Trieneiron Tricarbonyl and Bisallyldi-iron Hexacarbonyl π-Complexes from Photolysis of Divinylcyclopropanes Induced by Iron Pentacarbonyl

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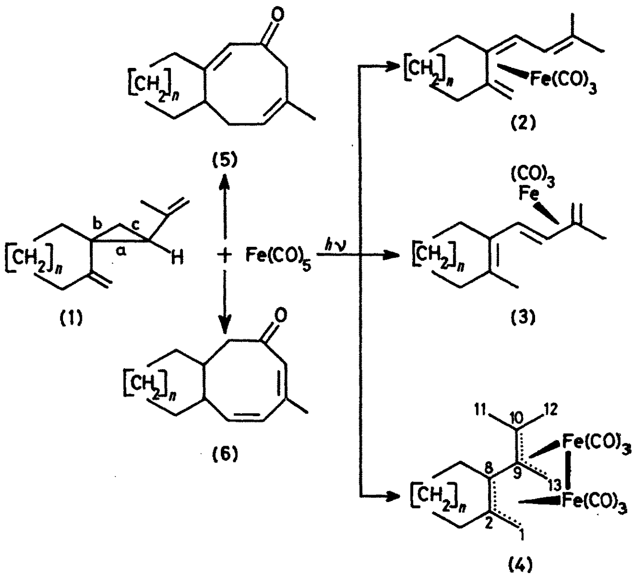
Summary The photolysis of *trans*-1-isopropenyl-4-methylenespiro[2.*x*]alkanes (**1**) ($x = 4,5$, or 6) in presence of $Fe(CO)_5$ at room temperature leads to formation (60%) of isomeric mononuclear irontricarbonyl π-complexes of linear trienes [(**2**) and (**3**)] and (10%) of a di-ironhexacarbonyl–bis-π-allyl complex of a branched triene (**4**).

IN a previous communication[1] we reported that the photolysis of *trans*-1-isopropenyl-4-methylenespiro[2.*x*]alkanes ($x = 4$, 5, or 6) in presence of $Fe(CO)_5$ at room temperature afforded a mixture comprising eight-membered-ring dienones, (**5**) and (**6**), and zerovalent iron complexes of formulae $[C_{n+10}H_{2n+14}{\cdot}Fe(CO)_3]$ and $[C_{n+10}H_{2n+14}{\cdot}Fe_2(CO)_6]$, respectively. This communication concerns the structures of these metal-containing products.



a; $n = 0$
b; $n = 1$
c; $n = 1$

Irradiation of a mixture of (**1**) ($n = 0$, 1, or 2) (10 mmol) and $Fe(CO)_5$ (40 mmol) in petroleum–ether (100 ml) for 4 h., under N_2 in a quartz apparatus by a Philips HPX 125 W lamp, followed by preparative t.l.c. (silica) afforded three fractions. The two of highest R_f values (*ca.* 0·9) comprised the metal-containing products, while the one of the lowest R_f values comprised metal-free bicyclic cyclo-octadienones, (**5**) (15%) and (**6**) (15%).[1]

^1H- and ^{13}C-N.m.r. analysis indicated that the first fraction essentially consisted of a 2:3-isomeric mixture of trieneirontricarbonyl π-complexes. These were shown to have structures (**2**) (36%) and (**3**) (24%) from: (i) elemental analysis of the top fraction indicating a ratio ligand: $Fe(CO)_3$ of 1:1; (ii) i.r. absorption bands (hexane) at 2040, 1980, and 1964 cm^{-1}; (iii) mass spectra exhibiting the corresponding molecular-ion peak in low intensity and peaks arising from successive losses of three carbonyls and one iron atoms;[2] and (iv) the 270 MHz ^1H-n.m.r. spectra ($CDCl_3$) indicating the presence of two sets of doublets at δ 0·56 and 1·21, corresponding to vinylic protons *endo* to the metal. The 180 MHz ^{13}C-n.m.r. spectra also exhibited double the number of carbons expected. Analysis of spin–spin decoupling together with ^1H–^{13}C coupling constants showed that the spectra were virtually the superimposed spectra of the two π-complexes, (**2**) and (**3**).

The minor metal-containing fraction (10%) was shown to be the triene–di-iron–hexacarbonyl bis-π-allyl complex (**4b**) (red crystals, m.p. 119—120 °C) on the basis of its analytical and spectral properties: (i) i.r. (KBr): 2055, 2015, 1992, 1889, 1999, and 1963 cm^{-1}; (ii) m/e 442 (9%) [M^{+}, $C_{12}H_{18}Fe_2(CO)_6$] and peaks at m/e 274 (100), 218 (96), and 162 (51%), arising from successive losses of 6CO, $Fe(CO)_6$, and $Fe_2(CO)_6$.[2] The same spectral cracking was shown by (**4a**) and (**4c**).

Table. ^{13}C N.m.r. spectral data of (**4b**) and (**4c**)

Compound	C(1)	C(2)	C(8)–C(9)-C(10)	C(11)	C(12)	C(13)	$^{2}J_{13}$	$^{2}J_{1}$	$^{2}J_{11-12}$	$^{2}J_{3-7}$
(**4b**)	44·1	106·7	80·0—86·7	30·4	25·2	37·4	157·0	157·0	127·0	*ca.* 124·0
(**4c**)	49·9	110·3	76·7—86·3	30·2	25·2	38·6	159·0	157·0	127·0	*ca.* 124·0

180 MHz ^{13}C-n.m.r. analysis showed that the ligands in (**4b**) and (**4c**) contained 12 and 13 carbon atoms, respectively. Six of these carbon atoms which pertain to two terminal methylenes and four quaternary carbon atoms are co-ordinated to the metal, while the other two carbons pertain to two vicinal methyl groups (see Table). The multiplicity of the metal-co-ordinated carbonyls is indicative of metal–metal bonding.[3] The stereochemistry followed from the ^{1}H-n.m.r. data (see Figure).

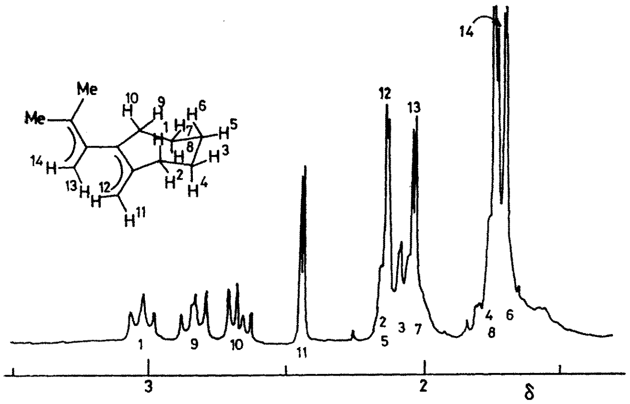
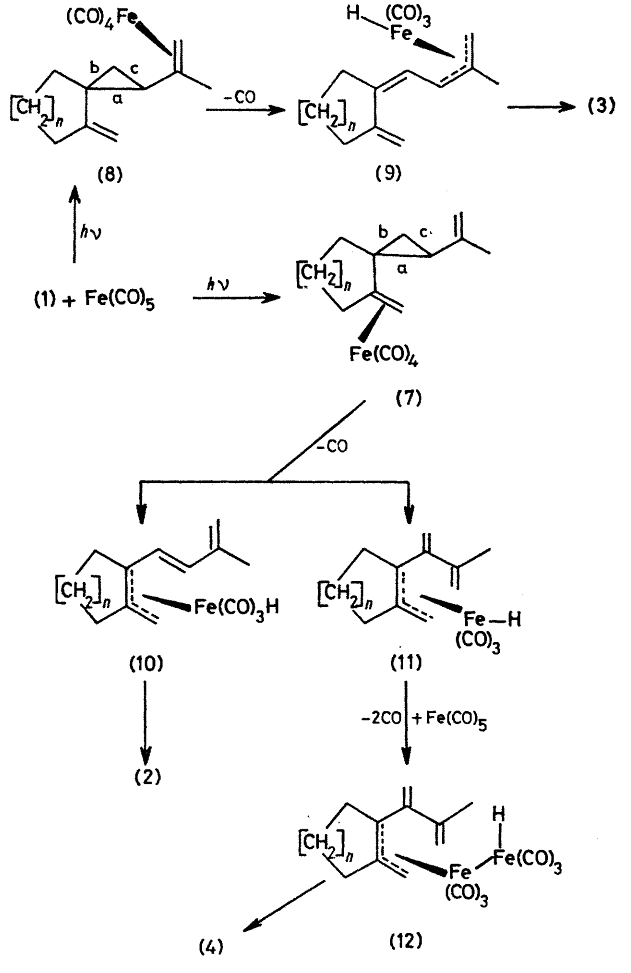


Figure. ^{1}H-N.m.r. spectrum of (**4c**) in $CDCl_3$ as determined on a Bruker WH-270-180 instrument.

The formation of the mononuclear π-complexes, (**2**) and (**3**) and of the bis-π-allyldi-ironhexacarbonyl complex (**4**) is thought to arise from two distinctly different reaction pathways. The predominant one is assumed to involve a metal-mediated breakage of the weakest cyclopropane σ-bond (a)† coupled with migration of a hydrogen across the ring (from the methylene group) to the metal.[4] This causes the hydrido–irontricarbonyl–π–allyl complex intermediates (**9**) or (**10**) to became unstable, probably because of a preference in the site of attachment of the metal to either vinylic group in the substrate (**1**): *i.e.* (**1**) → (**8**) → (**9**) as opposed to (**1**) → (**7**) → (**10**).

Hydride migration from the metal to the terminal non-co-ordinated olefinic methylene groups, (**9**) → (**3**) and (**10**) → (**2**), affords the linear triene π-complexes (**3**) and (**2**). An alternative breakage of the minor cyclopropane σ-bond (bond b) is accompanied with migration of the hydrogen which is attached to the methine carbon across the cyclopropane ring to yield a hydrido–tricarbonyliron–π–allyl complex of structure (**11**). This is prone to insert a $Fe(CO)_4$



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† The pronounced tendency of the multi-σ,π-electron system in (**1**) to undergo cycloaddition with tetracyanoethylene (S. Sarel and M. Langbeheim, *J.C.S. Chem. Comm.*, 1977, 593) and *N*-chlorosulphonylisocyanate (M. Langebeheim and S. Sarel, *Tetrahedron Letters*, 1978, 2613) indicates that the C–C σ-bond a of the cyclopropane ring in (**1**) is electronically richer than either the b or c bonds and that it breaks more easily. It has already been argued that carbonyliron prefers to insert into the weakest C–C σ-bond of the cyclopropane ring (R. M. Moriarty, C. L. Yeh, K. N. Chen, E. L. Yeh, K. C. Ramey, and C. W. Jefford, *J. Amer. Chem. Soc.*, 1973, **95**, 4756; see also: R. Hoffmann and W. D. Stohrer, *ibid.*, 1971, **93**, 6941).

to engender a hydrido–di-ironhexacarbonyl–π-allyl complex of structure (**12**) which tends to become stabilized by transformation into the crystalline non-linear di-π-allyl di-iron complex of structure (**4**). Of particular interest is the observed preference of the hydrogen to migrate to the distant vinylic methylene to produce a new methyl group rather than to an internal unsaturated carbon to form either a methine or a new methylene group. This sheds a new light on the well documented $Fe(CO)_5$-induced vinylcyclopropane→diene rearrangement.[5]

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[1] S. Sarel and M. Langbeheim, *J.C.S. Chem. Comm.*, 1977, 827.

[2] R. Victor, J. Deutsch, and S. Sarel, *J. Organometallic Chem.*, 1974, **71**, 65.

[3] L. Kruczynsky and J. Takats, *J. Amer. Chem. Soc.*, 1974, **96**, 933; O. A. Gansow, A. R. Burke, and W. D. Vernon, *ibid.*, 1972, **94**, 2551; K. Bachmann, Doctoral Dissertation, University of Zurich, 1977.

[4] *Cf.* T. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, 1971, **93**, 1049 and references cited therein.

[5] S. Sarel, R. Ben-Shoshan, and B. Kirson, *J. Amer. Chem. Soc.*, 1965, **87**, 2517; *Israel J. Chem.*, 1972, **10**, 787; S. Sarel, *Accounts Chem. Res.*, 1978, **11**, 204 and references cited therein.