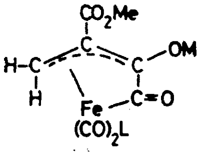
Reaction of η^4-Vinylketen Iron Complexes with Carbon Monoxide or Tertiary Phosphines. Intramolecular Carbonylation–Decarbonylation Rearrangement of the Vinylketen Skeleton Induced by Co-ordination of a Ligand: *X*-Ray Crystal Structure of $\overline{\mathrm{FeCOCH_2C(CO_2Me){=}C}}\mathrm{(OMe)(CO)_3(PPhMe_2)}$

By Take-aki Mitsudo,* Teruhiko Sasaki, Yoshihisa Watanabe, and Yoshinobu Takegami
(*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto, Japan*)

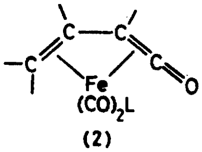
and Kazumi Nakatsu,* Kenji Kinoshita, and Yoshiki Miyagawa
(*Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo 662, Japan*)

Summary The (η^4-vinylketen)tricarbonyliron complexes (**1c**) and (**1d**) react with L′ (L′ = CO or PR_3) to afford the ferracyclopent-2-en-5-ones (**4**)—(**6**) by an unusual intramolecular carbonylation–decarbonylation rearrangement of the vinylketen skeleton, induced by the co-ordination of L′; the structure of (**5**) was determined by *X*-ray analysis.

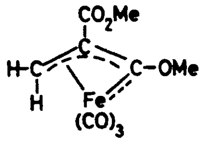
Recently the (η^4-vinylketen)iron complexes (**1a**) and (**1b**) were prepared by the reaction of (η^3-vinylcarbene)tricarbonyliron (**3**) with L (L = CO or PPh_3); *X*-ray molecular analysis of (**1b**) showed that structure (**1**) is preferable to (**2**).[1]†



(1) a; L = CO
b; L = PPh_3
c; L = PPh_2Me
d; L = $PPhMe_2$

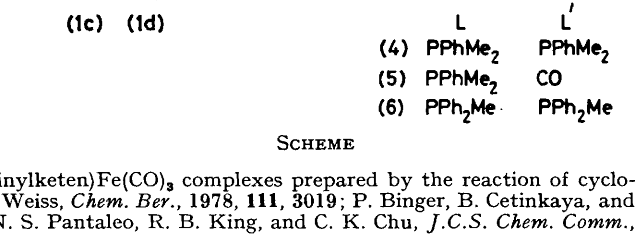


(2)



(3)

We now report an unusual intramolecular carbonylation–decarbonylation rearrangement of the η^4-vinylketen skeleton of (**1c**) (L = PPh_2Me) and (**1d**)‡ (L = $PPhMe_2$) induced by the co-ordination of an additional ligand L′ (L′ = CO, PPh_2Me, or $PPhMe_2$) affording the novel ferracyclopent-2-en-5-ones (**4**)—(**6**) (Scheme).



(1c) (1d)

	L	L′
(4)	$PPhMe_2$	$PPhMe_2$
(5)	$PPhMe_2$	CO
(6)	PPh_2Me	PPh_2Me

Scheme

---

† After the publication of ref. 1, the molecular structure of (η^4-vinylketen)$Fe(CO)_3$ complexes prepared by the reaction of cyclopropenes with $Fe_2(CO)_9$ was reported: G. Dettlaf, U. Behrens, and E. Weiss, *Chem. Ber.*, 1978, **111**, 3019; P. Binger, B. Cetinkaya, and C. Krueger, *J. Organometallic Chem.*, 1978, **159**, 63; M. G. Newton, N. S. Pantaleo, R. B. King, and C. K. Chu, *J.C.S. Chem. Comm.*, 1979, 10.

‡ (**1c**) and (**1d**) were prepared by the method similar to that for (**1b**) both in *ca.* 70% yield. Analytical and spectral data of these complexes were fully consistent with the structures given. The reaction of (**1a**) or (**1b**) with CO or PR_3 was very slow and no product was isolated.

Treatment of (**1d**) with 1 mol. equiv. of dimethylphenylphosphine or carbon monoxide (1 atm) in methylene dichloride at room temperature for several hours followed by recrystallization from light petroleum–diethyl ether gave yellow crystals of the 1 : 1 adducts (**4**) and (**5**),§ in 45 and 65% yields, respectively. The reaction of (**1c**) with methyldiphenylphosphine also gave the 1 : 1 adduct (**6**) in 13% yield. On the basis of the spectral data of (**4**)—(**6**), the formation of a novel series of ferracyclopent-2-en-5-ones was inferred and the complete structural characterization of (**5**) was accomplished by an *X*-ray single crystal analysis, the result of which is shown in the Figure. *Crystal data*: $C_{18}H_{19}FeO_7P$, $M = 434{\cdot}2$, monoclinic, space group $P2_1/n$, $a = 13{\cdot}393(4)$, $b = 16{\cdot}906(3)$, $c = 8{\cdot}774(2)$ Å, $\beta = 93{\cdot}10(2)°$, $Z = 4$, $D_c = 1{\cdot}454$ g cm^{-3}. Least-squares calculations on 2690 non-zero independent reflections (Mo-K_α radiation) gave an R value of 4·2%. The geometry of the co-ordination is pseudo-octahedral [$\angle$P–Fe–C(16) 167·9(1)°]. Both C(2) and C(5) are in the *cis* positions about the dimethylphenylphosphine. The phenyl group is oriented towards the ferracyclopentenone ring, which is not planar but envelope-like; C(2)=O(1) deviates from the plane Fe–C(5)–C(4)–C(3).¶ The molecule is thought to be formed by the co-ordination of carbon monoxide to the iron atom accompanied by the migratory insertion of carbon monoxide into the methylene carbon–iron bond of (**1d**) and by the decarbonylation of the acyl group in (**1d**).

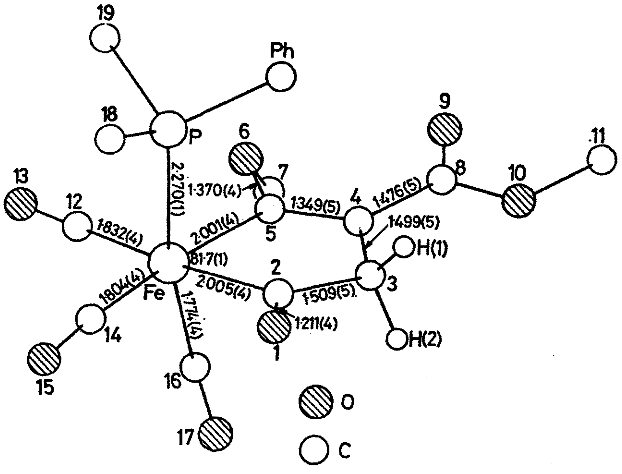


FIGURE. Molecular structure of $\overline{\mathrm{FeCOCH_2C(CO_2Me)=C}}$(OMe)-(CO)$_3$(PPhMe$_2$) (**5**). The phenyl group is not shown except for the carbon atom bonded to the phosphorus atom. Important distances (Å) and angles (°) are also given.

On the basis of the *X*-ray analysis and the following spectral observations for the complexes (**4**) and (**6**), the geometry of (**4**) and (**6**) was deduced to be as shown in the Scheme: (i) ^{1}H and ^{13}C n.m.r. spectra of (**4**) and (**6**) exhibited nonequivalence of the methyl groups of the methylphenylphosphines and the methylene protons showing the absence of a plane of symmetry in the complexes; (ii) the ^{13}C n.m.r. signals for the Fe–C(: O)– groups in (**4**) and (**6**) were triplets [$J_{\text{C–P}}$(L), $J_{\text{C–P}}$(L′) = 23·2 and 21·5 Hz, respectively].

A plausible reaction route can be deduced by comparison of the molecular structures of (**1**) and (**4**)—(**6**) (Scheme). The attack of the ligand L′ on the iron atom from the plane C(2)–C(16)–L (see Scheme) in (**1**) would cause movement of C(16)O, inducing fission of the C(3)–Fe bond and formation of the C(2)–C(3) bond accompanied by cleavage of the C(5)–C(12) bond.

Although several examples of ferracyclopentanones[2,3] and ferracyclopentenones[4–6] have been prepared and characterised, compounds (**4**)—(**6**) are the first examples of fully characterized ferracyclopent-2-en-5-ones.

(*Received*, 15*th March* 1979; *Com.* 261.)

---

§ Satisfactory analytical and spectral data for the complexes have been obtained. Detailed spectroscopic data for (**4**)—(**6**), which are completely consistent with the *X*-ray structure will be reported in a full paper.

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] T. Mitsudo, T. Sasaki, Y. Watanabe, Y. Takegami, S. Nishigaki, and K. Nakatsu, *J.C.S. Chem. Comm.*, 1978, 252.
[2] Y. Watanabe, T. Mitsudo, M. Yamashita, M. Tanaka, and Y. Takegami, *Chem. Letters*, 1973, 475.
[3] V. Heil, B. F. G. Johnson, J. Lewis, and D. J. Thompson, *J.C.S. Chem. Comm.*, 1974, 270.
[4] F. A. Cotton, J. M. Troup, W. E. Billups, L. P. Lin, and C. V. Smith, *J. Organometallic Chem.*, 1975, **102**, 345.
[5] R. C. Petterson, J. L. Cihonski, F. R. Young, and R. A. Levenson, *J.C.S. Chem. Comm.*, 1975, 370.
[6] T. Mitsudo, H. Watanabe, Y. Watanabe, and Y. Takegami, *J.C.S. Chem. Comm.*, 1979, 265.