYL)IRON TRICARBONYL COMPLEXES. I. TRANSFORMATION OF COMPLEXES FROM ELECTROPHILIC GEM-DIMETHYLCYCLOPROPENES INTO FUNCTIONALIZED ISOPRENIC DIENE-IRON TRICARBONYL COMPLEXES BY THERMOLYSIS OR PHOTOLYSIS (1).

M. FRANCK-NEUMANN,* C. DIETRICH-BUCHECKER, A. KHEMISS

Equipe de Recherche Associée au CNRS n° 687, Institut de Chimie
de l'Université Louis Pasteur, 1, rue Blaise Pascal 67008 Strasbourg, France.

*Electrophilic gem-dimethyl cyclopropenes react with diiron enneacarbonyl to give $(\eta^3:\eta^1$ allylcarbonyl)iron tricarbonyl complexes. These complexes, bearing in this work electron withdrawing substituents, are shown to be rather labile thermally and photochemically, leading easily to isoprenic diene-iron tricarbonyl complexes.*

Certain methyl- and phenyl- substituted cyclopropenes were shown to react with iron carbonyls via ring opening and carbonylation to $(\eta^3: \eta^1$allylcarbonyl)iron tricarbonyl complexes (2-4). Our own investigations of this carbonylating coordination reaction were done with different cyclopropenes, i.e., electrophilic ones (5). As a result, gem-dimethylcyclopropenic esters and ketones are producing the same kind of vinylketene ligand complexes (6) which show, however, a new property, the tendency to be easily transformed into isoprenic diene-iron tricarbonyl complexes. This result can be achieved thermally with loss of carbon monoxide or photochemically without carbon monoxide evolution, as will be seen in this communication.

In a first complexation attempt, the cyclopropenic ester $\underline{1}$ was heated for several hours in refluxing benzene with diiron enneacarbonyl. Under these conditions, the diene-iron tricarbonyl complexes $\underline{2}$, $\underline{3Z}$ and $\underline{3E}$, isolated in the approximate ratio of 3:2:1 with an overall yield of 80%, are the only products formed :
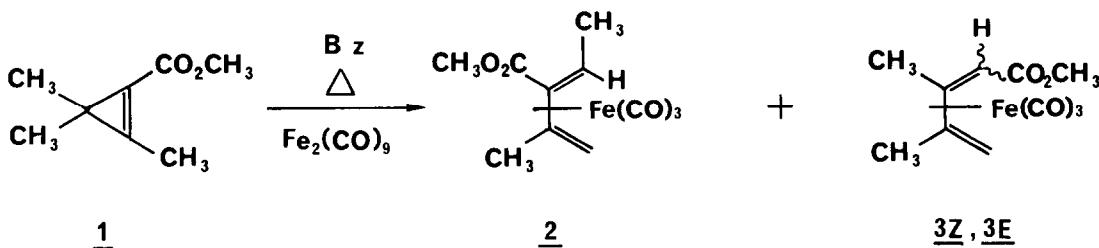


$$\underline{1} \qquad\qquad \underline{2} \qquad\qquad \underline{3Z}, \underline{3E}$$

2,3Z,3E : yellow liquids separated by column chromatography on silicagel (7).

2 : $\nu$(C=O) 1725 cm$^{-1}$ ; NMR : 0,22 ppm (1H, d, J=2Hz), 0,77 ppm (1H, q, J=5Hz), 1,66 ppm
(1H, d, J=2Hz), 1,44 ppm (3H, d, J=5Hz), 2,18 ppm (3H,s), 3,98 ppm (3H, s).

3Z: $\nu$(C=O) 1700 cm$^{-1}$ ; NMR : 1,50 ppm (1H, d, J=3Hz), 2,05 ppm (1H, d, J=3Hz), 2,87 ppm
(1H,s), 2,20 ppm (6H, s), 3,57 ppm (3H, s).

3E: $\nu$(C=O) 1710 cm$^{-1}$ ; NMR : 0,54 ppm (2H, m), 1,90 ppm (1H, d, J=3Hz), 2,17 ppm (3H, s),
2,48 ppm (3H, s), 3,66 ppm (3H, s).

At first the coordination chemistry of this cyclopropenic ester seems thus to be very dif-
ferent from that of unfunctionalized cyclopropenes ; the ligands of the complexes obtained
here are simple ring opening isomers of the starting material. This process is not, howe-
ver, a simple isomerization induced by complexation. Complexation of the cyclopropenic
ester 1 with Fe$_2$(CO)$_9$ in methylene chloride at room temperature leads, after 18 hours, to
a 1:1 mixture of the carbonylation complexes 4 and 5 (80%). The isolated complex 4, after
refluxing in benzene for one hour, quantitatively produces complex 2. Complex 5, which is
slightly more stable than 4, behaves similarly to produce, in a non-stereospecific manner,
however, complexes 3Z and 3E :
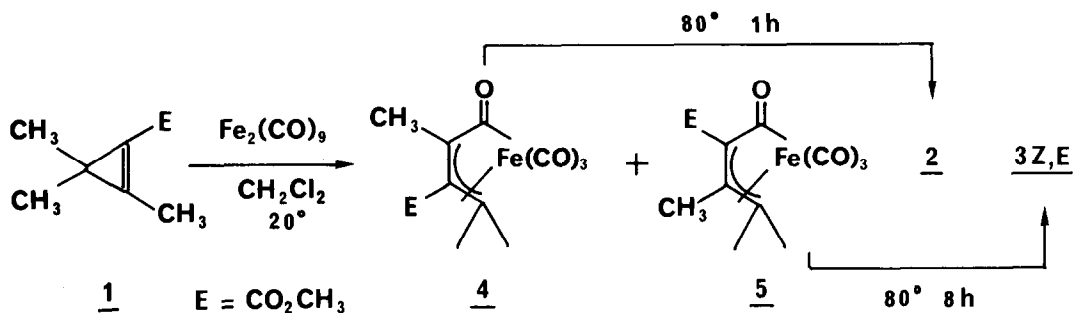


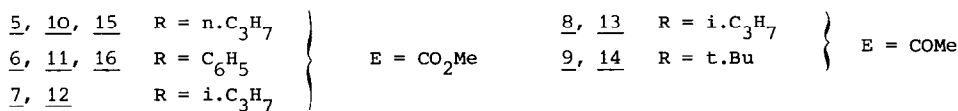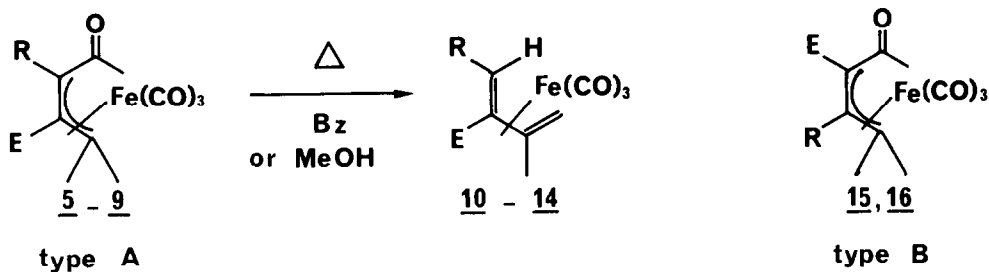4, 5 : separated by low pressure column chromatography (SiO$_2$).

4 : pale yellow crystals F = 40°C ; $\nu$(C=O) 1770 and 1725 cm$^{-1}$ ; NMR : four singlets at 1,23;
1,84 ; 1,92 and 3,94 ppm (each 3H).

5 : orange-yellow crystals F = 49°C ; $\nu$(C=O) 1780 and 1715 cm$^{-1}$ ; NMR : four singlets at
1,28 ; 1,92 ; 2,51 and 3,80 ppm (each 3H).

The formation of the diene complexes 2 and 3 from cyclopropene 1 results, therefore, not
from a simple isomerization and subsequent complexation but from the much more complicated
process of ring opening and carbonylation to vinylketene complexes followed by decarbonyla-
tion and hydrogen migration !

The lability of complex 4, as compared to the greater thermal stability of complex
5 or to the apparent stability of the unfunctionalized iron tricarbonyl vinylketene comple-
xes in the literature, is general for complexes bearing the carbomethoxyl or acetyl E sub-
stituent in the middle of the $\pi$-allylic ligand part (type A). Thus, the type A complexes
5 - 9 give quantitatively the diene complexes 10 - 14 by simple heating whereas the isomeric
complexes 15 and 16, which belong to the more stable type B (E substituent contiguous to the

cyclic carbonyl) again give mixtures where the sterically least favourable Z isomers predominate :



| 5, 10, 15 | R = n.C$_3$H$_7$ | | | | 8, 13 | R = i.C$_3$H$_7$ | |
| 6, 11, 16 | R = C$_6$H$_5$ | E = CO$_2$Me | | | 9, 14 | R = t.Bu | E = COMe |
| 7, 12 | R = i.C$_3$H$_7$ | | | | | | |

For complexes of type A the temperature where the decarbonylation is achieved up to 90% in 3 hours varies from less than 70°C for the complexes 4, 5 and 6 (R = CH$_3$, n.Pr, C$_6$H$_5$) to 80°C for the complexes 7 and 8 (R = i.Pr) to reach 110°C for the complex 9 (R = t.Bu). The decarbonylation rate thus clearly depends upon the size of the substituent R. A mechanism with an intermediate acyl hydrido complex such as that for aldehyde decarbonylations catalyzed by transition metal derivatives (8) is likely, especially since a similar rate variation was observed for the same substituents (9).

Clearly, since the presence of an electron-withdrawing substituent in the middle position of the π-allylic system makes the decarbonylation easier by activating the methylic hydrogens, the first step must indeed be the transfer of that hydrogen onto the metal :
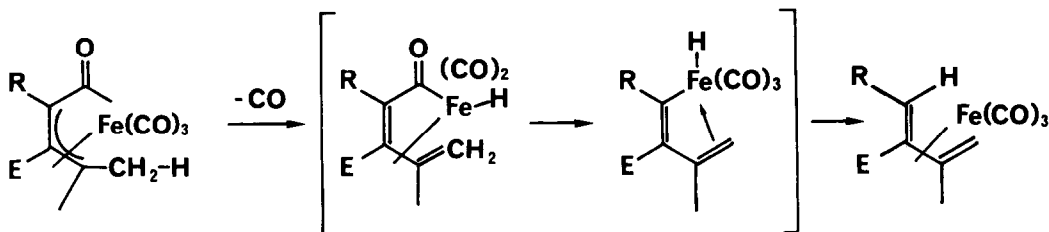


On the other hand, the fact that the sterically least favourable Z isomers like 3Z are preferentially obtained by thermolysis of complexes of type B can be rationalized if we admit the intermediate formation of heterodiene-iron tricarbonyl complexes.

Photochemical transformation into isoprenic diene complexes, starting with type B complexes, can also occur. The complex 17 solely formed from 3,3-dimethyl carbomethoxycyclopropene (1,6) thus gives a mixture of the isoprenic aldehyde complexes 18E and 18Z (∼1:1, overall yield 65%) after photolysis in benzene solution (10). These new complexes formal result from a [1,5] hydrogen shift. Similar sigmatropic shifts are responsible for the isomerization of uncomplexed methylated vinylketenes into dienals (11) but, unlike the present case, these reactions are not photochemical. Two consecutive [1,3] hydrogen shifts are, however, not involved as can be seen by deuteration. Again an iron hydrido complex

is a likely intermediate. The same photolysis in methanol solution leads to a completely different result since the diester 19 is now quantitatively isolated after work-up in presence of oxygen. The first step is therefore probably the rupture of the iron-acyl bond with formation of a free ketene.
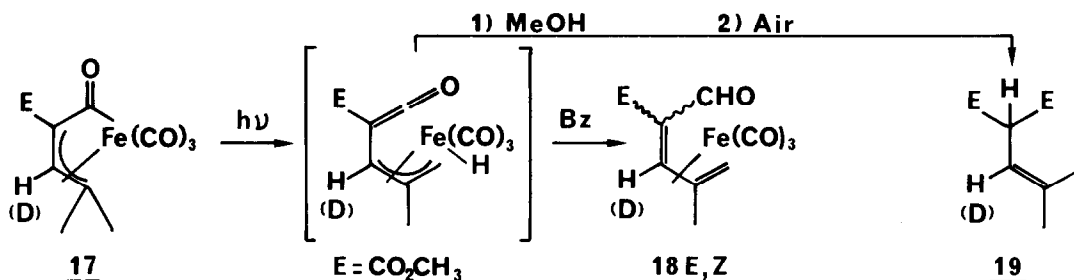


**17** orange-yellow crystals F = 84°C ; $\nu$(C=O) 1780 and 1710 cm$^{-1}$ ; NMR ($C_6D_6$/TMS) : 0,90 ppm (3H, s), 1,20 ppm (3H, s), 3,27 ppm (3H, s), 5,85 ppm (1H, large s).

**18** (one isomer) : $\nu$(C=O) 1705 and 1665 cm$^{-1}$ ; NMR ($C_6D_6$/TMS) : 1,30 ppm (1H, dd, J=1,5 and 3Hz), 1,76 ppm (1H,m), 1,47 ppm (3H, s), 3,28 ppm ( 3H, s), 5,73 ppm (1H,m), 9,90 ppm (1H, d, J=2Hz).

**18** (other isomer) : $\nu$(C=O) 1710 and 1670 cm$^{-1}$ ; NMR ($C_6D_6$/TMS) : 1,49 ppm (1H, m), 1,74 ppm (1H, m), 1,52 ppm (3H, s), 3,22 ppm (3H, s), 5,58 ppm (1H, m), 9,68 ppm (1H, large s).

**19** colourless liquid ; $\nu$(C=O) 1730 cm$^{-1}$ ; NMR : 1,69 ppm (3H, d, J=1,5Hz), 1,78 ppm (3H, d, J=1,5Hz), 3,74 ppm (6H, s), 4,28 ppm (Ha, d, Jab=10Hz), 5,48 ppm (Hb, dm, Jab=10Hz).

Both transformations described show that functionalized ($\eta^3$: $\eta^1$allylcarbonyl)iron tricarbonyl complexes are easily converted into diene-iron tricarbonyl complexes whenever the possibility of hydrogen migration exists, as here with the methyl substituents.

## REFERENCES AND NOTES.

1. Presented in part at the Journées de Chimie Organique de la Société Chimique de France (Palaiseau, 1979).
2. R.B. KING Inorg. Chem. 2, 642 (1963)
   M.G. NEWTON, N.S. PANTALEO, R.B. KING, C.K. CHU Chem. Comm. 1979, 10.
3. P. BINGER, B. CETINKAYA, C. KRUGER J. Organomet. Chem. 159, 63 (1978).
4. G. DETTLAF, U. BEHRENS, E. WEISS Chem. Ber. 111, 3019 (1978).
5. C. DIETRICH-BUCHECKER, M. FRANCK-NEUMANN Tetrahedron 33, 751 (1977).
6. M. FRANCK-NEUMANN, C. DIETRICH-BUCHECKER, A. KHEMISS : to be published in J. Organomet. Chem. ; L. RICARD, J. FISCHER : to be published in Acta Cryst.
7. All indicated products gave satisfactory microanalyses, IR (CHCl3) and NMR (CDCl3/TMS) spectra. The iron tricarbonyl complexes show all strong $\nu$ (C≡O) absorption bands at 2060 cm-1 (fine) and 1995-2000 cm$^{-1}$ (broad) in the IR.
8. M.C. BAIRD, C.J. NYMAN, G. WILKINSON J. Chem. Soc. (A) 1968, 348.
9. N.E. HOFFMANN, T. PUTHENPURACKAL J. Org. Chem. 30, 420 (1965).
10. Medium pressure mercury lamp Philips HPK 125 ; Pyrex glass filter ; 1 g complex 17 in 140 ml solvent, complete transformation ~5 hours. The complexes 18E and 18Z (yellow crystals) could not be obtained completely pure, being allways slightly contaminated by each other.
11. P. SCHIESS,C. SUTER Helv. Chim. Acta 54, 2636 (1971)
    P. SCHIESS, P. RADIMERSKI Angew. Chem. 84, 345 (1972).

(Received in UK 27 March 1981)