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# A Study of the Reactivity of Tricarbonyl(vinylketene)iron(0) Complexes Towards Alkynes

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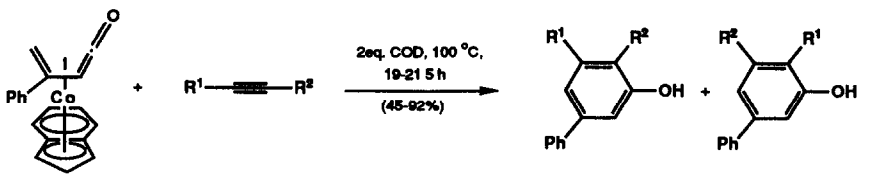
***Abstract:*** Alkynes add to tricarbonyl(vinylketene)iron(0) complexes to generate stable 1:1 adducts, the structures of which were determined by an *X*-ray crystal structure analysis of the adduct formed from tricarbonyl(5-phenyl-3-*iso*-propyl-1-oxapenta-1,2,4-triene)iron(0) and dimethyl acetylenedicarboxylate. Addition of unsymmetrical alkynes is regioselective and the regiochemistries of the adducts isolated from these reactions were determined by *X*-ray crystal structure analyses of the products derived from but-3-yn-2-one and tricarbonyl(3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0), and of the structurally modified product derived from diethylpropynylamine and tricarbonyl(5-phenyl-3-*iso*-propyl-1-oxapenta-1,2,4-triene)iron(0). Thermolysis of the adducts leads to either cyclopentenediones or phenols and its outcome is dependent on the electronic properties of the carbon-1 substituent of the adduct. The phenols may be synthesised directly and regioselectively from tricarbonyl(vinylketene)iron(0) complexes and the appropriate alkynes.

The reactivity of transition metal complexes of ketenes and vinylketenes is currently attracting significant attention. Of note from a synthetic viewpoint, is the conversion of transient chromium-bound ketenes to diverse organic products including β-lactams and amino acids.[1] Very recently there has been considerable interest in the reactions that take place between alkynes and transition metal complexes of vinylketenes. 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.[2] In contrast, the chromium-centred complex (2) has been shown to react with diethylpropynylamine to give a [2+2] cycloadduct (3), 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) after a reductive work-up.[3]

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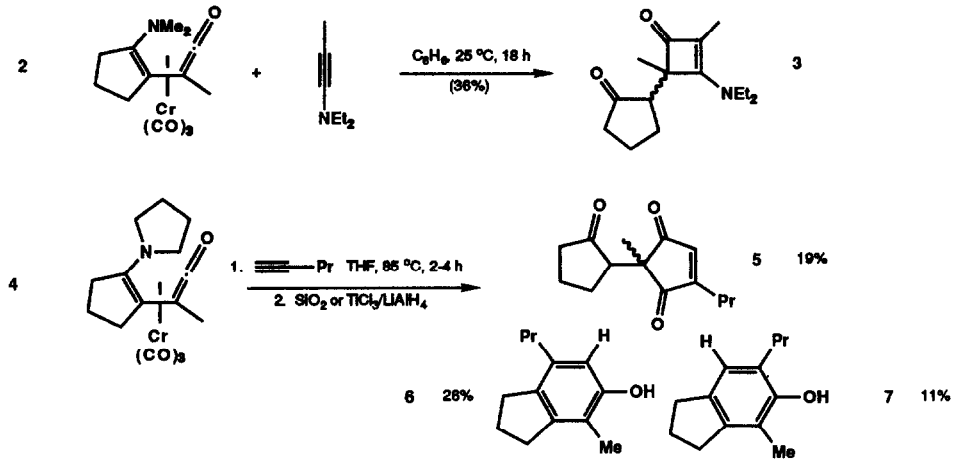
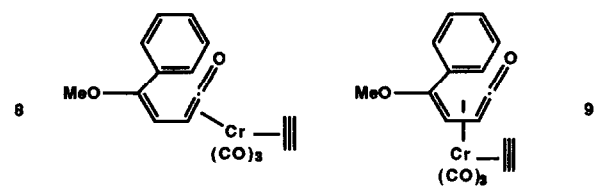



Complexes (2) and (4) are the first examples of chromium-centred vinylketene complexes to be isolated and as such are of considerable significance in view of the postulated pivotal rôle of chromium-centred vinylketene complexes in the multi-faceted and synthetically attractive reactions which take place 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 rôle 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 reacting the cobalt- and chromium-centred vinylketene complexes with alkynes, we recently initiated an investigation into the reactivity of tricarbonyl(vinylketene)iron(0) complexes towards alkynes. The results of this study, some of which have been published in Communication form,[9,10] are described below.

## RESULTS AND DISCUSSION

*Reactions of alkynes bearing π-acceptor substituents with tricarbonyl(vinylketene)iron(0) complexes*

The tricarbonyl(vinylketene)iron(0) complexes (10)-(12) were synthesised from the corresponding readily available alkyl styryl ketones (13) *via* tricarbonyl(vinylketone)iron(0) complexes (14) using a modification of a previously reported procedure.[6]

Initial experiments focussed on the symmetrical alkyne dimethyl acetylenedicarboxylate. It was quickly discovered that stirring each of the vinylketene complexes (10)-(12) with two equivalents of dimethyl acetylenedicarboxylate at 72-80 °C for 1-2 hours gave, after work-up, yellow air-stable crystals. These were identified as adducts (15)-(17), in which the alkyne had inserted into the bond between the iron and carbon-2

of the vinylketene complexes, by an *X*-ray crystal structure analysis of the product obtained from vinylketene complex (**12**) (see Figure 1). Adducts (**15**)-(**17**) were further characterised by IR, $^1$H NMR, $^{13}$C NMR spectroscopy, (see Tables 1-3) mass spectroscopy and combustion analysis (see Experimental section).

In order to study the regioselectivity of the alkyne insertion into the iron-ketene bond, we then examined the reactivity of tricarbonyl(vinylketene)iron(0) complexes towards monosubstituted electron-poor alkynes. Thus vinylketene complexes (**11**) and (**12**) were reacted with methyl propiolate and but-3-yn-2-one under similar conditions used for the dimethyl acetylenedicarboxylate reactions. Examination of the crude products obtained from each of the reactions by $^1$H NMR spectroscopy revealed that in each case essentially one adduct had been generated. Work-up led to the isolation of adducts (**18**)-(**21**), the regiochemistry of which was determined by an *X*-ray crystal structure analysis of adduct (**21**)[9] and comparison of its spectroscopic data with that obtained from adducts (**18**)-(**20**) (see Tables 1-3). Thus it transpired that the $MeO_2C$ and MeCO substituents derived from methyl propiolate and but-3-yn-2-one are in each case located on carbon-1 of the adducts.

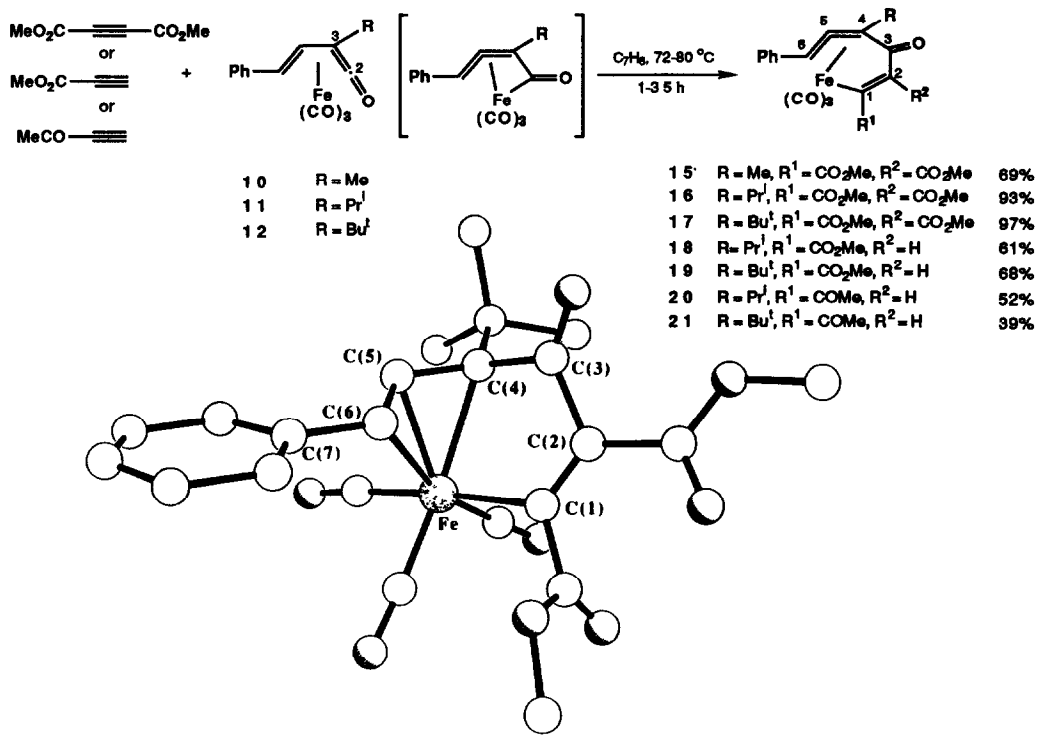


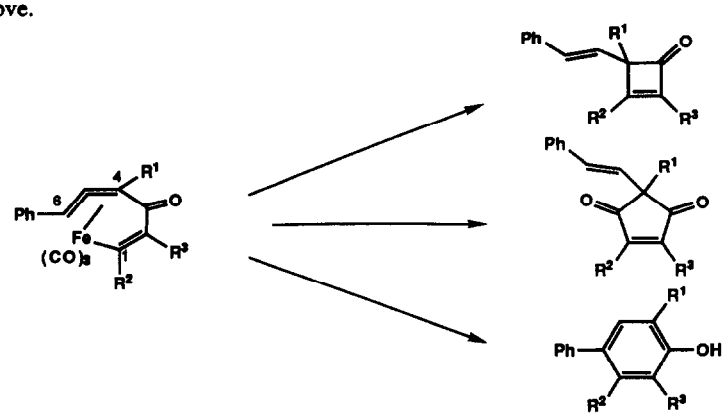

**Fig. 1.** Molecular structure of one of the pair of crystallographically independent molecules of complex (**17**) ($C_{23}H_{22}FeO_8$). Selected bond lengths (Å) and bond angles (°) (values in [] refer to the second independent molecule): C(1)-C(2) 1.339(10) [1.340(9)], C(2)-C(3) 1.471(13) [1.468(12)], C(3)-C(4) 1.554(8) [1.549(8)], C(4)-C(5) 1.421(8) [1.413(8)], C(5)-C(6) 1.385(9) [1.396(8)], Fe-C(1) 2.006(5) [2.017(5)], Fe-C(4) 2.179(7) [2.180(7)], Fe-C(5) 2.088(9) [2.095(8)], Fe-C(6) 2.203(8) [2.205(8)]; C(1)-C(2)-C(3) 116.2(5) [115.3(5)], C(2)-C(3)-C(4) 115.0(7) [114.8(7)], C(3)-C(4)-C(5) 116.3(5) [116.0(5)], C(4)-C(5)-C(6) 123.1(6) [123.4(5)], C(5)-C(6)-C(7) 124.7(5) [123.1(5)].

**Table 1.** IR data ($\nu/cm^{-1}$) for tricarbonyl(vinylketene)iron(0) - alkyne adducts

| Adduct | Solvent | $\nu C{\equiv}O$ | $\nu C{=}O$ | $\nu C(1)$ and/or C(2) substituent |
|---|---|---|---|---|
| **15** | $CH_2Cl_2$ | 2082vs, 2030vs | 1676s | 1740sh, 1719s |
| **16** | cyclohexane | 2078vs, 2029vs, 2015vs | 1678s | 1740sh, 1720s |
| **17** | $CH_2Cl_2$ | 2079vs, 2024vs | 1672s | 1740sh, 1717s |
| **18** | cyclohexane | 2075vs, 2022vs, 2008vs | 1667s | 1717m |
| **19** | $CH_2Cl_2$ | 2074vs, 2017vs | 1656s | 1707m |
| **20** | cyclohexane | 2074vs, 2025vs, 2006vs | 1665s | 1665s |
| **21** | cyclohexane | 2073vs, 2022vs, 2006vs | 1665s | 1665s |
| **27** | cyclohexane | 2066vs, 2011vs, 2000vs | 1657s | |
| **29** | cyclohexane | 2064vs, 2009vs, 1998vs | 1652s | |
| **30** | cyclohexane | 2073vs, 2019vs, 2005vs | 1655s | |
| **31** | cyclohexane | 2071vs, 2017vs, 2003vs | 1650s | |
| **34** | cyclohexane | 2002vs, 1935vs | 1578s | |
| **35** | cyclohexane | 2002vs, 1935vs | 1578s | |

The $^1H$ NMR spectra of the crude product mixtures from which complexes (**18**), (**19**) and (**21**) were isolated contained small signals [at $\delta$ 4.37 (1H, d, *J* 12), 5.46 (1H, d, *J* 12) and 8.01 (1H, s) in the case of adduct (**18**)] from a second product which could arguably originate from the other regioisomer of the adducts. The ratios of major product to minor product in these cases were 22:1, 10:1 and >100:1 respectively.

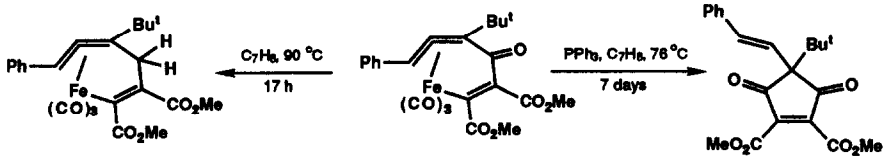
The adducts generated by adding alkynes to tricarbonyl(vinylketene)iron(0) complexes are, in principle, potential precursors of all the products observed in both the cobalt and chromium systems outlined in the Introduction above.




Reductive elimination across carbon-1 and carbon-4 would generate cyclobutenones, migration of carbon-1 to a carbonyl ligand followed by reductive elimination at carbon-4 or, alternatively, migration of carbon-4 to a carbonyl ligand followed by reductive elimination at carbon-1 would generate cyclopentenediones, whilst

reductive elimination across carbon-1 and carbon-6 followed by aromatisation would give phenols. Thus the outcome of thermolysis of the adducts generated from alkynes and tricarbonyl(vinylketene)iron(0) complexes was of significant interest.

Thermolysis of complex (17) at 90 °C for 17 hours in toluene led to an almost intractable mixture of organic and inorganic materials from which it eventually proved possible to isolate the reduced complex (22) in very low yield. To the best of our knowledge the product mixture did not contain any simple organic compounds derived directly from adduct (17). After the use of several different reaction temperature and times had given similar results, the effect of adding 2.2 equivalents of $PPh_3$ to the reaction mixture was examined. In this case, thermolysis at 76 °C for 7 days in toluene gave an organic product which was isolated and identified as the cyclopentenedione (23).




22 4% 17 23 22%

The cyclopentenedione (23) had therefore been constructed from the same components as cyclopentenedione (5) *i.e.* a vinylketene complex, an alkyne and a molecule of carbon monoxide, thus lending some support to the idea that the iron and chromium systems react with alkynes in a similar manner. The reaction conditions required for the formation of cyclopentenedione (23) from adduct (17) were, however, disappointingly forcing and so at this point our attention turned to reactions between tricarbonyl(vinylketene)iron(0) complexes and alkyl- and aryl-substituted alkynes.

*Reactions of oct-1-yne, phenylacetylene and 4-methoxyphenylacetylene with tricarbonyl(vinylketene)iron(0) complexes*

The second group of alkynes that was studied consisted of alkyl- and aryl-substituted alkynes. It was found that the reaction of the vinylketene complexes with the symmetrical disubstituted alkynes oct-4-yne and diphenylacetylene resulted in the decomposition of the vinylketene complexes leading to a complex mixture of organic and organometallic compounds. In contrast, the reactions of monosubstituted alkynes proceeded more smoothly.

The vinylketene complex (11) was stirred in toluene with two equivalents of oct-1-yne at 72 °C under an atmosphere of nitrogen. After 20 h, t.l.c. analysis indicated that there was still starting material present in the reaction mixture and so a further two equivalents of oct-1-yne was added and the reaction allowed to proceed to completion which required a further seven hours. Examination of the crude product mixture by $^1H$ NMR spectroscopy revealed that two products had been formed. These were isolated by column chromatography and identified on the basis of their spectroscopic data as 2-hexyl-5-*iso*-propyl-5-styrylcyclopent-2-en-1,4-dione (24) (22%) and 5-hexyl-4-phenyl-2-*iso*-propylphenol (25) (41%). The reaction between vinylketene complex (11) and oct-1-yne was repeated several times at 72 °C using different reaction times and equivalents of alkyne. Analysis of the crude products by $^1H$ NMR spectroscopy revealed

Table 2. $^1$H NMR data (δ)[a] for adducts formed from tricarbonyl(vinylketene)iron(0) complexes and alkynes

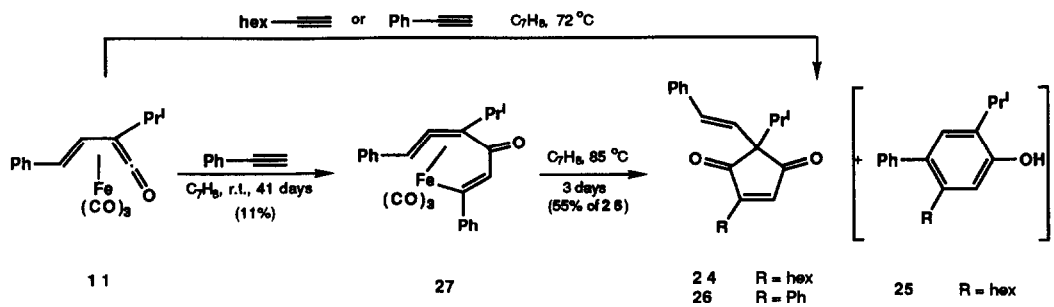
| Complex | C(2)H[b] | C(5)H | C(6)H | C(1) and/or C(2) substituent | C(4) substituent | Ph |
|---|---|---|---|---|---|---|
| **15** | - | 5.77 (1H, d, *J* 13) | 4.54 (1H, d, *J* 13) | 3.75 (3H, s), 3.93 (3H, s) | 2.24 (3H, s) | 7.35-7.5 (5H, m) |
| **16** | - | 5.83 (1H, d, *J* 12) | 4.43 (1H, d, *J* 12) | 3.75 (3H, s), 3.93 (3H, s) | 1.43 (3H, d, *J* 6), 1.60 (3H, d, *J* 6), 2.67 (1H, sept, *J* 6) | 7.35-7.5 (5H, m) |
| **17** | - | 5.70 (1H, d, *J* 12.5) | 3.96 (1H, d, *J* 12.5) | 3.61 (3H, s), 3.77 (3H, s) | 1.35 (9H, s) | 7.2-7.3 (5H, m) |
| **18** | 6.58 (1H, s) | 5.78 (1H, d, *J* 12.5) | 4.33 (1H, d, *J* 12.5) | 3.86 (3H, s) | 1.39 (3H, d, *J* 7), 1.53 (3H, d, *J* 7), 2.76 (1H, sept, *J* 7) | 7.3-7.4 (5H, m) |
| **19** | 6.67 (1H, s) | 5.78 (1H, d, *J* 12.5) | 4.06 (1H, d, *J* 12.5) | 3.85 (3H, s) | 1.46 (9H, s) | 7.35-7.4 (5H, m) |
| **20** | 6.50 (1H, s) | 5.79 (1H, d, *J* 13) | 4.28 (1H, d, *J* 13) | 2.38 (3H, s) | 1.40 (3H, d *J* 7), 1.53 (3H, d, *J* 7) 2.74 (1H, sept, *J* 7) | 7.3-7.4 (5H, m) |
| **21** | 6.57 (1H, s) | 5.77 (1H, d, *J* 12) | 3.99 (1H, d, *J* 12) | 2.36 (3H, s) | 1.45 (9H, s) | 7.3-7.35 (5H, m) |
| **27** | 6.36 (1H, s) | 5.82 (1H, d, *J* 13) | 4.42 (1H, d, *J* 13) | 7.2-7.5 (5H of 10H m) | 1.47 (3H, d, *J* 6), 1.60 (3H, d, *J* 6), 2.84 (1H, sept, *J* 6) | 7.2-7.5 (5H of 10H m) |
| **29** | 6.37 (1H, s) | 5.78 (1H, d, *J* 12) | 4.35 (1H, d, *J* 12) | 3.84 (3H, s), 6.92 (2H, d, *J* 9), 7.2-7.4 (2H of 7H m) | 1.45 (3H, d, *J* 7), 1.58 (3H, d, *J* 7), 2.82 (1H, sept, *J* 7) | 7.2-7.4 (5H of 7H m) |
| **30** | 5.52 (1H, s) | 5.62 (1H, d, *J* 12) | 4.33 (1H, d, *J* 12) | 1.41 (3H, t, *J* 7), 3.91 (1H, dq, *J* 14, 7) 4.06 (1H, dq, *J* 14,7) | 2.22 (3H, s) | 7.25-7.4 (5H, m) |
| **31** | 5.56 (1H, s) | 5.67 (1H, d, *J* 12) | 4.26 (1H, d, *J* 12) | 1.30 (3H, t, *J* 7), 3.80 (1H, dq, *J* 14, 7), 3.93 (1H, dq, *J* 14, 7) | 1.23 (3H, d, *J* 7), 1.36 (3H, d, *J* 7) 2.81 (1H, sept, *J* 7) | 7.1-7.3 (5H, m) |
| **34** | - | 5.57 (1H, d, *J* 10.5) | 3.85 (1H, d, *J* 10.5) | 1.34 (3H, s), 1.37 (3H, t, *J* 7), 1.54 (3H, t, *J* 7), 3.75 (2H, q, *J* 7), 4.05 (2H, q, *J* 7) | 1.08 (3H, d, *J* 7), 1.15 (3H, d, *J* 7) 1.98 (1H, sept, *J* 7) | 7.15-7.35 (5H, m) |
| **35** | - | 5.59 (1H, d, *J* 10.5) | 3.73 (1H, d, *J* 10.5) | 1.28 (3H, s), 1.38 (3H, t, *J* 7) 1.55 (3H, t, *J* 7), 3.73 (2H, m) 4.07 (2H, q, *J* 7) | 1.06 (9H, s) | 7.15-7.35 (5H, m) |

[a] $CDCl_3$, 300K, 270 MHz. [b] See Figure 1 for numbering

the reaction to be capricious - in some reactions only the cyclopentenedione was formed whilst in other cases both the cyclopentenedione and the phenol were generated.

The vinylketene complex (**11**) was subsequently reacted with two equivalents of phenylacetylene at 72 °C under an atmosphere of nitrogen. In this case the reaction required six days and the addition of two further equivalents of alkyne before all the vinylketene complex was consumed. Examination of the crude product by $^1$H NMR spectroscopy revealed the presence of a cyclopentenedione and the absence of a phenol. Chromatography led to the isolation of 2-phenyl-5-*iso*-propyl-5-styrylcyclopent-2-en-1,4-dione (**26**) (37%). Repetition of the reaction at 72 °C using different reaction times and equivalents of alkyne and examination of the crude products by $^1$H NMR spectroscopy showed that this reaction was also capricious. Once again, the crude product sometimes contained only the cyclopentenedione product and sometimes contained both the cyclopentenedione product and the corresponding phenol.

Whilst the unreliability of the reaction between the vinylketene complex and either oct-1-yne or phenylacetylene was somewhat frustrating, it was gratifying to see the generation of two of the classes of organic compound formed from the cobalt and chromium systems examined previously. In order to determine whether or not vinylketene complex - alkyne adducts were intermediates in the formation of the cyclopentenediones and/or the phenols, the reaction between vinylketene complex (**11**) and phenylacetylene was examined at room temperature. By sampling the reaction mixture at intervals and examining them by $^1$H NMR spectroscopy, it proved possible to observe the slow disappearance of complex (**11**), the formation of a vinylketene complex - alkyne adduct and the subsequent formation of cyclopentenedione (**26**). Work-up of a similar reaction led to the isolation and characterisation of the vinylketene complex - adduct (**27**). Subsequent thermolysis of adduct (**27**) at 85 °C for three days consumed the adduct and gave a crude product mixture containing cyclopentenedione (**26**) but not the corresponding phenol from which the cyclopentenedione in 55% yield.




Finally in this section, the reactivity of 4-methoxyphenylacetylene, prepared by adaptation of a published procedure,[11] was examined to determine whether or not the methoxy substituent would lead to any significant deviation from the chemistry observed using phenylacetylene. Reaction of vinylketene complex (**11**) with 4-methoxyphenylacetylene at 80 °C for 8 days gave a crude product which $^1$H NMR spectroscopy revealed contained the cyclopentenedione (**28**) but no corresponding phenol. Reaction of vinylketene complex (**11**) with 4-methoxyphenylacetylene at 40 °C for 30 h led to the isolation of vinylketene complex - alkyne adduct (**29**) which when heated at 80 °C for 3 days gave the cyclopentenedione (**28**). Thus the methoxy substituent

**Table 3.** $^{13}C\{^1H\}$ NMR data (δ)[a] for adducts formed from tricarbonyl(vinylketene)iron(0) complexes and alkynes

| Adduct | C(1)[b] | C(2) | C(3) | C(4) | C(5) | C(6) | C(1)/C(2) substituent(s) | C(4) substituent | $C_{ortho/meta}$ | $C_{para}$ | $C_{ipso}$ | C=O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **15** | 193.4 | 137.5 | 204.4-206.3 (see C=O) | 87.8 | 93.7 | 84.5 | 52.0, 52.1, 160.6, 175.2 | 24.2 | 126.4, 129.6 | 129.3 | 136.5 | 3 from 204.4, 205.4 206.0, 206.3 [see C(3)] |
| **16** | 193.1 | 139.2 | 204.4-206.3 (see C=O) | 103.9 | 92.3 | 83.6 | 51.9, 52.0, 160.6, 175.1 | 20.5, 26.8, 38.5 | 126.3, 129.5 | 129.1 | 136.5 | 3 from 204.4, 205.8 206.2, 206.3 [see C(3)] |
| **17** | 194.3 | 141.4 | 205.0-206.7 (see C=O) | 115.9 | 89.2 | 79.2 | 52.0, 52.1, 160.8, 175.5 | 32.1, 38.3 | 126.2, 129.0 | 128.8 | 136.7 | 3 from 205.0, 206.0 206.6, 206.7 [see C(3)] |
| **18** | 192.9 | 144.3 | 198.8 | 106.9 | 92.6 | 82.5 | 52.3, 174.0 | 20.5, 26.6, 37.2 | 126.3, 129.4 | 128.7 | 137.4 | 205.1, 207.4, 207.7 |
| **19** | 192.8 | 146.3 | 199.6 | 117.1 | 90.0 | 79.2 | 52.2, 174.0 | 32.0, 37.9 | 126.0, 129.4 | 128.4 | 137.5 | 205.4, 207.6, 208.1 |
| **20** | 199.0 | 141.6 | 204.0-207.7 (see C=O) | 106.6 | 92.7 | 82.2 | 28.1, 204.0-207.7 (see C=O) | 20.5, 26.7, 37.3 | 126.2, 129.5 | 128.7 | 137.3 | 3 from 204.0, 205.1, 207.3, 207.7, 207.7 [see C(3) and C(1)/(2) substituent] |
| **21** | 200.1 | 143.7 | 204.1-208.1 (see C=O) | 116.8 | 90.1 | 79.1 | 28.1, 204.1-208.1 (see C=O) | 32.1, 38.1 | 126.1, 129.5 | 128.5 | 137.7 | 3 from 204.1, 205.5 207.7, 207.9, 208.1 [see C(3) and C(1)/(2) substituent] |
| **27** | 205.0-210.2 (see C=O) | 141.7 | 198.2 | 107.0 | 93.2 | 82.1 | [c] | 20.5, 26.8, 37.3 | [c] | [c] | [c] | 3 from 205.0, 208.2 210.0, 210.2 [see C(1)] |
| **29** | 205.0-210.3 (see C=O) | 140.7 | 198.1 | 107.2 | 93.2 | 82.0 | 55.3, 113.8, 126.5, 142.4, 159.9 | 20.5, 26.7, 37.1 | 126.2, 129.3 | 128.3 | 137.7 | 3 from 205.0, 208.5, 209.7, 210.3 [see C(2)] |
| **30** | 229.7 | 114.4 | 198.8 | 92.0 | 94.5 | 80.0 | 14.8, 68.9 | 24.6 | 126.7, 129.7 | 128.7 | 138.4 | 205.6, 207.5, 209.5 |
| **31** | 229.0 | 116.1 | 198.3 | 109.0 | 91.2 | 78.3 | 14.4, 68.3 | 20.2, 26.3, 35.7 | 126.3, 129.3 | 128.2 | 138.1 | 205.4, 207.8, 209.4 |
| **34** | 242.7 | 55.7 | 165.7 | 108.0 | 91.0 | 71.2 | 12.6, 13.6, 13.8, 51.4, 52.7 | 20.8, 22.6, 31.6 | 216.6, 128.6 | 126.1 | 141.0 | 213.6, 216.3 |
| **35** | 243.9 | 55.4 | 166.8 | 112.4 | 90.8 | 71.2 | 12.9, 13.3, 13.3, 51.0, 53.3 | 27.7, 34.2 | 126.7, 128.6 | 126.2 | 141.2 | 213.7, 216.3 |

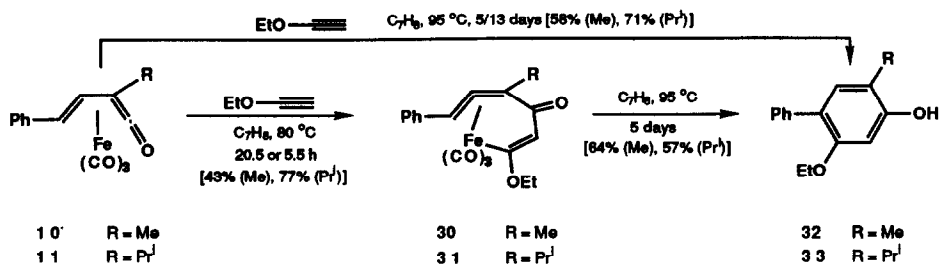
[a] $CDCl_3$, 297K, 125.8 or 67.9 MHz [b] See Figure 1 for numbering [c] Firm assignment difficult

did not appear to be exerting any significant effect and so attention turned to alkynes with relatively powerful π-donor substituents.

*Reactions of alkynes bearing π-donor substituents with tricarbonyl(vinylketene)iron(0) complexes*

The reactivity of relatively electron-rich alkynes towards tricarbonyl(vinylketene)iron(0) complexes was examined next. Thus the oxygen-substituted alkyne ethyl ethynyl ether was reacted with the vinylketene complexes (**10**) and (**11**) at 80 °C for 20.5 and 5.5 hours respectively. The organometallic products isolated from these reactions were regiochemically pure by 270 MHz $^1$H NMR spectroscopy and were tentatively assigned the structures (**30**) and (**31**) by comparison of their spectroscopic and analytical data with that obtained from the adducts (**15**)-(**21**), (**27**) and (**29**) (see Tables 1-3). Interestingly, the ethoxy substituent derived from the alkyne appeared to be located on the carbon atom α to the iron atom *i.e.* the regiochemistry of alkyne insertion does not appear to be controlled in a simple manner by the π-donor/acceptor effects of the alkyne substituents.

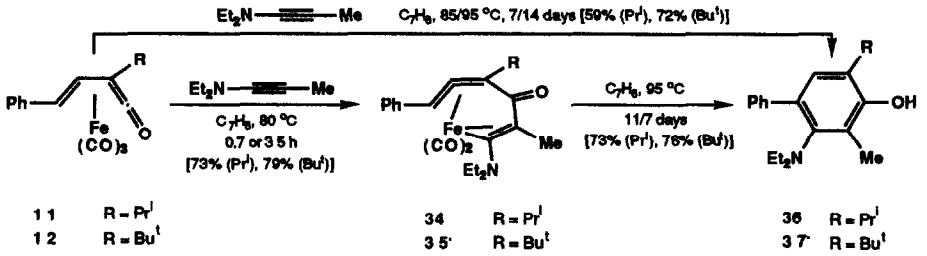
Complexes (**30**) and (**31**) were subsequently thermolysed. Heating these two complexes at 95 °C for 5 days followed by work-up led to the isolation of organic compounds which were identified as the phenols (**32**) and (**33**). [The regiochemistry of the phenols was determined by comparison of their $^1$H and $^{13}$C NMR spectroscopic data with values calculated for the two possible regioisomers. These comparisons led to an unambiguous assignment of the structure of phenols (**32**) and (**33**) which, its was noted, confirmed the regiochemical assignments made for adducts (**30**) and (**31**).] Careful examination of the crude product mixtures from which the two phenols were isolated established that the corresponding cyclopentenediones had not been formed in any of these reactions. It was also demonstrated that the vinylketene complexes can be converted directly into regiochemically-pure phenols (**32**) and (**33**) in moderate to good yield (58 and 71% respectively) simply by heating with ethyl ethynyl ether.




**10** R = Me **30** R = Me **32** R = Me
**11** R = Pi **31** R = Pi **33** R = Pi

Finally, the vinylketene complexes (**11**) and (**12**) were reacted with the disubstituted electron-rich alkyne diethylpropynylamine[12] at 80 °C for 0.7 and 3.5 h respectively. Although the organometallic products derived from these reactions were also regiochemically pure by 270 MHz $^1$H NMR spectroscopy, examination of their spectroscopic and analytical data revealed that they were structurally different from 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. An *X*-ray crystal structure analysis of the product obtained from the reaction between the vinylketene complex (**11**) and diethylpropynylamine[9] revealed that a) a carbon monoxide ligand had been displaced from the iron centre by co-ordination of the double bond derived from the alkyne, and b) the $Et_2N$ substituent was located on the carbon atom α to the metal centre.

Thermolysis of adducts (34) and (35) gave phenols (36) and (37) in good yield. Once again, careful examination of the crude product mixtures from which these phenols were isolated established that the corresponding cyclopentenediones had not been formed in either of these reactions. The two phenols were also generated directly under good regiochemical control from the vinylketene complexes (11) and (12) and diethylpropynylamine.



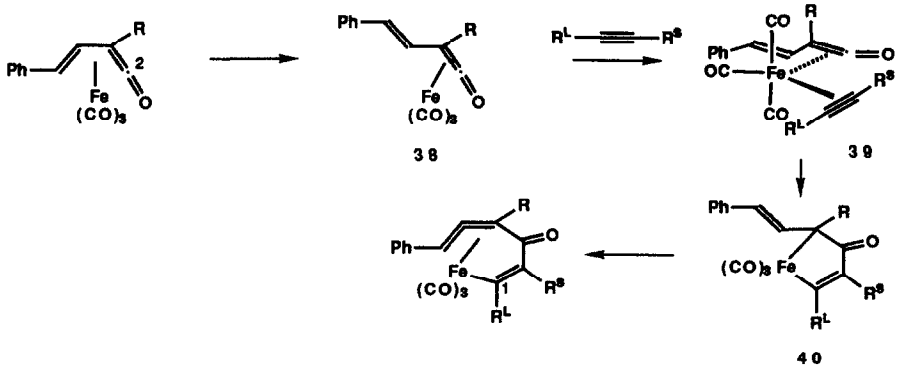

11 R = Pr$^i$
12 R = Bu$^t$

34 R = Pr$^i$
35 R = Bu$^t$

36 R = Pr$^i$
37 R = Bu$^t$

## CONCLUSIONS

Reaction of tricarbonyl(vinylketene)iron(0) complexes with alkynes has been shown to generate 1:1 adducts. Use of alkynes bearing strong $\pi$-acceptor and strong $\pi$-donor substituents produces very stable adducts in good to excellent yield whilst the use of alkynes bearing weak $\pi$-acceptor or donor substituents generates adducts which are difficult to isolate due to their instability with respect to organic products. A plausible pathway for the formation of these adducts is depicted below. Dissociation of the styryl section of the vinylketene ligand produces complex (38), which is coordinatively unsaturated and can bind the appropriate alkyne to generate the eighteen electron complex (39). Subsequent interaction of the metal centre, the alkyne, and the 'alkene' of the ketene ligand gives rise to the sixteen electron metallacyclopentenone (40) which after recoordination of the styryl group affords the product adduct.




The regioselectivity of insertion of the alkynes into the iron-carbon-2 bond of the vinylketene complexes does not correlate in a simple manner with electronic factors. Whilst it may be postulated that steric interactions between the alkyne substituents and the ketene ligand in intermediate (39) are responsible for the more sterically demanding alkyne substituent consistently being located on carbon-1 of the product adduct (an

explanation based on steric considerations has been used to rationalise the regioselectivity of alkyne incorporation in the benzannulation reaction of chromium arylcarbene complexes[13]), electronic influences (which have been used to explain the regioselectivity of alkyne insertion into a 2-ferra-3-azetine ring[14]) cannot be ruled out. Experiments to probe further the origin of the regioselectivity are underway.

The outcome of thermolysis of the adducts appears to be dependent on the π-acceptor/donor capacity of their carbon-1 substituent. The ethoxy-substituted adducts (30) and (31) ($\delta_{C\text{-}1}$ = 229.7 and 229.0 respectively) cleanly reductively eliminate to give phenols on thermolysis whilst the carbomethoxy-substituted adduct (17) ($\delta_{C\text{-}1}$ = 194.3) produces a cyclopentenedione on heating under forcing conditions. The observation that the phenyl-substituted adduct (27) ($\delta_{C\text{-}1}$ = 205.0-210.2) gives a cyclopentenedione on thermolysis whilst thermolysis of the precursor vinylketene complex in the presence of phenylacetylene generates both the phenyl-substituted cyclopentenedione and phenol leads to the prognosis that this system is close to the boundary between the two pathways which lead to the two observed classes of organic product. It is proposed that the strong π-donor ethoxy substituent reduces the strength of the iron-C-1 bond (by competing effectively with a filled metal orbital for interaction with the C=C-C=O fragment) and thus facilitates reductive elimination across C-1 and C-6. The stronger iron-C-1 bonds of adducts (17) and (27) render this pathway less favourable and migration of C-4 to a carbonyl ligand becomes accessible. Reductive elimination between the acyl ligand so formed and C-1 of complex (27) relatively readily produces a cyclopentenedione whilst reductive elimination of the acyl ligand formed from complex (17) and C-1 is inaccessible under simple thermolysis conditions because of the strength of the iron-C-1 bond in this system.

## EXPERIMENTAL

Reactions under nitrogen were performed using standard vacuum line and Schlenk tube techniques.[15] Dichloromethane was distilled from $P_4O_{10}$. Diethyl ether and toluene were dried over sodium wire. Ethyl acetate was distilled from $CaH_2$. Tetrahydrofuran was distilled from sodium benzophenone ketyl. $Fe_2(CO)_9$,[16] 4-methoxyphenylacetylene,[11] diethylpropynylamine,[12] and tricarbonyl(vinylketene)iron(0) complexes (10)-(12)[6] were prepared using published literature procedures. All other reagents were used as obtained from commercial sources. The concentration of MeLi was determined by titration against diphenylacetic acid.[17] M.p.s were obtained on a Reichert 7905 hot-stage microscope and a Gallenkamp capillary m.p. apparatus and are uncorrected. Elemental analyses were performed by MEDAC Ltd, Brunel University Chemistry Department and Imperial College Microanalytical Service. IR spectra were obtained on a Perkin-Elmer 1710 FTIR instrument. NMR spectra were recorded in $CDCl_3$ on Jeol GSX 270 (270 MHz $^1H$; 67.9 MHz $^{13}C$) and Bruker AM 500 (500 MHz $^1H$; 125.8 MHz $^{13}C$) spectrometers; *J* values are given in Hz. Mass spectra were recorded on VG Mass Lab 12/250 and VG Analytical ZAB/E instruments at the SERC Mass Spectrometry Service Centre, Swansea, and on a VG Micromass 7070E instrument at Imperial College using EI, CI and FAB techniques.

*Reactions of alkynes bearing π-acceptor substituents with tricarbonyl(vinylketene)iron(0) complexes*

**Procedure A** Reaction of vinylketene complex (10) with dimethyl acetylenedicarboxylate. - Complex (10) (93.9 mg, 0.315 mmol) was dissolved in toluene (16 $cm^3$) and the yellow solution was degassed and purged with nitrogen. Dimethyl acetylenedicarboxylate (77.5 μl, 0.63 mmol) was added and the solution stirred

under nitrogen at 72 °C for 1 h. The resulting dark brown mixture was filtered through a plug of deactivated alumina using diethyl ether as eluent and concentrated *in vacuo* to give a brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) and crystallisation afforded *adduct (15)* as yellow crystals (96.3 mg, 69%), m.p. 149-151 °C (Found: C, 54.76; H, 3.54. $C_{20}H_{16}FeO_8$ requires C, 54.57; H, 3.66%); *m/z* (FAB, MNBA) 441 ($MH^+$, 57%), 357 (100, MH-3CO) and 297 (47, M-3CO-$CO_2$Me). See Tables 1, 2, and 3 for relevant IR, $^1H$ and $^{13}C$ NMR data.

Reaction of vinylketene complex (11) with dimethyl acetylenedicarboxylate. - As Procedure A: Complex (11) - 50.0 mg, 0.15 mmol; toluene - 10 $cm^3$; dimethyl acetylenedicarboxylate - 37.7 µl, 0.31 mmol; 72 °C; 1.5. Concentration gave a yellow solid which was crystallised from 60-80 °C petroleum ether-diethyl ether to give *adduct (16)* as yellow crystals (66.8 mg, 93%), m.p. 121-123 °C (Found: C, 56.21; H, 4.18. $C_{22}H_{20}FeO_8$ requires C, 56.43; H, 4.30%); *m/z* (FAB, NOBA): 469 ($MH^+$, 49%), 385 (100, MH-3CO) and 325 (34, M-3CO-$CO_2$Me).

Reaction of vinylketene complex (12) with dimethyl acetylenedicarboxylate. - As Procedure A: Complex (12) - 210.0 mg, 0.62 mmol; toluene - 16 $cm^3$; dimethyl acetylenedicarboxylate - 152.0 µl, 1.23 mmol; 80 °C; 1.75 h. Concentration gave a yellow oil that was crystallised from 60-80 °C petroleum ether-diethyl ether to afford *adduct (17)* as yellow crystals (288.0 mg, 97%), m.p. 151-152 °C (Found: C, 57.14; H, 4.47. $C_{23}H_{22}FeO_8$ requires C, 57.28; H, 4.60%); *m/z* (FAB, MNBA) 483 ($MH^+$, 10%), 399 (100, MH-3CO) and 339 (45, M-3CO-$CO_2$Me).

X-Ray crystallographic analysis of adduct (17). - *Crystal data.* Single crystals of (17), suitable for *X*-ray crystallography were grown from 60-80 °C petroleum ether-diethyl ether. $C_{23}H_{22}FeO_8$, $M$ = 482.3, monoclinc, $a$ = 17.294(6), $b$ = 17.182(13), $c$ = 17.379(8) Å, β = 116.43(3)°, $U$ = 4624Å$^3$, space group $P2_1/c$, $Z$ = 8 (2 crystallographically independent molecules), $D_c$ = 1.39 g $cm^{-3}$. Yellow air stable plates, dimensions 0.36 x 0.40 x 0.50 mm, µ(Mo-$K\alpha$) = 6.97 $cm^{-1}$, $F(000)$ = 2000. 4357 Independent measured reflections were collected on a Siemens P4 diffractometer, ω-scan method, ($3 \leq 2\theta \leq 50°$), graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) with 2940 observed [$|F_o| > 3\sigma(|F_o|)$] and corrected for Lorentz and polarisation factors. No absorption corrections were applied. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealised (C-H = 0.96 Å), assigned isotropic thermal parameters $U$(H) = 0.08 and allowed to ride on their parent carbons. Refinement was by full-matrix least squares to give $R$ = 0.047, $R_w$ = 0.045 ($\omega^{-1} = \sigma^2(F) + 0.0007F^2$). The maximum residual electron density in the final $\Delta F$ maps was 0.23 e Å$^{-3}$ and the mean and maximum shift/error in the final refinement cycle were 0.001 and 0.658 respectively. Computations were carried out on an IBM PS/2 386 using the SHELXTL PC program system.[18] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Reaction of vinylketene complex (11) with methyl propiolate. - As Procedure A: Complex (11) - 101.0 mg, 0.31 mmol; toluene - 15 $cm^3$; methyl propiolate - 55.0 µl, 0.62 mmol; 72 °C; 2 h. Concentration gave a brown oil (116.0 mg, 91%; ratio of major product : minor product by $^1H$ NMR spectroscopy, 22:1) which was chromatographed ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) to give the regiochemically pure *adduct (18)* as a brown oil (78.1 mg, 61%), (Found: *m/z* 411.0530. $C_{20}H_{19}FeO_6$ (MH) requires 411.0531); *m/z* (FAB, NOBA) 411 ($MH^+$, 23%), 382 (8, M-CO), 355 (7, MH-2CO) and 327 (100, MH-3CO).

Reaction of vinylketene complex (12) with methyl propiolate. - As Procedure A: Complex (12) - 85.0 mg, 0.25 mmol; toluene 12.5 $cm^3$; methyl propiolate - 42.0 µl, 0.50 mmol; 72 °C; 2.5 h. Concentration gave an

orange yellow oil (ratio of major product : minor product by $^1$H NMR spectroscopy, 10:1). Chromatography ($SiO_2$; 40-60 °C petroleum ether-diethyl ether, 4:1) afforded the regiochemically pure *adduct (19)* as a bright yellow crystalline solid (75 mg, 68%), m.p. 128-131 °C (decomp) (Found: *m/z* 425.0688. $C_{21}H_{21}FeO_6$ (MH) requires 425.0688); *m/z* (CI, $NH_3$) 425 ($MH^+$, 14%), 397 (23, MH-CO), 358 (8, M+$NH_4$-3CO), 341 (27, MH-3CO) 302 (58, M+$NH_4$-Fe(CO)$_3$) and 285 (100, MH-Fe(CO)$_3$).

Reaction of vinylketene complex (11) with but-3-yn-2-one. - As Procedure A: Complex (11) - 100.0 mg, 0.307 mmol; toluene - 16 cm$^3$; but-3-yn-2-one - 48.0 µl, 0.613 mmol; 72 °C; 3 h. Concentration gave a yellow oil. $^1$H NMR spectroscopy of this crude product indicated that the minor product observed in the reactions above had not been formed. The oil was solidified by immersing it in liquid nitrogen and allowing to warm to -4 °C overnight. The yellow crystals thus obtained were washed with 60-80 °C petroleum ether and dried *in vacuo*. *Adduct (20)* was obtained as a single regioisomer (by $^1$H NMR spectroscopy) (63.0 mg, 52%), m.p. 95-98 °C (Found: C, 60.88; H, 4.54. $C_{20}H_{18}FeO_5$ requires C, 60.93; H, 4.6%); *m/z* (EI): 394 ($M^+$, 0.3%), 366 (27, M-CO), 338 (36, M-2CO), 310 (100, M-3CO) and 254 (97, M-Fe(CO)$_3$).

Reaction of vinylketene complex (12) with but-3-yn-2-one. - As Procedure A: Complex (12) - 205.3 mg, 0.63 mmol; toluene - 20 cm$^3$; but-3-yn-2-one - 98.5 µl, 1.26 mmol; 80 °C; 3.5 h. Concentration gave a yellow oil. $^1$H NMR spectroscopy of this crude product indicated that the ratio of major product : minor product was >100:1.) Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) and crystallisation afforded *adduct (21)* as a yellow regiochemically pure crystalline solid (96.1 mg, 39%), m.p. 154-156 °C (Found: C, 61.63; H, 4.94. $C_{21}H_{20}FeO_5$ requires C, 61.78; H, 4.94%); *m/z* (LSIMS, MNBA) 409 ($MH^+$, 19%), 380 (16, M-CO), 352 (15, M-2CO) and 325 (100, MH-3CO).

Thermolysis of tricarbonyl(3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) - dimethyl acetylene-dicarboxylate adduct (17) - Adduct (17) (0.70 g, 1.45 mmol) was heated at 90 °C in dry toluene (25 cm$^3$) for 17 h. After cooling, the brown turbid mixture was passed through a short plug of alumina (Brockmann 1, neutral; diethyl ether). Evaporation of the solvent gave a brown oil which was then subjected to preparative TLC (Kieselgel 60 $GF_{254}$; diethyl ether-60-80 °C petroleum ether, 1:4). Extraction of material from the band of $R_f$ 0.25 gave a yellow oil which was subsequently identified as *the reduced adduct (22)* (0.030 g, 4%) (Found: *m/z* 469.0950. $C_{23}H_{25}FeO_7$ (MH) requires 469.0950); $\nu_{max}(CCl_4)/cm^{-1}$ 2050vs, 2000vs, and 1990vs (C≡O), 1750m and 1710m (C=O); $\delta_H$ 1.29 (9H, s, $C(CH_3)_3$), 2.49 (1H, d, *J* 9.3, H-6), 3.38 (1H, d, *J* 17, 1H of $CH_2$), 3.51 (1H, d, *J* 17, 1H of $CH_2$), 3.64 (3H, s, 1 $CH_3$ of 2 x $CO_2CH_3$), 3.86 (3H, s, 1 $CH_3$ of 2 x $CO_2CH_3$), 6.02, (1H, d, *J* 9.3, H-5) and 7.2-7.25 (5H, m, Ph); $\delta_C$ 30.8 ($C(CH_3)_3$), 33.0 ($C(CH_3)_3$), 41.3 ($CH_2$), 51.7 and 51.9 (2 x $CO_2CH_3$), 64.0 (C-6), 87.2 (C-5), 94.9 (C-4), 116.2 (C-2), 126.5 ($C_{ortho}/C_{meta}$), 127.3 ($C_{para}$), 128.9 ($C_{ortho/meta}$), 138.3 ($C_{ipso}$), 167.7 and 171.5 (2 x $CO_2Me$), 183.5 (C-1), 206.3, 209.1 and 212.9 (3 x C≡O); *m/z* (CI/$NH_3$) 469 ($MH^+$, 60%), 441 (7, MH - CO), 385 (44, MH - 3CO) and 329 (100, MH - Fe(CO)$_3$).

Thermolysis of tricarbonyl(3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) - dimethyl acetylene-dicarboxylate adduct (17) in the presence of triphenylphosphine. - Adduct (17) (0.100 g, 0.207 mmol) and triphenylphosphine (0.120 g, 0.458 mmol) were heated in dry toluene (15 cm$^3$) at 76 °C for 7 days. The resulting brown suspension was subjected to column chromatography (Kieselgel 60; diethyl ether-60-80 °C petroleum ether, 1:3) and the first yellow band to be eluted was collected. This was purified further by preparative TLC (Kieselgel 60 $GF_{254}$; diethyl ether-60-80 °C petroleum ether, 1:3). Extraction of the yellow band of $R_f$ 0.25 gave *5-tert-butyl-2,3-dicarbomethoxy-5-styryl-cyclopent-2-en-1,4-dione (23)* as a yellow oil

(0.017 g, 22%) (Found: *m/z* 388.1760. $C_{21}H_{26}NO_6$ ($M+NH_4$) requires 388.1760); $\nu_{max}(CCl_4)/cm^{-1}$ 1744s ($CO_2Me$), 1712s (unsaturated ketone); $\delta_H$ 1.08 (9H, s, $C(CH_3)_3$), 3.94 (6H, s, 2 x $CO_2CH_3$), 6.19 (1H, d, *J* 16.4, PhCH=C*H*), 6.70 (1H, d, *J* 16.4, PhC*H*=CH), 7.2-7.4 (5H, m, Ph); $\delta_C$ 26.1 ($C(CH_3)_3$), 39.8 ($C(CH_3)_3$), 53.4 (2 x $CO_2CH_3$), 62.0 ($CBu^t$), 120.8 (PhCH=CH) 126.6 ($C_{ortho/meta}$), 128.2 ($C_{para}$), 128.6 ($C_{ortho/meta}$), 134.3 (PhCH=CH), 136.1 ($C_{ipso}$), 146.2 (2 x $CCO_2Me$), 161.0 (2 x $CO_2Me$) and 198.5 (2 x unsaturated ketone C=O); *m/z* (CI, $NH_3$) 388 ($MH^+$+$NH_3$, 53%) and 315 (100, MH-isobutene).

*Reactions of oct-1-yne, phenylacetylene and 4-methoxyphenylacetylene with tricarbonyl(vinylketene)iron(0) complexes*

Reaction of complex (11) with oct-1-yne. - As Procedure A: Complex(**11**) - 96.6 mg, 0.296 mmol; toluene - 15 $cm^3$; oct-1-yne - 87 µl, 0.59 mmol; 72 °C; 20 h; further oct-1-yne added - 90 µl, 0.60 mmol; 7 h. Concentration gave a brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) gave *2-hexyl-5-*iso*-propyl-5-styrylcyclopent-2-en-1,4-dione (24)* (20.9 mg, 22%) $\nu_{max}$(cyclohexane)/$cm^{-1}$ 1704 (C=O); $\delta_H$ 0.9 (3H, m, $(CH_2)_5CH_3$), 0.96 (6H, d, *J* 7 Hz, $CH(CH_3)_2$), 1.2-1.4 (6H, m, $CH_2CH_2(CH_2)_3Me$), 1.6 (2H, m, $CH_2CH_2(CH_2)_3Me$), 2.28 (1H, sept, *J* 7 Hz, $CHMe_2$), 2.46 (2H, m, $CH_2CH_2(CH_2)_3Me$), 6.1 (1H, d, *J* 16 Hz, PhCH=C*H*), 6.5 (1H, d, *J* 16 Hz, PhC*H*=CH), 6.9 (1H, m, O=CC(hex)=C*H*C=O) and 7.2-7.35 (5H, m, Ph); $\delta_C$ 14.1 ($(CH_2)_5CH_3$), 17.9 and 18.0 ($CH(CH_3)_2$), 22.6, 25.6, 27.1, 29.0 and 31.5 ($(CH_2)_5Me$), 34.5 ($CHMe_2$), 60.1 ($CCHMe_2$), 125.3 (PhCH=CH), 126.5 ($C_{ortho/meta}$), 127.9 ($C_{para}$), 128.6 ($C_{ortho/meta}$), 132.1 (PhCH=CH), 136.5 ($C_{ipso}$), 143.2 (O=CC(hex)=CHC=O), 164.9 (O=CC(hex)=CHC=O), 204.4 and 205.6 (C=O); *m/z* (EI) 324 ($M^+$, 100%), 282 (39, M-propene) and 211 (47, M-$C_8H_{17}$); and *5-hexyl-4-phenyl-2-*iso*-propylphenol (25)* (35.8 mg, 41%) (Found: 296.214. $C_{21}H_{28}O$ ($M^+$) requires 296.214); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3600 (OH); $\delta_H$ 0.85 (3H, m, $(CH_2)_5CH_3$), 1.1-1.5 (14H, m, $(CH_2)_4Me$ and $CH(CH_3)_2$), 2.48 (2H, m, $CH_2(CH_2)_4Me$), 3.2 (1H, sept, *J* 7 Hz, $CHMe_2$), 4.8 (1H, brs, OH), 6.7 (1H, s, H-6), 7.0 (1H, s, H-3), 7.3-7.4 (5H, m, Ph); $\delta_C$ 14.1 ($(CH_2)_5CH_3$), 22.6 ($CH(CH_3)_2$), 22.5, 26.7, 29.2, 31.2, 31.7, 32.6 ($(CH_2)_5Me$ and $CHMe_2$), 115.6 (C-6), 126.3 ($C_{para}$), 127.9 ($C_{ortho}$), 128.1 (C-3), 129.6 ($C_{meta}$), 131.4 and 135.0 (C-2 and C-4), 138.8 and 142.0 (C-5 and $C_{ipso}$) and 152.0 (C-1); *m/z* (EI) 296 ($M^+$, 100%), 281 (68, M-Me) and 183 (49, M-$C_8H_{17}$).

Reaction of vinylketene complex (11) with phenylacetylene to give 2-phenyl-5-*iso*-propyl-5-styrylcyclopent-2-en-1,4-dione (26). - As Procedure A: Complex (**11**) - 101.8 mg, 0.312 mmol; toluene - 16 $cm^3$; phenylacetylene - 68.5 µl, 0.624 mmol; 72 °C; 48 h; further phenylacetylene added - 68.5 µl, 0.624 mmol; 72 h. Concentration gave a brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 9:1) afforded *2-phenyl-5-*iso*-propyl-5-styrylcyclopent-2-en-1,4-dione (26)* as a yellow oil (36.2 mg, 37%) (Found: 316.1463. $C_{22}H_{20}O_2$ ($M^+$) requires 316.1463); $\nu_{max}$ (cyclohexane)/$cm^{-1}$ 1702vs (C=O); $\delta_H$ 1.03 (3H, d, *J* 7, $CH_3$), 1.05 (3H, d, *J* 7, $CH_3$), 2.38 (1H, sept, *J* 7, $CHMe_2$), 6.20 (1H, d, *J* 16.5, PhCH=C*H*), 6.60 (1H, d, *J* 16.5, PhC*H*=CH) and 7.2-7.95 [11H, m, 2 x Ph and C(O)C(Ph)=C*H*C(O)]; $\delta_C$ 18.0 ($CH(CH_3)_2$), 34.9 ($CH(CH_3)_2$), 61.2 ($CCH(CH_3)_2$), 125.3 (PhCH=CH), 126.5 ($C_{ortho/meta}$), 128.0 ($C_{para}$), 128.6 ($C_{ortho/meta}$), 129.0 ($C_{ortho/meta}$), 129.3 ($C_{ortho/meta}$), 131.7 (O=CC(Ph)=CHC=O/$C_{para}$), 131.8 ($C_{ipso}$) 132.4 (O=CC(Ph)=CHC=O/$C_{para}$), 136.2 ($C_{ipso}$), 141.1 (PhCH=CH), 156.4 (O=CC(Ph)=CHC=O), 203.9 and 204.5 (2 x C=O); *m/z* (CI, $NH_3$) 317 ($MH^+$, 42%), 248 (100), 232 (90).

Reaction of vinylketene complex (11) with phenylacetylene to give adduct (27). - As Procedure A: Complex (11) - 294.0 mg, 0.90 mmol; toluene - 48 $cm^3$; phenylacetylene - 594.0 µl, 5.40 mmol; 41 days; r.t. Concentration gave a mixture of complex (11) and adduct (27) (17:3 by $^1H$ NMR spectroscopy). Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2 followed by 60-80 °C petroleum ether-dichloromethane, 7:3) afforded *adduct (27)* as a regiochemically pure brown oil (45 mg, 11%), (Found: *m/z* 429.0790. $C_{24}H_{21}FeO_4$ (MH) requires 429.0789); *m/z* (FAB, NOBA) 429 ($MH^+$, 15%), 401 (5, MH-CO), 372 (7, M-2CO) and 345 (100, MH-3CO).

**Procedure B** Thermolysis of tricarbonyl(5-phenyl-3-*iso*-propyloxapenta-1,2,4-triene)iron(0) - phenylacetylene adduct (27). - Adduct (27) (0.045 g, 0.105 mmol) was dissolved in toluene (8 $cm^3$) and the solution degassed and purged with nitrogen. The yellow solution was stirred under nitrogen at 85 °C for 3 days and the resulting dark brown mixture filtered through a plug of deactivated alumina and concentrated *in vacuo* to afford a brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-dichloromethane, 7:3) afforded a yellow oil which was identified as 2-phenyl-5-*iso*-propyl-5-styrylcyclopent-2-en-1,4-dione (26) (0.018 g, 55%) by comparison of its IR and $^1H$ NMR spectra with those obtained from an authentic sample (see above).

Reaction of vinylketene complex (11) with 4-methoxyphenylacetylene to give 2-(4-methoxyphenyl)-5-*iso*-propyl-5-styrylcyclopent-2-en-1,4-dione (28). - As Procedure A: Complex (11) - 163 mg, 0.50 mmol; toluene - 10 $cm^3$; 4-methoxyphenylacetylene - 120 mg, 2.00 mmol; 80 °C; 8 days. Concentration gave a dark brown oil. Chromatography ($SiO_2$; 40-60 °C petroleum ether-diethyl ether, 99:1 decreasing to 95:5 in 1% increments) afforded *2-(4-methoxyphenyl)-5-*iso*-propyl-5-styrylcyclopent-2-en-1,4-dione (28)* as a green-yellow oil (27 mg, 16%) (Found: 346.1569. $C_{23}H_{22}O_3$ ($M^+$) requires 346.1569); $\nu_{max}$ (solvent)/$cm^{-1}$ 1691s (C=O); $\delta_H$ 1.02 (3H, d, *J* 7, $CH_3$), 1.05 (3H, d, *J* 7, $CH_3$), 2.37 (1H, sept, *J* 7, C*H*$Me_2$), 3.87 (3H, s, $OCH_3$), 6.20 (1H, d, *J* 16, PhCH=C*H*), 6.61 (1H, d, *J* 16, PhC*H*=CH), 6.99 (2H, d, *J* 9, H-3 of 4-MeOAr), 7.2-7.4 (5H, m, Ph) and 7.99 (2H, d, *J* 9, H-2 of 4-MeOPh); $\delta_C$ 18.7 ($CH(CH_3)_2$), 34.8 ($CH(CH_3)_2$), 55.5 ($OCH_3$), 61.1 ($CCH(CH_3)_2$), 114.5 ($C_{ortho/meta}$), 121.5 ($C_{ipso}$ of 4-MeOPh), 125.6 (PhCH=CH), 126.4 ($C_{ortho/meta}$), 127.8 ($C_{para}$ of Ph), 128.5 ($C_{ortho/meta}$), 131.2 ($C_{ortho/meta}$), 132.2 (O=CC(4-OMeAr)=CHC=O), 136.5 ($C_{ipso}$ of Ph), 138.7 (PhCH=CH), 155.4 (O=CC(4-MeOAr)=CHC=O), 162.5 (C-4 of 4-MeOAr), 203.6 and 205.0 (2 x C=O); *m/z* (CI, $NH_3$) 347 ($MH^+$, 100%).

Reaction of vinylketene complex (11) with 4-methoxyphenylacetylene to give adduct (29). - As Procedure A: Complex (11) - 163 mg, 0.50 mmol; toluene - 10 $cm^3$; 4-methoxyphenylacetylene - 120. mg, 2.00 mmol; 40 °C; 30 h. Concentration gave a brown oil which contained starting complex (11) and adduct (29) (1.2:1 by $^1H$ NMR spectroscopy). Chromatography ($SiO_2$; 40-60 °C petroleum ether-dichloromethane, 0:100 increasing to 100:0 in 5% increments) yielded regiochemcially pure *adduct (29)* as a yellow powder (57 mg, 25%). Recrystallisation from hexane-dichloromethane afforded yellow needle crystals (22 mg, 10%), m.p. 93-96 °C (dec) (Found: *m/z* 459.0854. $C_{25}H_{22}FeO_5$ ($M^+$) requires 459.0895); *m/z* (FAB, NOBA) 459 ($MH^+$, 29%) and 375 (100, MH-3CO).

Thermolysis of tricarbonyl(5-phenyl-3-*iso*-propyloxapenta-1,2,4-triene)iron(0) - 4-methoxyphenylacetylene adduct (29). - As Procedure B: Adduct (29) - 45 mg, 0.10 mmol; toluene - 8 $cm^3$; 80 °C; 3 days. Concentration gave a light brown oil which by $^1H$ NMR spectroscopy contained a cyclopentenedione but not a phenol. Chromatography ($SiO_2$; 40-60 °C petroleum ether - diethyl ether, 99:1 decreasing to 95:5 in 1% increments) yielded a green yellow oil which was identified as 2-(4-methoxyphenyl)-5-*iso*-propyl-5-

styrylcyclopent-2-en-1,4-dione (**28**) (23.4 mg, 68%) by comparison of its TLC and IR and $^1$H NMR spectra with those obtained from an authentic sample (see above).

*Reactions of alkynes bearing π-donor substituents with tricarbonyl(vinylketene)iron(0) complexes*

Reaction of vinylketene complex (**10**) with ethyl ethynyl ether. - As Procedure A: Complex(**10**) - 106.8 mg, 0.358 mmol; toluene - 15 cm$^3$; ethyl ethynyl ether - 100.5 μl, 1.43 mmol; 80 °C; 20.5 h. Concentration gave a yellow oil. $^1$H NMR spectroscopy of this crude product indicated that only one regioisomer of adduct (**30**) had been formed. Purification by column chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) and crystallisation from 60-80 °C petroleum ether-diethyl ether afforded *adduct (30)* as yellow flakes (57.0 mg, 43.5%), m.p. 152-154 °C (Found: *m/z* 369.0410. $C_{18}H_{17}FeO_5$ ($MH^+$) requires 369.0425); *m/z* (FAB, MNBA) 369 ($MH^+$, 20%) and 285 (100, MH-3CO).

Reaction of complex(**11**) with ethyl ethynyl ether. - As Procedure A: Complex (**11**) - 77.1 mg, 0.236 mmol; toluene - 12 cm$^3$; ethyl ethynyl ether - 66.3 μl, 0.945 mmol; 80 °C; 5.5 h. Concentration gave a yellow oil. $^1$H NMR spectroscopy of this crude product indicated that only one regioisomer of adduct (**31**) had been formed. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) followed by crystallisation from 60-80 °C petroleum ether-diethyl ether afforded *adduct (31)* as yellow flakes (72.2 mg, 77%), m.p. 95-98 °C (Found: *m/z* 397.0738. $C_{20}H_{21}FeO_5$ ($MH^+$) requires 397.0738); *m/z* (FAB, NOBA) 397 ($MH^+$, 82%), 369 (10, MH-CO), 340 (19, M-2CO) and 313 (100, MH-3CO).

Thermolysis of tricarbonyl(3-methyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) - ethyl ethynyl ether adduct (**30**). - As Procedure B: Adduct (**30**) - 0.0361 g, 0.098 mmol; toluene - 12 cm$^3$; 95 °C; 6 days. Concentration gave a pale yellow oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) afforded a white solid which was identified as 5-ethoxy-2-methyl-4-phenylphenol (**32**) (0.014 g, 64%) by comparison of its $^1$H NMR spectrum with that obtained from an authentic sample (see below).

Thermolysis of tricarbonyl(5-phenyl-3-*iso*-propyl-1-oxapenta-1,2,4-triene)iron(0) - ethyl ethynyl ether adduct (**31**). - As Procedure B: Adduct (**31**) - 0.0654 g, 0.165 mmol; toluene - 15 cm$^3$; 95 °C; 5 days. Concentration gave a dark brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) afforded *5-ethoxy-4-phenyl-2-iso-propylphenol (33)* as a white solid (0.0241 g, 57%) m.p. 79-81 °C (Found: 256.146. $C_{17}H_{20}O_2$ requires 256.146); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3590s (OH); $\delta_H$ 1.27 (6H, d, *J* 7, $CH(CH_3)_2$), 1.33 (3H, t, *J* 7, $CH_2CH_3$), 3.15 (1H, sept, *J* 7, $CHMe_2$), 3.98 (2H, q, *J* 7, $CH_2Me$), 4.88 (1H, s, OH), 6.45 (1H, s, H-6), 7.15 (1H, s, H-3), 7.27 (1H, t, *J* 7, $H_{para}$), 7.38 (2H, t, *J* 7, $H_{meta}$) and 7.55 (2H, d, *J* 7, $H_{ortho}$); $\delta_C$ 14.8 ($CH_2CH_3$), 22.9 ($CH(CH_3)_2$), 26.7 ($CHMe_2$), 64.3 ($CH_2Me$), 101.0 (C-6), 123.6 (C-4), 126.2 (C-2), 126.3 ($C_{para}$), 127.9 ($C_{ortho}$), 128.7 (C-3), 129.5 ($C_{meta}$), 138.9 ($C_{ipso}$), 152.8 and 154.6 (C-1 and C-5); *m/z* (EI) 256 ($M^+$, 77%), 241 (100, M-Me) and 213 (95, M-Me-CO).

Reaction of vinylketene complex (**10**) with ethyl ethynyl ether to give 5-ethoxy-2-methyl-4-phenylphenol (**32**). - As Procedure A: Complex (**10**) - 0.0488 g, 0.164 mmol; toluene -15 cm$^3$; ethyl ethynyl ether - 183 μl, 0.655 mmol; 95 °C; 5 days. Concentration gave a red-brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) afforded *5-ethoxy-2-methyl-4-phenylphenol (32)* as a white solid (0.0218 g, 58%) m.p. 89-91 °C (Found: 228.115. $C_{15}H_{16}O_2$ ($M^+$) requires 228.115); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3590s (OH); $\delta_H$ 1.33 (3H, t, *J* 7, $CH_2CH_3$), 2.22 (3H, s, Ar-$CH_3$), 3.97 (2H, q, *J* 7, $CH_2CH_3$), 4.75 (1H, s, OH), 6.48 (1H, s, H-6), 7.08 (1H, s, H-3), 7.26 (1H, t, *J* 7, $H_{para}$), 7.32 (2H, t, *J* 7, $H_{meta}$), 7.52 (2H, d, *J* 7, $H_{ortho}$); $\delta_C$ 14.8 and 14.9 ($CH_3$ and $CH_2CH_3$), 64.3 ($CH_2Me$), 100.7 (C-6), 115.2 (C-2), 123.5 (C-4),

126.3 ($C_{para}$), 127.9 ($C_{ortho}$), 129.5 ($C_{meta}$), 132.9 (C-3), 138.5 ($C_{ipso}$), 153. and 155.0 (C-1 and C-5); *m/z* (EI) 228 ($M^+$, 100%), 200 (93, M-CO) and 199 (83, M-CHO).

Reaction of vinylketene complex (11) with ethyl ethynyl ether to give 5-ethoxy-4-phenyl-2-*iso*-propylphenol (33). - As Procedure A: Complex (11) - 0.101 g, 0.31 mmol; toluene - 12 $cm^3$; ethyl ethynyl ether - 87 µl, 0.945 mmol; 95 °C; 3 days. Concentration gave a brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 9:1) afforded an orange oil which was identified as 5-ethoxy-4-phenyl-2-*iso*-propylphenol (33) (0.056 g, 71%) by comparison of its IR and $^1H$ NMR spectra with those of an authentic sample (see above).

Reaction of vinylketene complex (11) with diethylpropynylamine. - As Procedure A: Complex (11) - 80.4 mg, 0.247 mmol; toluene - 15 $cm^3$; diethylpropynylamine - 54.7 µl, 0.49 mmol; 80 °C; 0.7 h. Concentration gave a brown oil. $^1H$ NMR spectroscopy of this crude product indicated that only one regioisomer of adduct (34) had been formed. Chromatography ($SiO_2$; diethyl ether and then ethyl acetate) followed by crystallisation from 60-80 °C petroleum ether-diethyl ether afforded *adduct (34)* as yellow crystals (76.1 mg, 73%), m.p. 92-94 °C (Found: C, 64.45; H, 6.71; N, 3.40. $C_{22}H_{27}FeNO_3$ requires C, 64.56; H, 6.65; N, 3.42%); *m/z* (FAB) 410 ($MH^+$, 93%), 381 (27, M-CO) and 353 (100, M-2CO).

Reaction of vinylketene complex (12) with diethylpropynylamine. - As Procedure A: Complex (12) - 107.2 mg, 0.33 mmol; toluene - 16 $cm^3$; diethylpropynylamine - 73 µl, 0.66 mmol; 80 °C; 1 h; further diethylpropynylamine - 73 µl, 0.66 mmol; 2.5 h. Concentration gave a dark brown oil. $^1H$ NMR spectroscopy of this crude product indicated that only one regioisomer of adduct (35) had been formed. Chromatography ($SiO_2$; diethyl ether then ethyl acetate) followed by crystallisation from 60-80 °C petroleum ether-diethyl ether afforded *adduct (35)* as yellow crystals (112.0 mg, 79%), m.p. 105-107 °C (Found: C, 65.18; H, 6.94; N, 3.26. $C_{23}H_{29}FeNO_3$ requires C, 65.26; H, 6.90; N, 3.31%); *m/z* (FAB, MNBA) 424 ($MH^+$, 100%), 395 (21, M-CO) and 367 (89, M-2CO).

Thermolysis of tricarbonyl(5-phenyl-3-*iso*-propyl-1-oxapenta-1,2,4-triene)iron(0) - diethylpropynylamine adduct (34). - As Procedure B: Adduct (34) - 0.0615 g, 0.150 mmol; toluene - 8 $cm^3$; 95 °C; 11 days. Concentration *in vacuo* gave a dark brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 9:1) afforded *5-diethylamino-6-methyl-4-phenyl-2-*iso*-propylphenol (36)* as a brown oil (0.0328 g, 73%) (Found: 297.209. $C_{20}H_{27}NO$ ($M^+$) requires 297.209); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3600 (OH); $\delta_H$ 0.91 (6H, t, *J* 7, $N(CH_2CH_3)_2$), 1.25 (6H, d, *J* 7, $CH(CH_3)_2$), 2.27 (3H, s, $CH_3$), 2.79 (4H, q, *J* 7, $N(CH_2Me)_2$), 3.16 (1H, sept, *J* 7, $CHMe_2$), 4.69 (1H, s, OH), 6.84 (1H, s, H-3), 7.25-7.4 (5H, m, Ph); $\delta_C$ 12.3 ($CH_3$), 14.4 ($N(CH_2CH_3)_2$), 22.8 ($CH(CH_3)_2$), 27.2 ($CHMe_2$), 47.7 ($N(CH_2Me)_2$), 122.6 (C-6), 125.9 (C-3), 126.1 ($C_{para}$), 126.9 (C-2), 127.6 ($C_{ortho}$), 129.7 ($C_{meta}$), 134.2 (C-4), 143.2 ($C_{ipso}$), 146.0 (C-5) and 151.0 (C-1); *m/z* (EI) 297 ($M^+$, 44%), 282 (100, M-Me), 269 (30, M-CO) and 254 (87, M-Me-CO).

Thermolysis of tricarbonyl(3-*tert*-butyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(0) - diethylpropynylamine adduct (35). - As Procedure B: Adduct (35) - 0.138g, 0.326 mmol; toluene - 15 $cm^3$; 95 °C; 11 days. Concentration gave a dark brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) afforded *2-tert-butyl-5-dimethylamino-6-methyl-4-phenylphenol (37)* as a brown oil (0.072 g, 76%) (Found: 311.225. $C_{21}H_{29}NO$ ($M^+$) requires 311.225); $\nu_{max}$ $(CH_2Cl_2)/cm^{-1}$ 3600 (OH); $\delta_H$ 0.91 (6H, t, *J* 7, $N(CH_2CH_3)_2$), 1.41 (9H, s, $C(CH_3)_3$), 2.25 (3H, s, $CH_3$), 2.75 (4H, q, *J* 7, $N(CH_2CH_3)_2$) 4.78 (1H, s, OH), 6.90 (1H, s, H-3), 7.25-7.35 (5H, m, Ph); $\delta_C$ 12.0 ($CH_3$), 14.5 ($N(CH_2CH_3)_2$), 29.9 ($C(CH_3)_3$), 34.3 ($CMe_3$), 47.7 ($N(CH_2Me)_2$), 122.7 (C-6), 126.1 ($C_{para}$), 126.9 (C-3), 127.6 ($C_{ortho}$), 129.7 ($C_{meta}$),

131.4 (C-2), 133.4 (C-4), 143.3 ($C_{ipso}$), 146.2 (C-5) and 152.4 (C-1); *m/z* (EI) 311 ($M^+$, 62%), 296 (100, M-Me), 283 (18, M-CO) and 268 (38, M-Me-CO).

Reaction of vinylketene complex (11) with diethylethynylamine to give 5-diethylamino-4-phenyl-2-*iso*-propylphenol (36). - As Procedure A: Complex (11) - 0.095 g, 0.29 mmol; toluene - 15 $cm^3$; diethylpropynylamine - 74 µl, 0.67 mmol; 85 °C; 7 days. Concentration gave a brown-red oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) afforded a brown oil which was identified as 5-diethylamino-4-phenyl-2-*iso*-propylphenol (36) (0.0513 mg, 59%) by comparison of its IR and $^1H$ NMR spectra with those of an authentic sample (see above).

Reaction of vinylketene complex(12) with diethylethynylamine to give 5-diethylamino-4-phenyl-2-*tert*-butylphenol (37). - As Procedure A: Complex (12) - 0.099 g, 0.29 mmol; toluene - 15 $cm^3$; diethylpropynylamine - 64.6 µl, 0.58 mmol; 95 °; 14 days. Concentration gave a dark brown oil. Chromatography ($SiO_2$; 60-80 °C petroleum ether-diethyl ether, 5:2) afforded a brown oil which was identified as 2-*tert*-butyl-5-dimethylamino-6-methyl-4-phenylphenol (37) (0.0685 g, 72%) by comparison of its IR and $^1H$ NMR spectra with those of an authentic sample (see above).

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