

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

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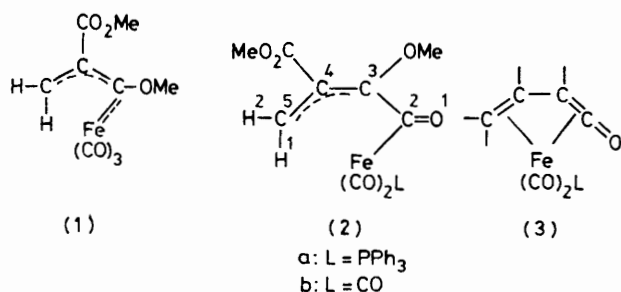
Summary In the reaction of $(\eta^3\text{-vinylcarbene})\text{Fe}(\text{CO})_3$ with triphenylphosphine or carbon monoxide (L), the η^3 -vinylcarbene ligand was carbonylated affording an apparent ' η^4 -vinylketen complex,' which was shown by X-ray analysis to have the alternative $(\eta^3\text{-allyl}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

RECENTLY the first example (1) of an $(\eta^3\text{-vinylcarbene})\text{iron}$ complex was prepared¹ and its structure was established by

X-ray analysis.² We now report an unusual carbonylation of the η^3 -vinylcarbene ligand of (1) affording an ' η^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,[†] after evaporation of the solvent, in 78 and 38% yield.

[†] Satisfactory analytical data for the complexes have been obtained. (2a): m.p. 113 °C, *M* 484; i.r. (CHCl_3) 2020 vs and 1968 vs; (KBr) 1713 s, br and 1705 m cm^{-1} ; ^1H n.m.r. [$(\text{CD}_3)_2\text{CO}$, τ , J/Hz] 9.77 [H^1 , t, $J(\text{H}^1\text{-H}^2)$ 2.2, $J(\text{H}^1\text{-P})$ 2.2], 7.57 [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 (CO_2Me , s), 2.2–2.8 (Ph, m); ^{13}C n.m.r. (δ , Me_4Si , CDCl_3 , J/Hz) 24.4 (C^5 , t, $J_{\text{C-H}}$ 163.6), 85.5 (C^4 , s), 103.5 (C^3 , s), 167.4 (ester C=O, s), 210.0 (Fe-C-O, d, $J_{\text{C-P}}$ 17.1), 214.0 (Fe-C-O, d, $J_{\text{C-P}}$ 12.2), and 241.7 [$\text{Fe-C}(\text{:O})$ -, 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*-ylide) $\text{M}(\text{CO})_n$ and (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.



X-Ray analysis of (2a) revealed the novel molecular arrangement shown in the Figure. *Crystal data*: C₂₇H₂₃FeO₆P, *M* = 530.3; monoclinic, space group *P*2₁/*c*; *a* = 13.926(2), *b* = 10.227(2), *c* = 35.835(7) Å, β = 101.81(2)°; *Z* = 8 (two independent molecules in the cell); *D*_m = 1.410 g cm⁻³. 5473 non-zero independent reflections (Mo-*K*_α radiation) were refined by standard heavy atom procedures to a current conventional *R* value of 8.0%. The two independent molecules are very similar to each other except for the orientation of the CO₂Me groups. The molecules are formed by the co-ordination of triphenylphosphine to the iron atom accompanied by the insertion of one CO molecule into the iron-carbene carbon bond of (1). The complex appears to contain a stabilized vinylketen skeleton. However, the following findings show that the complex can be best described as a novel (η³-allyl + η¹-acyl)-Fe^{II} system (2a) rather than an (η⁴-vinylketen)Fe⁰ complex (3). (i) The bond lengths C(3)-C(4) and C(4)-C(5) (1.41 and 1.43 Å) are in the range of those found in known (η³-allyl)Fe complexes.³ (ii) The C(2)-C(3) bond (1.48 Å) is longer than typical co-ordinated carbon-carbon double bonds and its length is typical of C(*sp*²)-C(*sp*²) single bonds.⁴ (iii) The C(2)-Fe bond length (1.90 Å) is much shorter than that expected for a normal π-complex. It is also shorter than normal acyl-Fe bond lengths (1.96-1.97 Å)⁵ and is comparable to that found in [(PPh₃)₂N]⁺[(η³-acryloyl)Fe(CO)₃]⁻ (1.897 Å).⁶

Although η⁴-vinylketen metal complexes were claimed to be formed in low yields (<10%) in the reaction of Fe₂-

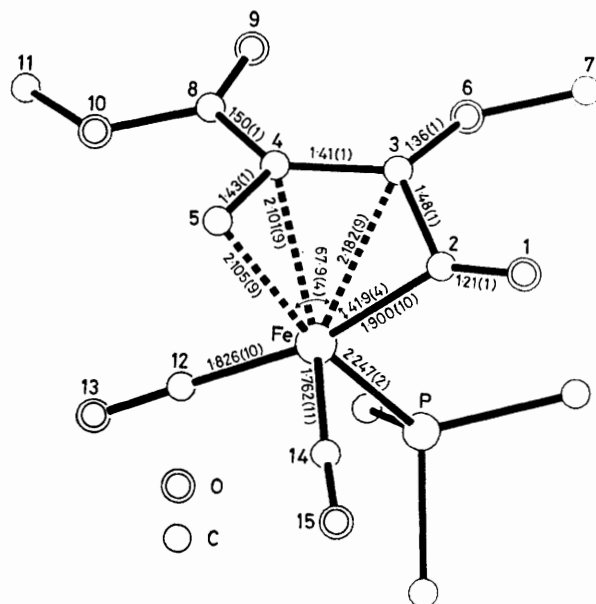


FIGURE. Stereochemistry of the (η³-allyl + η¹-acyl)Fe^{II}(CO)₂-PPh₃ complex (2a). Phenyl groups are not shown for clarity, except for the three carbon atoms bonded to the P atom. Only one of the two crystallographically independent molecules is illustrated. Important distances (Å) and angles (°) (averaged) are also given. ∠ 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)°.

(CO)₉ with cyclopropenyl compounds⁷ or 1-chloro-2-methoxypropane,⁸ their structures have not so far been established. These complexes would probably have structures similar to (2a).

The present carbonylation of the η³-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).⁹

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