Ring Opening of 2,3-Bis(hydroxymethyl)methylenecyclopropanes with [Fe$_2$(CO)$_9$]; the Molecular Structure of a 1,4-Diene Complex of Iron(0), Tricarbonyl-η^4-(3-methylene-4-vinyldihydrofuran-2(3*H*)-one)iron

By Michael Green,* Russell P. Hughes, and Alan J. Welch
(*Department of Inorganic Chemistry, University of Bristol, Bristol* BS8 1TS)

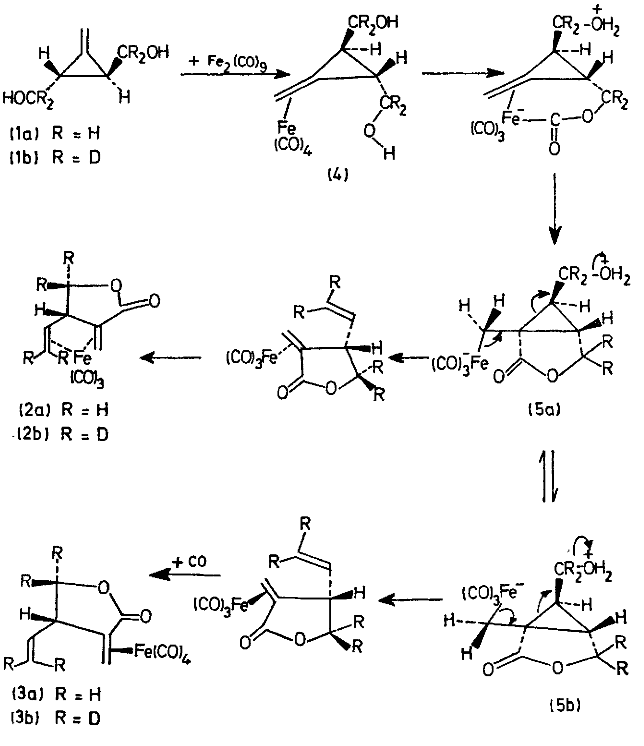
Summary *trans*- or *cis*-2,3-Bis(hydroxymethyl)methylenecyclopropanes react with [Fe$_2$(CO)$_9$] to yield ring-opened products containing the 3-methylene-4-vinyldihydrofuran-2(3*H*)-one ligand; η^2- and η^4-complexes of this ligand have been characterised, the latter by *X*-ray crystallography.

Reactions of *trans*- or *cis*-bis(methoxycarbonyl)methylenecyclopropanes with [Fe$_2$(CO)$_9$] have been shown to yield (η^2-methylenecyclopropane)Fe(CO)$_4$ complexes of remarkable thermal stability, rearrangement to substituted (η^4-1,3-diene)Fe(CO)$_3$ complexes, *via* an opening of the 1,2-bond of cyclopropane ring, occurring only slowly in refluxing toluene.[1,2] In contrast, reactions with [Fe$_2$(CO)$_9$] of methylenecyclopropanes containing phenyl substituents occur readily *via* cleavage of the 2,3-bond, to yield substituted (trimethylenemethane)Fe(CO)$_3$ complexes.[3] We now report a particularly facile ring-opening reaction of a methylenecyclopropane derivative by [Fe$_2$(CO)$_9$], in which cleavage of the ring occurs at the 1,2-bond.

trans-2,3-Bis(hydroxymethyl)methylenecyclopropane (**1a**)[4] reacted smoothly with [Fe$_2$(CO)$_9$] (16 h; 20°; Et$_2$O) to yield, as the major product (48% yield) [(**2a**), m.p. 104—105°, ν_{CO}(hexane) 2056, 2006, 1976, and 1760 cm^{-1}], as air-stable orange crystals. A single-crystal *X*-ray crystallographic study of (**2a**) established the structure shown in the Figure. Complex (**2a**) represents the first example of an η^4-1,4-diene complex of iron(0) in which the olefinic ligands are not incorporated into a ring system.[5,6]

A minor reaction product (16%) was [(**3a**), m.p. 76—77°, ν_{CO} (hexane) 2103, 2039, 2015, 1997, and 1756 cm^{-1}] obtained as pale yellow crystals. Notably, the yield of (**3a**) was greatly improved (30%) by carrying out the original reaction under an atmosphere of CO. Preliminary

X-ray crystallographic results for (**3a**) show that the $[Fe(CO)_4]$ unit is attached to the vinylidene olefin of the ligand on the opposite face of the lactone ring system to the pendant vinyl function; η^4-co-ordination in (**3a**) is thus sterically precluded.[7]



SCHEME

Reaction of $[Fe_2(CO)_9]$ with the deuterium labelled methylenecyclopropane (**1b**) yielded the analogous complexes (**2b**) and (**3b**), in which no deuterium scrambling had occurred, as evidenced by ^1H n.m.r. spectroscopy. A similar reaction of $[Fe_2(CO)_9]$ with *cis*-bis(hydroxymethyl)-methylenecyclopropane[4] also yielded (**2a**) and (**3a**); the ring-opening reaction and product stereochemistry are therefore independent of the substituent stereochemistry in the starting material.

Complexes (**2a**) and (**3a**) are not thermally interconvertible, although both rearrange under mild conditions *via* extremely regiospecific H-shifts.[8] A plausible mechanism for the formation of (**2a**) and (**3a**) is shown in the Scheme, and presumably proceeds *via* formation of an intermediate η^2-bonded methylenecyclopropane complex (**4**);[1,2] molecular models show the *endo*-CH_2OH group to be ideally situated for an intramolecular nucleophilic attack on a co-ordinated CO,† which together with intramolecular cyclisation generates the lactone ring system (**5**) in which the $Fe(CO)_3$ system is σ-bonded to a cyclopropylmethyl group, which undergoes a facile ring-opening reaction to produce the 3-methylene-4-vinyldihydrofuran-2(3*H*)-one ligand. It is noteworthy that the detailed configuration of the transition state for this ring-opening reaction (**5a** or **5b**) controls whether the iron atom is situated on the same, or on the opposite, face of the lactone to the vinyl olefin, and consequently whether the final product is (**2**) or (**3**). The mechanism also accounts for the formation of (**2**) and (**3**) from either the *trans*- or *cis*-bis(hydroxymethyl)methylenecyclopropane, since the stereochemistry of one of the ring-carbons must be lost in the ring-opening process.‡ Notably, the stereochemistry of the other ring carbon must be retained; this feature has been verified by use of optically active (**1a**).[8]

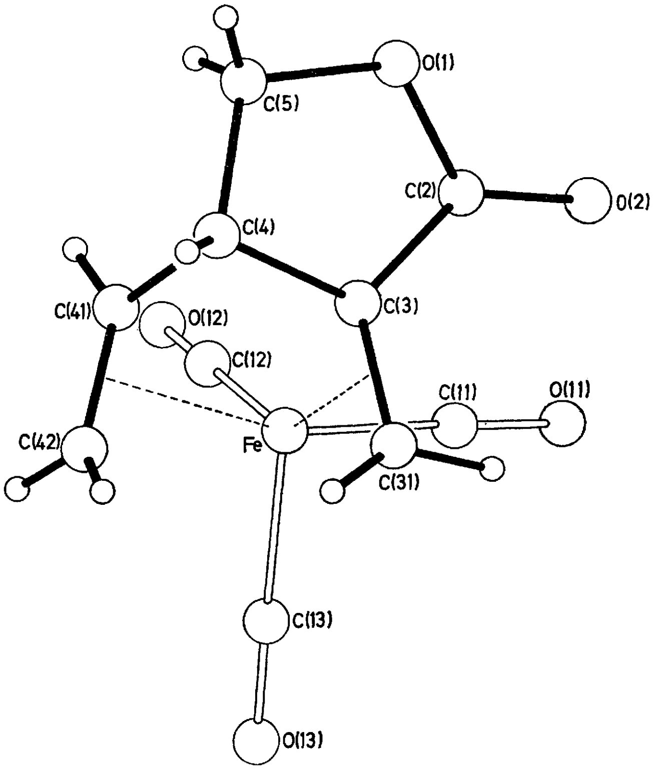


FIGURE. Perspective view of *X*-ray structure of (**2a**). *Crystal data:* $C_{10}H_8FeO_5$, $M = 264{\cdot}02$, triclinic, $a = 7{\cdot}745(5)$, $b = 6{\cdot}787(3)$, $c = 9{\cdot}873(4)$ Å, $\alpha = 96{\cdot}46(3)$, $\beta = 86{\cdot}79(4)$, $\gamma = 94{\cdot}05(4)^\circ$, $U = 513{\cdot}8(4)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1{\cdot}706$, $\mu(\text{Mo-}K_\alpha) = 15{\cdot}1\ \text{cm}^{-1}$. $R = 0{\cdot}029$ for 1435 reflections to $2\theta = 50^\circ$ (Syntex $P2_1$ diffractometer). Important bond lengths are Fe–C(11), 1·779(4); Fe–C(12), 1·803(4); Fe–C(13), 1·789(4); Fe–C(3), 2·114(3); Fe–C(31), 2·105(4); Fe–C(41), 2·205(4); Fe–C(42), 2·201(4); C(3)–C(31), 1·402(5); C(41)–C(42), 1·369(6) Å.

The facility of the methylenecyclopropane ring-openings reported here, in contrast with the results of Whitesides and Slaven,[1] underlines the requirement for either an internal,

---

† Attacks by alkoxide ions on co-ordinated CO molecules are well known, though not under the mild, non-basic, conditions reported here. It is possible that the lack of a positive entropy term in this situation, due to the forced proximity of CO and CH_2OH, lowers the overall activation energy for nucleophilic attack.

‡ The intermediate analogous to (**4**), arising from the *cis*-bis(hydroxymethyl)methylenecyclopropane must have both CH_2OH groups *endo*- with respect to the metal for this mechanism to operate (see ref. 2).

or external, nucleophile to attack the co-ordinated methylenecyclopropane and generate a substituted cyclopropylmethyl–metal intermediate in order for 1,2-cleavage to occur.[9]

Finally, it should be noted that this novel iron-promoted transformation of (**1**) into a substituted 3-methylenedihydrofuran-2(3*H*)-one ligand may prove a useful route into this skeletal system; compounds containing α-methylene-γ-lactone units are important *in vivo* antitumour agents.[10]

Acknowledgement is made to the S.R.C. for financial support.

(*Received, 3rd April* 1975; *Com.* **384**.)

[1] T. H. Whitesides and R. W. Slaven, *J. Organometallic Chem.*, **1974**, **67**, 99,

[2] T. H. Whitesides, R. W. Slaven, and J. C. Calabrese, *Inorg. Chem.*, 1974, **13**, 1895.

[3] R. Noyori, T. Nishigama, and H. Takaya, *Chem. Comm.*, 1969, 89.

[4] J. J. Gajewski, *J. Amer. Chem. Soc.*, 1971, **93**, 4450.

[5] J. Ashley-Smith, D. V. Howe, B. F. G. Johnson, J. Lewis, and I. E. Ryder, *J. Organometallic Chem.*, 1974, **82**, 257.

[6] B. F. G. Johnson, J. Lewis, T. W. Matheson, I. E. Ryder, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1974, 269.

[7] B. Chisnall, P. Woodward, and A. J. Welch, unpublished observations.

[8] M. Green and R. P. Hughes, to be published.

[9] M. Green and R. P. Hughes, *J.C.S. Chem. Comm.*, 1974, 686.

[10] S. M. Kupchan, M. A. Eakin, and A. M. Thomas, *J. Medicin. Chem.*, 1971, **14**, 1147.