Addition of Alkynes to (Vinylketene)tricarbonyliron(0) Complexes

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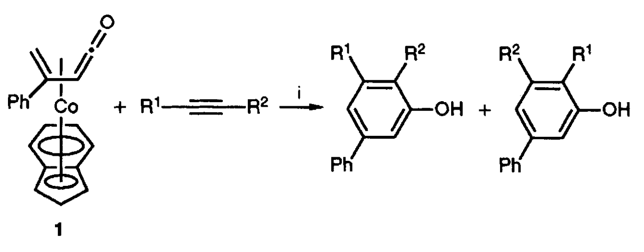
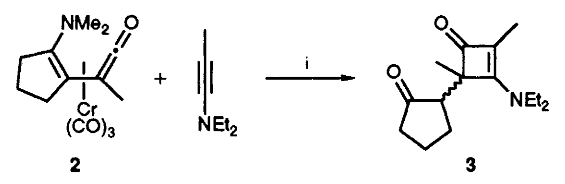
Alkynes add to (vinylketene)tricarbonyliron(0) complexes to generate stable adducts; addition of unsymmetrical alkynes is highly regioselective and the regiochemistries of the adducts produced in these reactions were determined by X-ray crystal structure analyses of the major isomer derived from but-3-yn-2-one and (3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)tricarbonyliron(0), and of the structurally modified product derived from diethylpropynylamine and (3-isopropyl-5-phenyl-1-oxapenta-1,2-4-triene)tricarbonyliron(0).

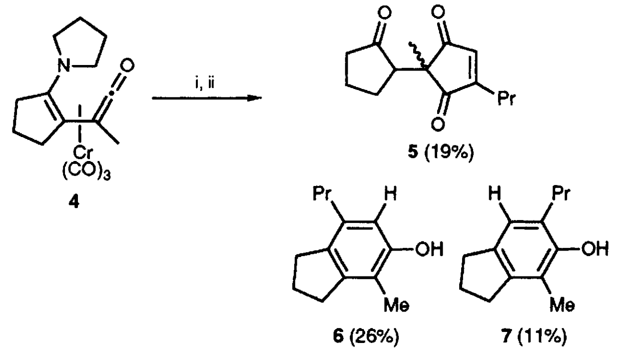
Very recently there has been considerable interest in the reactions that take place between transition metal complexes of vinylketenes and alkynes. Thus, it has been demonstrated that the cobalt-centred vinylketene complex **1** reacts with hex-3-yne, pent-1-yne, dimethyl acetylenedicarboxylate and ethyl but-2-ynoate to give phenols[1,2] (Scheme 1). In contrast, the chromium-centred complex **2** has been shown to react with diethylpropynylamine to give a [2 + 2] cycloadduct **3** (Scheme 2), and the closely related chromium-centred complex **4** has been shown to react with pent-1-yne to give the cyclopentenedione **5** and the isomeric indanols **6** and **7** (Scheme 3) after reductive work-up.[3] Complexes **2** and **4** are the first examples



Scheme 1 *Reagents and conditions*: i, cycloocta-1,5-diene (2 equiv.), 100 °C, 19–21.5 h, (45–92%)



Scheme 2 *Reagents and conditions*: i, benzene, 25 °C, 18 h, (36%)

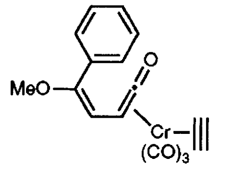


Scheme 3 *Reagents and conditions*: i, pent-1-yne, tetrahydrofuran, 85 °C, 2–4 h; ii, SiO_2 or $TiCl_3$–$LiAlH_4$

Table 1 Addition of alkynes to (vinylketene)tricarbonyliron(0) complexes **10** to give insertion products **11** or **12**[a]

Entry	R^1	R^2	R^3	Equiv. alkyne	Solvent	T/°C	t/h	Product structure	Yield (%)
1	MeO_2C	CO_2Me	Pr^i	2	Toluene	72	1.5	**11**	93
2	MeO_2C	CO_2Me	Bu^t	2	Toluene	80	1.75	**11**	96
3	MeO_2C	H	Pr^i	2	Toluene	72	2	**11**	91
4	MeCO	H	Bu^t	2	Toluene	80	5	**11**	39
5	EtO	H	Me	2	Toluene	80	20.5	**11**	43
6	EtO	H	Pr^i	4	Hexane	80	5.5	**11**	77
7	Et_2N	Me	Pr^i	2	Toluene	80	0.7	**12**	73
8	Et_2N	Me	Bu^t	4	Toluene	80	3.5	**12**	79
9	Ph	H	Pr^i	6	Toluene	25	1176	**11**	12

[a] A typical reaction procedure is illustrated by experimental details for entry 1: To a nitrogen-saturated solution of the vinylketene complex **10** ($R^3 = Pr^i$) (0.050 g, 0.15 mmol) in toluene (10 cm^3) was added dimethyl acetylenedicarboxylate (0.038 cm^3, 0.31 mmol). After stirring at 72 °C for 1.5 h under a nitrogen atmosphere, the resulting orange–brown solution was filtered through deactivated alumina and concentrated *in vacuo* to give a yellow oil. The oil was crystallised from diethyl ether–light petroleum (60–80 °C) to give complex **11** ($R^1 = MeO_2C$, $R^2 = CO_2Me$, $R^3 = Pr^i$) as yellow crystals (0.067 g, 93%).



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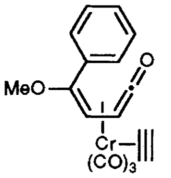

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of chromium-centred vinylketene complexes to be isolated and as such are of considerable significance in view of the postulated pivotal role of chromium-centred vinylketene complexes in the multi-faceted and synthetically attractive reactions that take place between chromium Fischer carbene complexes and alkynes.[4] Recently it has been postulated that alkyne-substituted chromium-centred vinylketene complexes such as the hypothetical structures **8** and **9** may also play a significant role in these reactions.[5]

We are currently interested in the fundamental reactivity of easily accessible and highly stable iron-centred vinylketene complexes and have reported the results of their reactions with isonitriles,[6] phosphonoacetate anions[7] and a range of nucleophiles.[8] In view of our interests and the intriguing but contrasting results obtained by treating the cobalt- and chromium-centred vinylketene complexes with alkynes, we have recently examined the hitherto uninvestigated reactivity of iron-centred vinylketene complexes towards alkynes. Our experiments, the results of which are reported below, have led to the isolation and characterisation of novel alkyne–vinylketene complex adducts. Cobalt- and chromium-centred analogues of these adducts may well be important intermediates in some of the reactions outlined above.

The (vinylketene)tricarbonyliron(0) complexes **10** (R^3 = Me, Pr^i and Bu^t) were synthesised in good to excellent yield (77, 82 and 93%, respectively) from the corresponding readily available (vinylketone)tricarbonyliron(0) complexes using a previously reported procedure.[6] In an initial experiment, complex **10** ($R^3 = Bu^t$) was stirred with two equivalents of the electron-poor alkyne dimethyl acetylenedicarboxylate in toluene at 80 °C for 1.75 h under a nitrogen atmosphere (Table 1, entry 2). Subsequent work-up of the product mixture gave air-stable yellow crystals which were identified as complex **11** ($R^1 = MeO_2C$, $R^2 = CO_2Me$, $R^3 = Bu^t$) on the basis of their spectroscopic and microanalytical data† and an X-ray crystal structure analysis. Similarly a complex of the novel structural type **11** was also produced in excellent yield when dimethyl acetylenedicarboxylate was treated with the (vinylketene)tricarbonyliron(0) complex **10** ($R^3 = Pr^i$) (Table 1, entry 1).

In order to examine the regioselectivity of the alkyne insertion into the iron–ketene bond, we then studied the reactivity of (vinylketene)tricarbonyliron(0) complexes towards monosubstituted electron-poor alkynes. Thus, vinylketene complex **10** ($R^3 = Pr^i$) was treated with methyl propiolate, and vinylketene complex **10** ($R^3 = Bu^t$) was treated with but-3-yn-2-one (Table 1, entries 3 and 4). In the former case the ratio of major isomer to minor isomer in the crude product was found to be >95 : 5 by 270 MHz ^1H NMR spectroscopy, whilst in the latter case the ratio was found to be >100 : 1. On the basis of ^1H and ^{13}C NMR spectroscopic data, the MeO_2C and MeCO substituents were tentatively assigned to C-1 (*i.e.* the carbon atom α to the iron atom) in their respective major regioisomers. This assignment was confirmed by an X-ray crystal structure analysis‡ of the major regioisomer formed from complex **10** ($R^3 = Bu^t$) and but-3-yn-2-one (Fig. 1; Table 1, entry 4).§

The reactivity of relatively electron-rich alkynes towards (vinylketene)tricarbonyliron(0) complexes was also examined. Thus, the oxygen-substituted alkyne ethyl ethynyl ether was treated with the vinylketene complexes **10** (R = Me, Pr^i) (Table 1, entries 5 and 6), and the nitrogen-substituted alkyne diethylpropynylamine was treated with vinylketene complexes **10** (R = Pr^i, Bu^t) (Table 1, entries 7 and 8). The products derived from ethyl ethynyl ether were regiochemically pure by 270 MHz ^1H NMR spectroscopy and were

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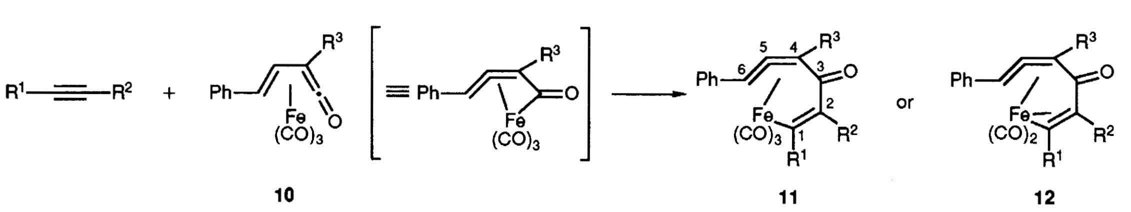
† All products of structural types **11** and **12** gave satisfactory IR, ^1H NMR, ^{13}C NMR, low resolution mass spectral and microanalytical/high resolution mass spectral data.

‡ *Crystal data* for adduct **11** (R^1 = MeCO, R^2 = H, $R^3 = Bu^t$): $C_{21}H_{20}FeO_5$, M = 408.2, orthorhombic, space group $P2_1ca$, a = 7.767(2), b = 12.729(4), c = 19.828(6) Å, V = 1960 $Å^3$, Z = 4, D_c = 1.38 g cm^{-3}, $\mu(Cu\text{-}K\alpha) = 64\ cm^{-1}$. Data were measured on a Siemens P3/PC diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.059, R_w = 0.054 for 1318 independent observed reflections $[|F_o| > 3\sigma(|F_o|), 2\theta \leqslant 116°]$.

§ Typical analytical and spectroscopic data were obtained for product **10** (R^1 = MeCO, R^2 = H, $R^3 = Bu^t$): m.p. 154–156 °C; satisfactory elemental analyses were obtained; ν_{max} (cyclohexane)/cm^{-1} 2073vs, 2022vs, 2006s (C≡O) and 1665m [MeCO and $C(R^3)C(=O)C(R^2)$]; δ_H (270 MHz) 1.45 (9H, s, Bu^t), 2.36 (3H, s, MeCO), 3.99 (1H, d, J 12.2, H-6), 5.77 (1H, d, J 12.2, H-5), 6.57 (1H, s, H-2) and 7.3–7.35 (5H, m, Ph); δ_C {^1H} (67.9 MHz) 28.1 ($COCH_3$), 32.1 [$C(CH_3)_3$], 38.1 [$C(CH_3)_3$], 79.1 (C-6), 90.1 (C-5), 116.8 (C-4), 126.1 (C_{ortho} or C_{meta}), 128.5 (C_{para}), 129.5 (C_{ortho} or C_{meta}), 137.7 (C_{ipso}), 143.7 (C-2), 200.1 (C-1), 204.1, 205.5, 207.7, 207.9, 208.1 (C-3, COMe, 3 x C≡O); m/z (FAB) 409 (M^+ + H, 20%), 380 (M − CO), 17), 352 (M − 2CO, 15), 325 (M − 3CO + H, 100).



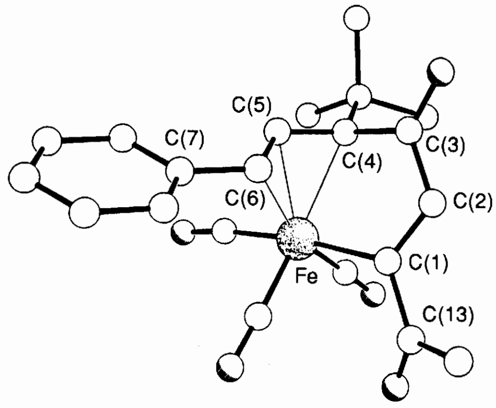


Fig. 1 Molecular structure of complex **11** (R^1 = MeCO, R^2 = H, R^3 = $\mathrm{Bu^t}$) ($C_{21}H_{20}FeO_5$). Selected bond lengths (Å) and bond angles (°): C(1)–C(2) 1.350(13), C(2)–C(3) 1.441(13), C(3)–C(4) 1.552(13), C(4)–C(5) 1.412(11), C(5)–C(6) 1.404(12), Fe–C(1) 2.017(10), Fe–C(4) 2.205(8), Fe–C(5) 2.079(8), Fe–C(6) 2.182; Fe–C(1)–C(13) 122.2(7), Fe–C(1)–C(2) 117.2(7), C(1)–C(2)–C(3) 118.5(9), C(2)–C(3)–C(4) 115.3(8), C(3)–C(4)–C(5) 114.0(8), C(4)–C(5)–C(6) 123.3(8), C(5)–C(6)–C(7) 123.8(8).

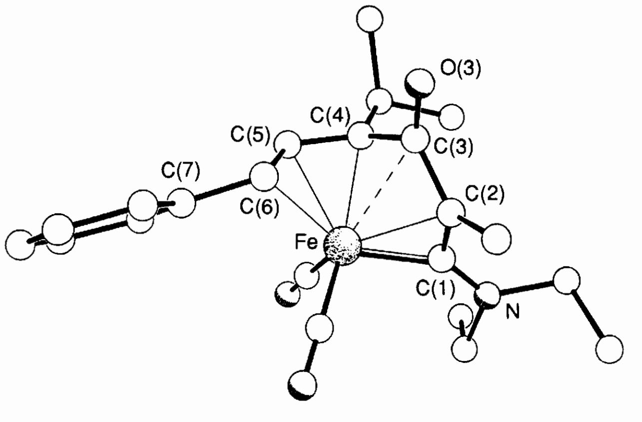


Fig. 2 Molecular structure of one of the pair of crystallographically independent molecules of **12** (R^1 = Et_2N, R^2 = Me, R^3 = $\mathrm{Pr^i}$) [$2(C_{22}H_{27}FeNO_8)\cdot H_2O$]. Selected bond lengths (Å) and bond angles (°) (values in [ ] refer to the second independent molecule): C(1)–C(2) 1.408(7) [1.424(6)], C(2)–C(3) 1.430(7) [1.430(9)], C(3)–C(4) 1.507(8) [1.513(7)], C(4)–C(5) 1.416(9) [1.417(8)], C(5)–C(6) 1.398(5) [1.355(7)], Fe–C(1) 1.833(6) [1.841(7)], Fe–C(2) 2.184 [2.187(5)], Fe–C(3) 2.436(6) [2.436(5)], Fe–C(4) 2.073(5) [2.061(5)], Fe–C(5) 2.080(5) [2.072(7)], Fe–C(6) 2.174(5) [2.156(6)], C(1)–N 1.301(7) [1.297(8)], C(3)–O(3) 1.235(6) [1.241(6)]; Fe–C(1)–N 145.1(5) [146.1(4)], Fe–C(1)–C(2) 83.6(4) [83.0(4)], C(1)–C(2)–C(3) 118.0(4) [117.8(5)], C(2)–C(3)–C(4) 111.8(5) [111.9(4)], C(3)–C(4)–C(5) 114.6(4) [113.1(4)], C(4)–C(5)–C(6) 121.9(5) [123.7(5)], C(5)–C(6)–C(7) 122.6(5) [124.1(5)].

assigned the structural type **11** by comparison of their spectroscopic and analytical data with the data obtained from the products of entries 1–4. Interestingly, the ethoxy substituent derived from the alkyne was located on the carbon atom α to the iron atom *i.e.* the regiochemistry of alkyne insertion does not appear to be controlled by the overall electronic effect of the alkyne substituents. The products derived from diethylpropynylamine were also regiochemically pure (by 270 MHz ^1H NMR spectroscopy) but examination of their analytical and spectroscopic data revealed that they were structurally different to the products obtained previously. Although they were still essentially adducts formed from the vinylketene complex and the alkyne, one equivalent of carbon monoxide had been lost in forming the product molecule. X-Ray crystal analysis¶ of the product obtained from the reaction between vinylketene complex **10** (R^3 = $\mathrm{Pr^i}$) and diethylpropynylamine generated the structure **12** (R^1 = Et_2N, R^2 = Me, R^3 = $\mathrm{Pr^i}$) (Fig. 2) which revealed that (*i*) a carbon monoxide ligand had been displaced from the iron centre by coordination of the double bond derived from the alkyne, and (*ii*) the Et_2N substituent was located on the carbon atom α to the metal centre.

Phenylacetylene behaved quite differently from the alkynes used in the reactions described above when it was added to the vinylketene complex **10** (R = $\mathrm{Pr^i}$). When the reaction was carried out at 72 °C, the adduct formed between the alkyne and the vinylketene complex underwent further reaction thus making isolation of the adduct problematic. At room temperature, however, adduct formation and decomposition were extremely slow and under these conditions it did prove possible to isolate the adduct albeit in low yield (Table 1, entry 9). Characterisation of the adduct confirmed that its structure was of type **11** and revealed that the phenyl substituent derived from the alkyne component was located on the carbon atom α to the iron atom.

A plausible pathway for the reactions described above is depicted in Scheme 4. Dissociation of the styryl section of the vinylketene ligand produces complex **13**, which is coordinatively unsaturated and can bind the appropriate alkyne to generate the 18-electron complex **14**. Subsequent interaction of the metal centre, the alkyne, and the 'alkene' section of the vinylketene ligand gives rise to the 16-electron metallacyclopentenone **15** which after recoordination of the styryl alkene affords the product adduct **11**.

Finally, the adducts generated by adding alkynes to (vinylketene)tricarbonyliron(0) complexes are, in principle, potential precursors of all the products observed in both the cobalt and chromium systems outlined initially; reductive elimination across C-1 and C-4 would generate cyclobutenones, migration of C-1 to a carbonyl ligand followed by reductive elimination at C-4 or migration of C-4 to a carbonyl ligand followed by reductive elimination at C-1 would generate cyclopentenediones, and reductive elimination

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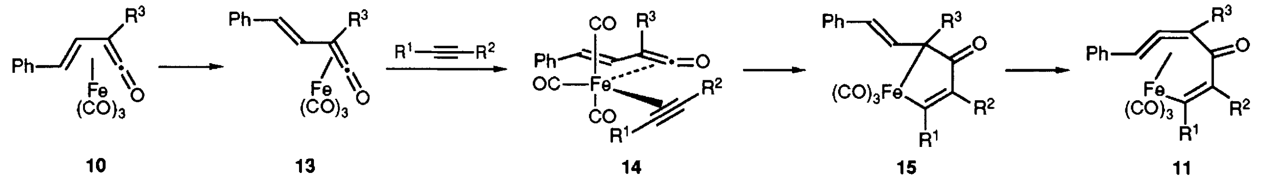
¶ *Crystal data* for adduct **12** (R^1 = Et_2N, R^2 = Me, R^3 = $\mathrm{Pr^i}$): $2(C_{22}H_{27}FeNO_8)\cdot H_2O$, M = 996.6, triclinic, space group $P\bar{1}$, a = 11.928(5), b = 13.370(5), c = 15.928(8) Å, α = 113.32(2), β = 106.43(2), γ = 89.87(2)°, V = 2220 Å^3, Z = 2, D_c = 1.49 g cm^{-3}, μ(Cu-Kα) = 59 cm^{-1}. Data were measured on a Siemens P3/PC diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.054, R_w = 0.051 for 4222 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 116°$].

Atomic coordinates, bond lengths and angles, and thermal parameters for structures **11** and **12** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 4

across C-1 and C-6 followed by aromatisation would give phenols. The thermal decomposition pathways and products of the adducts reported in this Communication are currently being studied and will be reported in a subsequent publication.

The authors thank the SERC and ICI Strategic Research Fund for financial support.

Received, 14th September 1992; Com. 2/04926K

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