

## Carbonylation of the $\eta^3$ -Vinylcarbene Ligand. Synthesis and X-Ray Crystal and Molecular Structure of an ' $\eta^4$ -Vinylketen' Iron Complex

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**Summary** In the reaction of  $(\eta^3\text{-vinylcarbene})\text{Fe}(\text{CO})_3$  with triphenylphosphine or carbon monoxide (L), the  $\eta^3$ -vinylcarbene ligand was carbonylated affording an apparent ' $\eta^4$ -vinylketen complex,' which was shown by X-ray analysis to have the alternative  $(\eta^3\text{-allyl} + \eta^1\text{-acyl})\text{Fe}^{\text{II}}(\text{CO})_2\text{L}$  structure.

RECENTLY the first example (1) of an  $(\eta^3\text{-vinylcarbene})\text{iron}$  complex was prepared<sup>1</sup> and its structure was established by

X-ray analysis.<sup>2</sup> We now report an unusual carbonylation of the  $\eta^3$ -vinylcarbene ligand of (1) affording an ' $\eta^4$ -vinylketen' iron complex and the molecular structure of this complex.

Treatment of (1) with 1 mol. equiv. of triphenylphosphine or carbon monoxide (1 atm) in methylene dichloride at room temperature for several hours gave yellow crystals of (2a) and (2b), respectively,<sup>†</sup> after evaporation of the solvent, in 78 and 38% yield.

<sup>†</sup> Satisfactory analytical data for the complexes have been obtained. (2a): m.p. 113 °C, *M* 484; i.r. ( $\text{CHCl}_3$ ) 2020vs and 1968vs; (KBr) 1713 s, br and 1705 m  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. [ $(\text{CD}_3)_2\text{CO}$ ,  $\tau$ ,  $J/\text{Hz}$ ] 9.77 [ $\text{H}^1$ , t,  $J(\text{H}^1\text{--H}^2)$  2.2,  $J(\text{H}^1\text{--P})$  2.2], 7.57 [ $\text{H}^2$ , dd,  $J(\text{H}^1\text{--H}^2)$  2.2,  $J(\text{H}^2\text{--P})$  1.0], 6.93 (OMe, s), 6.23 ( $\text{CO}_2\text{Me}$ , s), 2.2–2.8 (Ph, m);  $^{13}\text{C}$  n.m.r. ( $\delta$ ,  $\text{Me}_4\text{Si}$ ,  $\text{CDCl}_3$ ,  $J/\text{Hz}$ ) 24.4 ( $\text{C}^5$ , t,  $J_{\text{C--H}}$  163.6), 85.5 ( $\text{C}^4$ , s), 103.5 ( $\text{C}^3$ , s), 167.4 (ester  $\text{C=O}$ , s), 210.0 ( $\text{Fe--C--O}$ , d,  $J_{\text{C--P}}$  17.1), 214.0 ( $\text{Fe--C--O}$ , d,  $J_{\text{C--P}}$  12.2), and 241.7 [ $\text{Fe--C}(\text{:O})\text{--}$ , d,  $J_{\text{C--P}}$  7.3] p.p.m. Further detailed spectroscopic data for (2a) and (2b), which are fully in consistent with the X-ray molecular structure, will be reported in a full paper. Expected products such as  $(P\text{-ylide})\text{M}(\text{CO})_n$  and  $(\text{vinylcarbene})\text{M}(\text{CO})_n\text{L}$  (H. Fischer and E. O. Fischer, *Chem. Ber.*, 1974, 107, 673) could not be detected. 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.

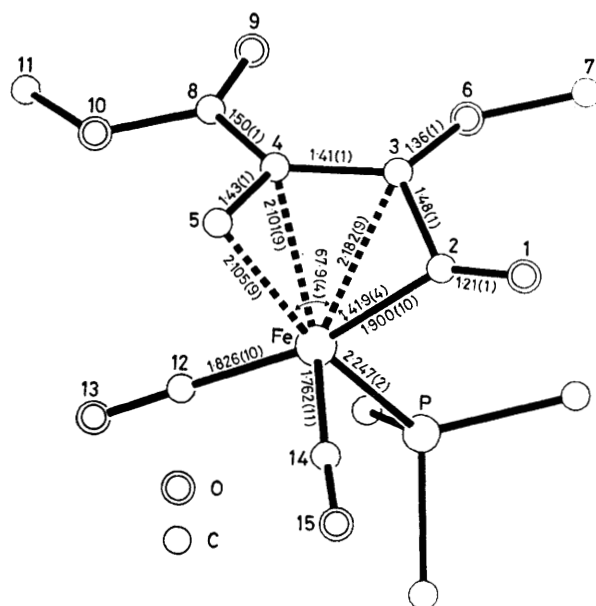


FIGURE. Stereochemistry of the ( $\eta^3$ -allyl +  $\eta^1$ -acyl)Fe<sup>II</sup>(CO)<sub>2</sub>PPh<sub>3</sub> complex (**2a**). Phenyl groups are not shown for clarity, except for the three carbon atoms bonded to the P atom. Only one of the two crystallographically independent molecules is illustrated. Important distances (Å) and angles (°) (averaged) are also given.  $\angle$  C(3)–C(4)–C(5) 115.3(9), C(2)–C(3)–C(4) 111.1(8), C(3)–C(2)–Fe 79.3(6)°.

The present carbonylation of the  $\eta^3$ -vinylcarbene ligand supports the proposal for the formation of keten in the reaction of (phenylalkoxycarbene)pentacarbonylchromium with vinyl compounds under pressure in carbon monoxide (150 atm).<sup>9</sup>

(Received, 24th November 1977; Com. 1207.)

<sup>9</sup> B. Doerer and E. O. Fischer, *Chem. Ber.*, 1974, **107**, 2683.