Conversion of (Vinylketene)tricarbonyliron(0) Complexes into (Vinylallene)tricarbonyliron(0) Complexes

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Addition of phosphonoacetate anions to (vinylketene)tricarbonyliron(0) complexes gave (vinylallene)tricarbonyliron(0) complexes; stereoselectivity as high as 98 : 2 was observed and the relative stereochemistry of the major stereoisomers was elucidated by X-ray crystal structure analysis of the major isomer of [PhCH=CHC(Me)=C=CHCO$_2$Bu^t](CO)$_3$Fe^0 **3d**, the product obtained from the reaction between [PhCH=CHC(Me)=C=O](CO)$_3$Fe^0 **1a** and the anion of (EtO)$_2$P(O)CH$_2$CO$_2$Bu^t **2b**.

Transition metal complexes of vinylketenes are frequently postulated as key intermediates in a wide range of transition metal-mediated organic reactions.[1] Thus it is surprising that although several types of vinylketene complexes have been known for some time,[2] it is only very recently that studies of their reactivity have been initiated. These investigations have shown to date that (*a*) iron-,[3] chromium-[1a] and cobalt-centred[4] vinylketene complexes react with nucleophiles at the carbon atom adjacent to the oxygen atom, (*b*) an iron-based vinylketene complex reacts with an electrophile through its oxygen atom,[5] (*c*) cobalt-centred vinylketene complexes react with alkynes to give phenols,[1b] whereas a chromium-based vinylketene complex reacts with an alkyne to give a cyclobutenone,[1a] and (*d*) iron-centred vinylketene complexes combine with isonitriles to give metal complexes of vinylketenimines.[6]

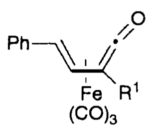
We report herein that (vinylketene)tricarbonyliron(0) complexes react with anions derived from phosphonoacetates to give (vinylallene)tricarbonyliron(0) complexes. These Wadsworth–Emmons type reactions not only represent a hitherto unreported class of reaction of vinylketene complexes, but also, in view of the ease of preparation and stability of the vinylketene complexes used,[7] constitute the first versatile and synthetically useful approach to (vinylallene)tricarbonyliron(0) compounds.[8]

Attention initially focused on the reaction between the methyl-substituted vinylketene complex **1a**[7] and the anion derived from commercially available trimethyl phos-

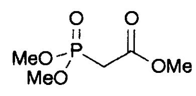
Table 1 Synthesis of (vinylallene)tricarbonyliron(0) complexes by addition of phosphonoacetate anions to (vinylketene)tricarbonyliron(0) complexes[a]

Entry	Vinylketene complex	Phosphonoacetate	Vinylallene complex	Stereoisomeric ratio of **3**; major : minor[b]	Yield of analytically pure major stereoisomer of **3**[c] (%)
1	**1a**	**2a**	**3a**	70:30	25
2	**1b**	**2a**	**3b**	50:50	38[d]
3	**1c**	**2a**	**3c**	70:30	30
4	**1a**	**2b**	**3d**	98:2	71
5	**1b**	**2b**	**3e**	80:20	43
6	**1c**	**2b**	**3f**	85:15	39

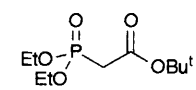
[a] In a typical reaction, the phosphonoacetate (8.66 mmol) was added to 60% NaH dispersion (8.66 mmol) in THF (25 ml) and the solution stirred for 0.5 h. A yellow solution of the vinylketene complex (4.33 mmol) in THF (15 ml) was then added to the phosphonoacetate anion solution and the red solution generated was stirred for 17 h. The resulting yellow solution was added to H_2O (20 ml). The mixture was extracted with Et_2O (2 × 20 ml) and the combined ether layers dried (Na_2SO_4), and evaporated *in vacuo* to give a yellow oil. This was examined by ^1H NMR spectroscopy and then crystallized from light petroleum (b.p. 60–80 °C) at 5 °C. [b] Determined by analysis of the ^1H NMR spectrum of the crude product. [c] The major stereoisomers of **3a** and **3c–3f** all gave satisfactory, IR, ^1H NMR, ^{13}C NMR, low resolution MS and microanalytical data and were subsequently assigned the relative stereochemistry depicted for the major stereoisomer of **3d**, in Fig. 1. [d] Yield of stereoisomeric mixture (attempts to obtain pure samples of each stereoisomer were unsuccessful for **3b**).



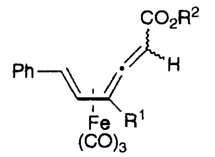
1a; R^1 = Me
1b; R^1 = Bu^n
1c; R^1 = Bu^t



2a



2b



3a; R^1 = Me, R^2 = Me
3b; R^1 = Bu^n, R^2 = Me
3c; R^1 = Bu^t, R^2 = Me
3d; R^1 = Me, R^2 = Bu^t
3e; R^1 = Bu^n, R^2 = Bu^t
3f; R^1 = Bu^t, R^2 = Bu^t

phonoacetate **2a**. On addition of a tetrahydrofuran (THF) solution of the vinylketene complex **1a** to the anion of phosphonoacetate **2a** in THF, the yellow vinylketene solution instantaneously turned red. The reaction mixture was stirred at room temperature for 17 h and the resulting yellow solution was subsequently treated with water, extracted with ether and filtered through a short plug of alumina. Solvent removal gave a yellow oil which was examined by ^1H NMR spectroscopy and tentatively assigned as a 70:30 mixture of the two possible stereoisomers of the vinylallene complex **3a** (Table 1, entry 1). Crystallisation of the yellow oil from light petroleum produced stable yellow crystals which gave spectroscopic data (IR, ^1H NMR, ^{13}C NMR, and mass) and microanalytical data entirely consistent with structure **3a**. Comparison of the ^1H NMR data of the cyrstals with the ^1H NMR spectrum of the crude product revealed that the crystals were a pure sample of the major stereoisomer.

Addition of the anion derived from phosphonoacetate **2a** to both the *n*-butyl-substituted vinylketene complex **1b**[7] and to the *tert*-butyl-substituted vinylketene complex **1c**,[7] using the procedure outlined above, gave in each case a yellow oil containing two stereoisomers. These were assigned as vinylallene complexes **3b** (stereoisomer ratio 50:50) and **3c** (stereoisomer ratio 70:30) respectively (Table 1, entries 2 and 3). Attempts to crystallise the oil containing the two stereoisomers of **3b** were unsuccessful but crystallisation of the oil containing the two stereoisomers of **3c** gave pure crystals of the major stereoisomer.

Although the results obtained using trimethyl phosphonoacetate **2a** demonstrate that the carbon–oxygen double bond of (vinylketene)tricarbonyliron(0) complexes may be replaced by carbon–carbon double bonds to give (vinylallene)tricarbonyliron(0) complexes, the production of two stereoisomers in approximately equal amounts is synthetically undesirable. Hence it was proposed that an increase in the steric demands of the phosphonoacetate should lead to improved stereoselectivity in the reaction. Accordingly *tert*-butyl diethyl phosphonoacetate (**2b**) was synthesised from diethyl chlorophosphate and *tert*-butyl acetate,[9] and its anion treated with vinylketene complexes **1a**, **1b** and **1c** (Table 1, entries 4–6). The results obtained revealed that, gratifyingly, the butoxycarbonyl-substituted vinylallene products, **3d**, **3e** and **3f** were all formed more stereoselectively than the corresponding methoxycarbonyl-substituted allene complexes **3a**, **3b** and **3c**. In each case crystallisation of the crude product led to the isolation of pure samples of the major diastereoisomer.

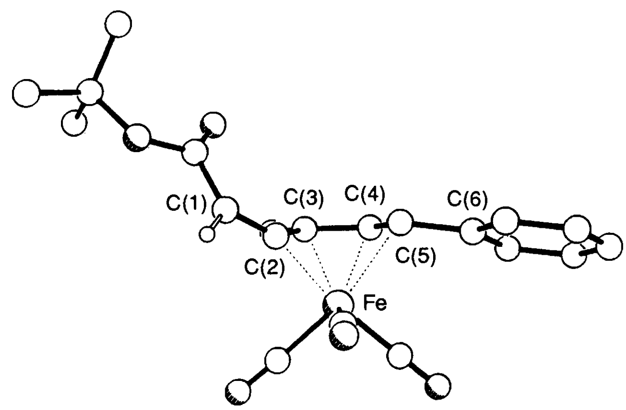


Fig. 1 Molecular structure of [PhCH=CHC(Me)=C=CHCO$_2$Bu^t](CO)$_3$Fe^0 **3d**. Selected bond lengths (Å) and bond angles (°): C(1)–C(2) 1.331(8), C(2)–C(3) 1.417(8), C(3)–C(4) 1.424(8), C(4)–C(5) 1.401(8), C(5)–C(6) 1.483(8), Fe–C(2) 1.953(6), Fe–C(3) 2.096(5), Fe–C(4) 2.089(5), Fe–C(5) 2.152(6); C(1)–C(2)–C(3) 137.8(5), C(2)–C(3)–C(4) 112.4(5), C(3)–C(4)–C(5) 118.4(5), C(4)–C(5)–C(6) 123.7(6); C(1)–C(2)–C(3)–C(4) 133.4(8), C(2)–C(3)–C(4)–C(5) −8.0(8), C(3)–C(4)–C(5)–C(6) 170.3(5).

Finally, the relative stereochemistry of the major and minor stereoisomers of the vinylallene complexes was determined by an X-ray crystal structure analysis† of the major stereoisomer

† *Crystal data* for [PhCH=CHC(Me)=C=CHCO$_2$Bu^t](CO)$_3$Fe^0 **3d**: $C_{20}H_{20}FeO_5$, M = 396.2, monoclinic, a = 12.504(6), b = 10.661(5), c = 15.389(7) Å, β = 106.42(3)°, V = 1968 Å^3, space group $P2_1/a$, Z = 4, D_c = 1.34 g cm^{-3}, μ = 64 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and refined anisotropically using absorption-corrected data to give R = 0.064, R_w = 0.065 for 2036 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 116°$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

of vinylallene complex **3d** and correlation of ^{1}H NMR data. The X-ray analysis (Fig. 1) revealed that in the major stereoisomer of **3d**, the bulky butoxycarbonyl group is directed away from the tricarbonyliron(0) unit. Comparison of the ^{1}H NMR shift values of the proton attached to the allene terminus in the major and minor stereoisomers of complexes **3d** and **3a**, **3c**, **3e** and **3f** (for major stereoisomer, δ 5.71–5.87; for minor stereoisomer, δ 6.37–6.47) revealed that all the major stereoisomers had the same relative stereochemistry as the major stereoisomer of **3d**.

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References

1 See, for example, (*a*) B. A. Anderson, W. D. Wulff and A. L. Rheingold, *J. Am. Chem. Soc.*, 1990, **112**, 8615 and references therein; (*b*) M. A. Huffman and L. S. Liebeskind *J. Am. Chem. Soc.*, 1990, **112**, 8617 and references therein; (*c*) W. D. Wulff, *Adv. Metal-Org. Chem.*, 1989, **1**, 209; (*d*) K. H. Dotz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587.

2 G. L. Geoffroy and S. L. Bassner, *Adv. Organomet. Chem.*, 1988, **28**, 1.

3 L. Hill, C. J. Richards and S. E. Thomas, *J. Chem. Soc., Chem. Commun.*, 1990, 1085.

4 W. D. Wulff, S. R. Gilbertson and J. P. Springer, *J. Am. Chem. Soc.*, 1986, **108**, 520.

5 T. Valeri, F. Meier and E. Weiss, *Chem. Ber.*, 1988, **121**, 1093.

6 C. J. Richards and S. E. Thomas, *J. Chem. Soc., Chem. Commun.*, 1990, 307.

7 N. W. Alcock, C. J. Richards and S. E. Thomas, *Organometallics*, 1991, **10**, 231.

8 The first example of a (vinylallene)tricarbonyliron(0) complex was synthesised recently in 15% yield by irradiating $Ph_2C{=}C{=}\overline{CCH_2CH_2OC}{=}O$ in the presence of $Fe(CO)_5$: L. S. Trifonov, A. S. Orahovats, R. Prewo and H. Heimgartner, *Helv. Chim. Acta*, 1988, **71**, 551.

9 T. J. Brocksom, N. Petragnani and R. Rodrigues, *J. Org. Chem.*, 1974, **39**, 2114.