

Addition of Alkenes to Tricarbonyl(vinylketene)iron(o) Complexes and the Synthesis of Cyclopropanes

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The tricarbonyl(vinylketene)iron(o) complex **1** reacts with electron-poor alkenes to give decarbonylated adducts **3** and these are oxidised to tetrasubstituted cyclopropanes **4** using CAN; an X-ray crystal structure analysis of the adduct formed from **1** and dimethyl fumarate define its relative stereochemistry.

The high levels of reactivity exhibited by ketenes and vinylketenes combined with the frequent postulation of metal-bound ketenes and vinylketenes as reaction intermediates,^{1,2} renders the reactivity of isolable metal-bound vinylketenes of considerable interest.^{3,4} We are currently interested in the fundamental reactivity of easily accessible and highly stable iron-centred vinylketene complexes and to date we have reported the results of their reactions with isonitriles,⁵ phosphonoacetate anions,⁶ nucleophiles⁷ and alkynes.⁸⁻¹⁰ In view of current interest in (a) the reactions that take place between *in situ* generated chromium-centred vinylketene complexes and alkenes,¹¹ and (b) the reactivity of *in situ* generated chromium carbene complexes towards alkenes,¹² we wish to report herein how tricarbonyl(vinylketene)iron(o) complexes react with alkenes.[†]

Our initial studies focussed on the reaction between tricarbonyl(3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(o) **1** and dimethyl maleate **2a**. A solution of complex **1** and 2 equiv. of dimethyl maleate in toluene was heated at reflux under an atmosphere of nitrogen for 3 d. Filtration of the product mixture through a short column of deactivated alumina using diethyl ether as eluent, followed by column chromatography (SiO₂; diethyl ether:40–60 light petroleum, 1:19) and crystallisation gave golden yellow air stable crystals. These were identified, on the basis of their microanalytical and spectroscopic data,[‡] as a decarbonylated adduct formed

from the complex and the alkene. The connectivity and relative stereochemistry of the decarbonylated adduct were elucidated by an X-ray crystal structure analysis[§] and the yield of the novel adduct **3a** was calculated to be 53%.

Reaction of complex **1** with dimethyl fumarate **2b** under identical conditions to those used in the dimethyl maleate experiment gave a 54% yield of adduct **3b**, the relative stereochemistry of which was also determined by X-ray crystallography (Fig. 1).[¶] Thus, it is apparent that the stereochemical integrity of the alkene is maintained during the formation of the decarbonylated adducts. Similarly, reaction of complex **1** with alkenes **2c** and **2d** gave adducts **3c** and **3d** in 57 and 64% respectively. The regiochemistry of **3c** was determined by ¹H–¹³C heteronuclear shift correlation spectroscopy and the regiochemistry of **3d** was apparent from its ¹H–¹⁹F coupling pattern. The relative stereochemistry of **3c** and **3d** were determined by comparison of their spectroscopic data with the data obtained from adducts **3a** and **3b**.

We then turned our attention to the generation of organic products from adducts **3**. Thermolysis and photolysis conditions led to very slow and complex reactions but after some experimentation it was discovered that oxidation of adducts **3** with 10 equiv. of ceric ammonium nitrate (CAN) in *N,N*-dimethylformamide for 30 min at room temperature gave a relatively fast and clean reaction. The white crystalline products isolated from adducts **3a** and **3b** were found to be identical and the common product was identified from its microanalytical and spectroscopic data as the tetrasubstituted cyclopropane **4b**. It was isolated in 53% and 50% yield from

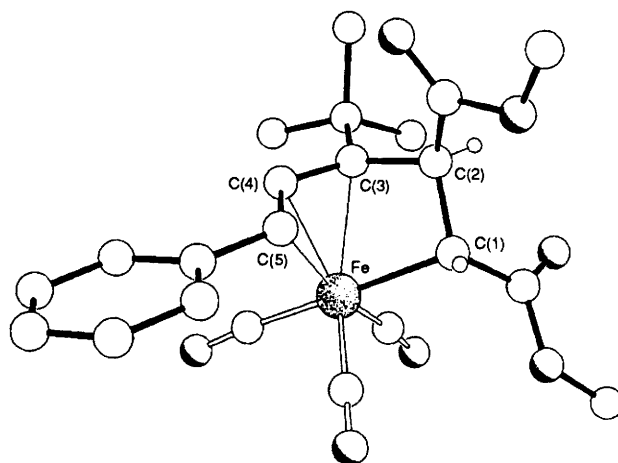
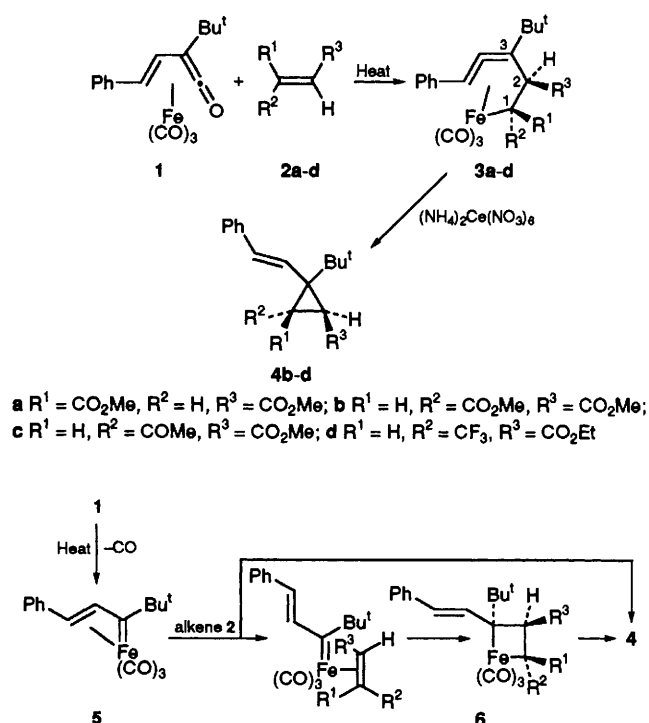


Fig. 1 Molecular structure of complex **3b** (R¹ = H, R² = CO₂Me, R³ = CO₂Me) (C₂₂H₂₄O₇Fe). Selected bond lengths (Å) and bond angles (°): Fe–C(1) 2.105(2), Fe–C(3) 2.230(2), Fe–C(5) 2.166(2), C(1)–C(2) 1.522(3), C(2)–C(3) 1.520(3), C(3)–C(4) 1.403(3), C(4)–C(5) 1.407(3); Fe–C(1)–C(2) 95.6(1), C(1)–C(2)–C(3) 105.7(2), C(2)–C(3)–C(4) 117.8(2), C(3)–C(4)–C(5) 123.2(2).

the reactions of the maleate and fumarate adducts, respectively. Similarly reductive elimination between C-1 and C-3 occurred on oxidation of adducts **3c** and **3d**, and cyclopropanes **4c** and **4d** were isolated in 13% and 52% yield respectively.

It is proposed that the reaction between the vinylketene complex **1** and the alkenes proceeds as follows. Decarbonylation of the vinylketene complex gives the vinylcarbene intermediate **5** [the interconversion of tricarbonyl(vinylketene)iron(o) complexes and tricarbonyl(η^3 -vinylcarbene)iron(o) complexes has been demonstrated¹⁴]. This is then followed by styryl dissociation, external alkene coordination and a formal [2 + 2] cycloaddition to give the 16 electron ferracyclobutane **6**. This then collapses to the 18 electron product **3** by recoordination of its styryl double bond. Alternatively direct interaction between the vinylcarbene complex **5** and the external alkene would lead straight to product **3**.

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Footnotes

† The reactions of tricarbonyl(3-methyl-5,5-dimethyl-1-oxapenta-1,2,4-triene)tricarbonyliron(o) with tetracyanoethylene and maleic anhydride have been reported to give an unidentified metal-free 1 : 1 adduct and an unidentified iron-containing 1 : 1 adduct respectively.¹³

‡ All products of structural types **3** and **4** were found to be novel and they all gave satisfactory IR, ¹H NMR, ¹³C NMR, low resolution mass spectral and microanalytical/high resolution mass spectral data.

§ Details of this analysis will be reported in the full account of this work.

¶ Crystal data for **3b** (R¹ = CO₂Me, R² = H, R³ = CO₂Me): C₂₂H₂₄O₇Fe, *M* = 456.3, monoclinic, *a* = 10.199(2), *b* = 15.084(3), *c* = 28.905(6) Å, β = 95.68(3)°, *V* = 4425(4) Å³, space group *C2/c*, *Z* = 8, *D*_c = 1.37 g cm⁻³, μ (Mo-K α) = 7.2 cm⁻¹, *F*(000) = 1904. Data were measured on a Siemens P4/PC diffractometer with Mo-K α

radiation (graphite monochromator) using ω -scans. The structure was solved by direct methods and the nonhydrogen atoms refined anisotropically to give *R* = 0.0355, *R*_w = 0.0416 for 3222 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50^\circ$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

|| The major product (59%) from this reaction has been identified as a cyclobutane-1,2-dione. Further details of this product will be reported in the full account of this work.

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