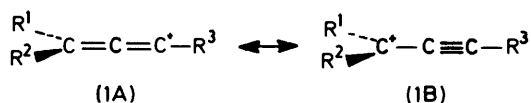


## Stable Carbocations. Part 14.<sup>1</sup> Ferrocenyl-substituted Allenyl $\leftrightarrow$ Propynyl Cations

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Whereas 3-ferrocenylprop-2-yn-1-ol undergoes protonation of the triple bond in trifluoroacetic acid to give a ferrocenylvinyl cation, the secondary alcohol 1,3-diferrocenylprop-2-yn-1-ol and the tertiary 3-ferrocenyl-1,1-dimethyl- and -diphenylpropynols undergo dehydroxylation giving mesomeric allenyl  $\leftrightarrow$  propynyl cations which are rapidly converted into trifluoroacetoxyallylium ions by solvent addition. Under similar conditions, the secondary alcohol 1-ferrocenyl-3-phenylprop-2-yn-1-ol gives the stable 1-ferrocenyl-3-phenylprop-2-ynylium ion, which can also be generated inefficiently in dichloromethane solution by hydride abstraction from 3-ferrocenyl-1-phenylpropyne. The (ferrocenylethynyl)tropylium cation has been prepared as a stable salt. The products formed on quenching solutions of these cations have been identified.

ALLENYL cations (1A) represent the simplest examples of a class of carbocations which incorporate two orthogonal superimposed  $p_{\pi}$ -systems, one electron-deficient. In consequence of the likely orbital geometry, such cations can be represented alternatively as propynyl species (1B), the relative contributions of these limiting structures to the resonance hybrid (and hence the charge distribution) being sensitive<sup>2</sup> to the nature of the attached groups R. Since ferrocenylvinyl cations are sufficiently stable in trifluoroacetic acid to permit spectroscopic study,<sup>3</sup> a similar investigation of ferrocenyl-stabilised cations of the type (1A)  $\leftrightarrow$  (1B) was envisaged. To this end, a



series of ferrocenylalkynols was synthesised by methods detailed elsewhere.<sup>4</sup>

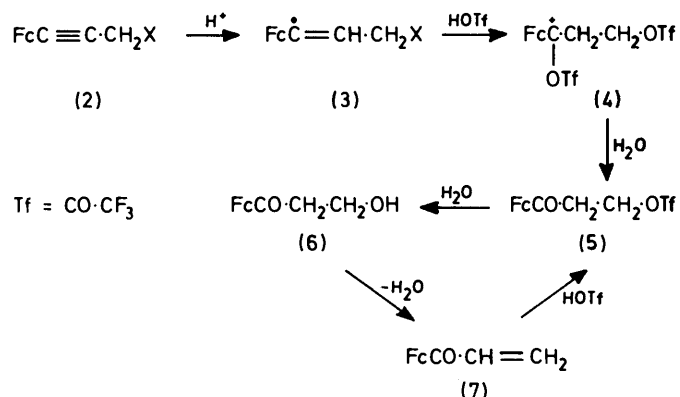
The <sup>1</sup>H n.m.r. spectra of solutions of the primary alcohols (2a and b) in trifluoroacetic acid gave no indication of the presence of cations of the type (1A)  $\leftrightarrow$  (1B) but instead corresponded to the trifluoroacetoxy allylium ions (4a and b).<sup>†</sup> When these solutions were hydrolysed (aqueous sodium hydrogen carbonate), the oxoesters (5a and b) were obtained. These could be converted under mild conditions into the oxo-alcohols (6a and b) which underwent ready dehydration to the  $\alpha\beta$ -unsaturated ketones (7a and b). The oxo-ester (5a) was synthesised independently by treatment of acryloylferrocene (7a) with trifluoroacetic acid followed by hydrolysis with aqueous sodium hydrogen carbonate.

These reactions follow the course indicated in Scheme 1, the first step involving protonation of the triple bond to give a vinyl cation. In the case of the alcohol (2b), the capture by solvent of this intermediate was retarded by the 1',2-di-*t*-butylferrocenyl group<sup>3</sup> to such an extent

<sup>†</sup> The <sup>1</sup>H n.m.r. spectra of the trifluoroacetoxyallylium ions (4a and b), (9c–f), and (13) in trifluoroacetic acid at 33 °C were characteristically broad and poorly defined. These spectra were closely similar, however, to those of the corresponding ketones (5a and b), (10c–f), and (14) in trifluoroacetic acid. Earlier variable-temperature <sup>1</sup>H n.m.r. studies<sup>5</sup> of protonated acylferrocenes [*i.e.* Fc<sup>+</sup>(OH)R] have shown that well defined spectra can be obtained only for solution temperatures lower than *ca.* –50 °C.

that the vinyl cation (3b) could be identified spectroscopically (Table). Initially, two stereoisomers of this cation (*exo*- and *endo*-CH<sub>2</sub>OH) were formed in approximately equal proportions. Rapid torsional equilibration, favouring the *exo*-CH<sub>2</sub>OH stereoisomer, then occurred [*cf.* behaviour of (3c)<sup>3</sup>] followed by much slower solvent addition and esterification to give (4b).

The tertiary alcohols (2c–f) behaved differently in trifluoroacetic acid solution. In these cases the first-formed



- a; Fc = ferrocenyl, X = OH  
b; Fc = 2,1'-di-*t*-butylferrocenyl, X = OH  
c; Fc = 2,1'-di-*t*-butylferrocenyl, X = H

SCHEME 1

carbocations, which were just observable by <sup>1</sup>H n.m.r. spectroscopy, rapidly added solvent, giving finally trifluoroacetoxyallylium ions (9c–f).<sup>†</sup> The appropriate  $\alpha\beta$ -unsaturated ketones (10c–f) were obtained following hydrolysis of these solutions. Unfortunately, the very short lifetimes of the first-formed species, even at low solution temperatures (*ca.* –10 °C), precluded spectroscopic characterisation. However, in view of the properties of the vinyl cation (3b) studied earlier, the corresponding cation resulting from protonation of the triple bond

<sup>1</sup> Part 13, T. S. Abram and W. E. Watts, preceding paper.

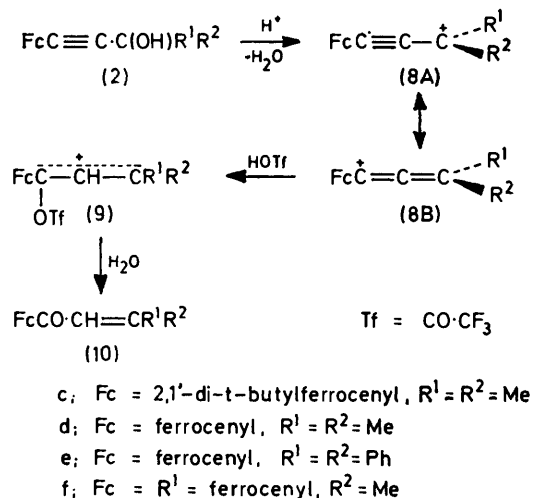
<sup>2</sup> G. A. Olah, R. J. Spear, P. W. Westerman, and J.-M. Denis, *J. Amer. Chem. Soc.*, 1974, **96**, 5855.

<sup>3</sup> T. S. Abram and W. E. Watts, *J.C.S. Perkin I*, 1977, 1522.

<sup>4</sup> T. S. Abram and W. E. Watts, *Synthesis and Reactivity in Inorganic and Metal-Organic Chem.*, 1976, **6**, 31.

<sup>5</sup> G. A. Olah and Y. K. Mo, *J. Organometallic Chem.*, 1973, **60**, 311.

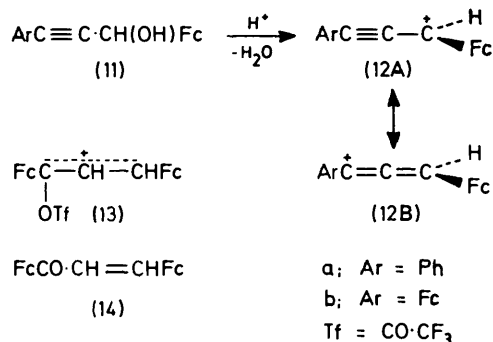
of (2c) would have been expected to be much more stable towards solvent addition than the species actually formed. It seems likely therefore that the alkynols (2c and d) undergo acid-promoted dehydroxylation to give mesomeric cations (8c and d) which are rapidly converted into allylium ions (9c and d) by addition of trifluoroacetic acid. Furthermore, since the hydroxy-groups of the other alkynols (2e and f) would be much more labile in acidic



SCHEME 2

media than that of (2c), a similar reaction pathway *via* the cations (8e and f) is indicated (Scheme 2).

In contrast to the instability of the cations (8c—f) towards solvent addition, the propynyl cation (12a) obtained by dissolution of the alkynol (11a) in trifluoroacetic acid was stable and showed no tendency to react with solvent. The resonance pattern and associated proton chemical shifts of Fc $\overset{\cdot}{\text{C}}\text{H}$  in the <sup>1</sup>H n.m.r. spectrum (Table) were very similar to those of secondary ferrocenylallylium ions (*e.g.* Fc $\overset{\cdot}{\text{C}}\text{HMe}$ ),<sup>6</sup> indicating that

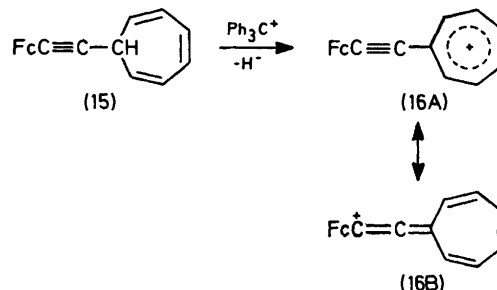


SCHEME 3

the allenyl resonance form (12Ba) makes negligible contribution to the electronic character of the ion (12Aa). Surprisingly, the related cation (12b) formed from the diferrocenylpropynol (11b) had only fleeting existence in trifluoroacetic acid, collapsing quickly by solvent addition to the allylium ion (13) † [*cf.* behaviour of (8f)].

The propenone (14) was formed on hydrolysis of the solution.

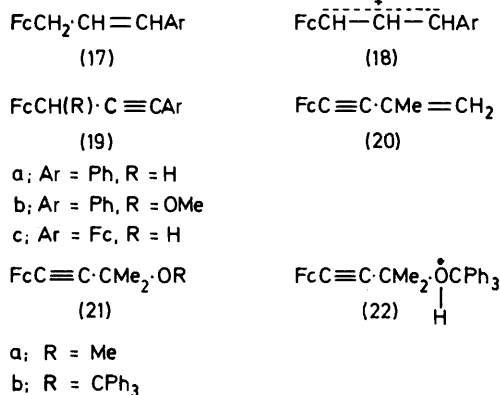
These results suggest that, for mesomeric cations of the type (1; R<sup>3</sup> = Fc), the contribution of the allenyl form (1A) to the structure leads to a substantial allocation of charge at the (*sp*)-terminal carbon atom, stabilised by the attached ferrocenyl group. Such allenic carbocations [*e.g.* (8c—f) and (12b)], however, are susceptible to nucleophilic addition (*cf.* behaviour of ferrocenylvinyl cations<sup>3</sup>) and collapse in trifluoroacetic acid to more stable trifluoroacetoxyallylium ions. In the case of related cations of the type (1; R<sup>1</sup> = Fc, R<sup>3</sup> ≠ Fc), the contribution



SCHEME 4

of the allenyl form (1A) is insignificant and these species [*e.g.* (12a)] behave as ferrocenylallylium ions which are stable in trifluoroacetic acid.<sup>6</sup>

An understandable exception to the above generalisation is the (ferrocenylethynyl)tropylium cation (16), obtained as a stable salt by treatment of the alkynylcycloheptatriene (15) with trityl tetrafluoroborate (Scheme 4). The spectroscopic properties of this cation establish a tropylium-like structure (16A) with negligible contribution from the allenyl form (16B). Accordingly, this



cation undergoes protonation of the triple bond in trifluoroacetic acid<sup>3</sup> and nucleophilic addition of hydride (from lithium aluminium hydride) exclusively at the tropylium ring giving a mixture of isomeric (ferrocenylethynyl)cycloheptatrienes, including the precursor (15).

Generation of cations of the type (1) in an aprotic non-nucleophilic medium was also investigated. Since (aryl-

<sup>6</sup> M. Hisatome and K. Yamakawa, *Tetrahedron*, 1971, **27**, 2101.

allyl)ferrocenes (17) undergo immediate and quantitative hydride-abstraction on reaction with trityl tetrafluoroborate in dichloromethane solution, giving stable allylium ions (18),<sup>7</sup> a similar reaction of the prop-2-ynylferrocene (19a) was attempted. Hydride abstraction from this alkyne proceeded sluggishly, however, in competition with one-electron oxidation<sup>8</sup> of the ferrocenyl group by the trityl cation to give a ferricenium ion inert to hydride transfer. Nevertheless, addition of sodium methoxide in methanol to the reaction solution

(lit.,<sup>11</sup> 73—75°);  $\nu_{\max}$  (KBr) 3 420 (OH) and 2 242  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ );  $\tau(\text{CDCl}_3)$  2.27—2.75 (5 H, m, Ph), 4.44br (1 H, d,  $\text{CH}\cdot\text{OH}$ ), 5.58 (2 H, t), and 5.72—5.93 (7 H, t + s) (ferrocenyl), and 7.75br (1 H, d, OH).

(b) Ferrocenecarbaldehyde (0.65 g, 3 mmol) was added to lithium phenylacetylide, prepared in ether (50 ml) from ethynylbenzene (0.51 g, 5 mmol) and methyl-lithium (4.8 mmol). The mixture was stirred for 0.5 h, then poured into water, and the product was extracted with ether. The alcohol (11a) (0.93 g, 98%) was purified by chromatography ( $\text{Al}_2\text{O}_3$ ).

<sup>1</sup>H N.m.r. spectra ( $\tau$  values) of ferrocenyl carbocations<sup>a</sup>

Cation (3b)	Ferrocenyl protons			Bu <sup>t</sup> protons	Other protons
	H-2, -5	H-3, -4	H-1'-5'		
(3b)	5.60 (t)	3.5—3.7	4.55—5.05	8.84br (s)	2.64 (t, <i>exo</i> -vinyl), 5.07 (d, <i>endo</i> -CH <sub>2</sub> ), 3.37 (t, <i>endo</i> -vinyl), 5.04 (d, <i>exo</i> -CH <sub>2</sub> )
(3c) <sup>b</sup>	5.72 (t)	3.71—3.86	4.75—5.2	8.85br (s)	2.95 (q, <i>exo</i> -vinyl), 7.64 (d, <i>endo</i> -Me), 3.75 (q, <i>endo</i> -vinyl), 7.60 (d, <i>exo</i> -Me)
(12a)	4.55—4.7, 5.2—5.35	3.45—3.6, 3.68—3.9	4.85 (s)		2.80 (s, CH), 2.3—2.6 (Ph)
(Fc <sup>+</sup> CHMe) <sup>c</sup>	4.9—5.0, 5.45—5.6	3.6—3.8	4.97 (s)		2.88 (q, CH), 7.75 (d, Me)

<sup>a</sup> Solvent  $\text{CF}_3\text{CO}_2\text{H}$ ;  $\text{Me}_4\text{Si}$  as internal reference; integrated relative intensities of signals agreed with proton assignments; multiplets unless indicated otherwise. <sup>b</sup> Ref. 3. <sup>c</sup> T. S. Abram and W. E. Watts, *J.C.S. Perkin I*, 1975, 113.

gave the ether (19b) (12% yield) as the sole product. This compound, which did not isomerise in acidified methanol, must arise by addition of methoxide to the cation (12a), which apparently reacts exclusively at the ferrocenyl-substituted carbon atom [*cf.* (12Aa)]. Similar attempts to abstract hydride from the diferrocenylpropyne (19c) led only to oxidation of the ferrocenyl group(s).

Finally, hydroxide abstraction from the alcohol (2d) was attempted by using trityl tetrafluoroborate in dichloromethane solution. Addition of methanol to the reaction solution gave a mixture of the enyne (20) (6%) and the ethers (21a) (51%) and (21b) (8%). Since no product of nucleophilic addition to the ferrocenyl-substituted carbon atom was isolated, it seems probable that the products arise not from the cation (8d) but from reactions of the protonated ether (22) formed by addition of the trityl cation to the alcohol (2d).

#### EXPERIMENTAL

For general details, see Part 4.<sup>9</sup> With the exception of those compounds given below, the methods of preparation of the acetylenic ferrocenes used in this study have been described previously.<sup>4</sup>

**1-Ferrocenyl-3-phenylpropynone.**—This ketone was prepared in 75% yield by a standard Friedel-Crafts reaction of ferrocene with 3-phenylpropynoyl chloride and aluminium chloride in dichloromethane, and gave maroon needles, m.p. (from light petroleum-ether) 105–106° (lit.,<sup>10</sup> 103–106°);  $\nu_{\max}$  (KBr) 2 210 ( $\text{C}\equiv\text{C}$ ) and 1 628  $\text{cm}^{-1}$  (CO);  $\tau(\text{CDCl}_3)$  2.24—2.77 (5 H, m, Ph), 4.99 and 5.48 (2 H and 2 H, 2 × t,  $\text{C}_5\text{H}_4$ ), and 5.71 (5 H, s,  $\text{C}_5\text{H}_5$ ).

**1-Ferrocenyl-3-phenylpropynol (11a).**—(a) Treatment of 1-ferrocenyl-3-phenylpropynone with an excess of sodium borohydride in dioxan-water gave the alcohol (11a) (92%), yellow needles, m.p. (from light petroleum-ether) 72–74°

(*Ferrocenylethynyl*)tropylium Tetrafluoroborate.—A solution of trityl tetrafluoroborate (225 mg, 0.68 mmol) in dichloromethane (5 ml) was added to a solution of the alkyne (15)<sup>4</sup> (200 mg, 0.67 mmol) in dichloromethane (5 ml). The resulting deep green solution was stirred for 2 min then diluted with ether until precipitation ceased. The title salt (175 mg, 68%), a dark green powder, was filtered off, washed with a little dichloromethane then with ether, and dried, all operations being conducted under nitrogen. The salt, which was not purified to analytical standard, was characterised spectroscopically:  $\nu_{\max}$  (KBr) 2 165br ( $\text{C}\equiv\text{C}$ ), and 1 060br  $\text{cm}^{-1}$  ( $\text{BF}_4^-$ );  $\tau(\text{CD}_2\text{Cl}_2)$  1.50br (6 H, s, tropylium), 5.11br (4 H, s,  $\text{C}_5\text{H}_4$ ), and 5.60 (5 H, s,  $\text{C}_5\text{H}_5$ ).

Treatment of this salt with an excess of lithium aluminium hydride in ether gave an almost quantitative yield of a mixture of isomers of (ferrocenylethynyl)cycloheptatriene which resisted separation by chromatographic methods but whose <sup>1</sup>H n.m.r. spectrum ( $\text{CDCl}_3$ ) showed the presence of the alkyne (15) in the mixture.

**2-Ferrocenylethyl Trifluoroacetate (5a).**—A solution of acryloylferrocene<sup>12</sup> (200 mg, 0.83 mmol) in trifluoroacetic acid (5 ml) was stirred for 3 h then poured into an excess of saturated aqueous sodium hydrogen carbonate. The product was extracted with ether and crystallised from light petroleum-ether to give red-orange prisms (271 mg, 92%), m.p. (from light petroleum-ether) 59–60°;  $\nu_{\max}$  (KBr) 1 788 ( $\text{CO}\cdot\text{CF}_3$ ), and 1 666  $\text{cm}^{-1}$  (FcCO);  $\tau(\text{CDCl}_3)$  5.17 and 5.41 (2 H and 2 H, 2 × t,  $\text{C}_5\text{H}_4$ ), 5.20 and 6.86 (2 H and 2 H, 2 × t,  $\text{CH}_2\cdot\text{CH}_2$ ), and 5.77 (5 H, s,  $\text{C}_5\text{H}_5$ ), which decomposed slowly and could not be satisfactorily analysed.

**2-Ferrocenylethanol (6a).**—This was prepared in quantitative yield by hydrolysis of the ester (5a) and was obtained as orange liquid;  $\nu_{\max}$  (film) 3 450 (OH) and 1 670  $\text{cm}^{-1}$  (CO);  $\tau(\text{CDCl}_3)$  5.21 and 5.49 (2 H and 2 H, 2 × t,  $\text{C}_5\text{H}_4$ ), 5.80 (5 H, s,  $\text{C}_5\text{H}_5$ ), 5.87—6.14 (2 H, m,  $\text{CH}_2\cdot\text{OH}$ ), and 6.89—7.13 (3 H, m,  $\text{CO}\cdot\text{CH}_2$  and OH). On attempted purification by chroma-

<sup>7</sup> M. J. A. Habib, J. Park, and W. E. Watts, *J. Chem. Soc. (C)*, 1970, 2556.

<sup>8</sup> P. L. Pauson, M. A. Sandhu, and W. E. Watts, *J. Chem. Soc. (C)*, 1970, 251.

<sup>9</sup> T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

<sup>10</sup> K. Schlögl and A. Mohar, *Monatsh.*, 1962, **93**, 861.

<sup>11</sup> K. Schlögl and A. Mohar, *Monatsh.*, 1961, **92**, 219.

<sup>12</sup> T. D. Turbitt and W. E. Watts, *J. Organometallic Chem.*, 1972, **46**, 109.

tography (SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) it was rapidly dehydrated giving acryloylferrocene, a red solid, m.p. (from light petroleum) 71–72°, identical with an authentic sample.<sup>12</sup>

*Reactions of the Alkynols (2a–f) and (11b) with Trifluoroacetic Acid then Aqueous Sodium Hydrogen Carbonate.*—The alkynol (200–500 mg) was dissolved in cold trifluoroacetic acid (–10 °C initially) and the <sup>1</sup>H n.m.r. spectrum of the solution was recorded immediately. In the case of the alkynols (2c–f), signals attributable to the cations (8c–f) were detected but these quickly disappeared. The spectra of the cations (3b) and (12a) and related species are given in the Table. The solution was then poured into an excess of saturated aqueous sodium hydrogen carbonate and the product was extracted quickly with ether and purified by preparative t.l.c. (SiO<sub>2</sub>). In each reaction, decomposition products were formed. Yields of product were usually >70%.

(a) From the alkynol (2a), there was obtained the ester (5a), identical with the product already described.

(b) From the alkynol (2b), there was obtained 3-(1',2-di-*t*-butylferrocenyl)-3-oxopropyl trifluoroacetate (5b), an orange-red liquid;  $\nu_{\max}$  (film) 1788 (CO·CF<sub>3</sub>) and 1664 cm<sup>-1</sup> (FcCO);  $\tau$ (CDCl<sub>3</sub>) 5.33 (1 H, t) and 5.45–5.63 (2 H, m) (C<sub>5</sub>H<sub>3</sub>), 5.78–6.17 (6 H, m, C<sub>5</sub>H<sub>4</sub> + CH<sub>2</sub>·O<sub>2</sub>C·CF<sub>3</sub>), 6.86–7.21 (2 H, m, CO·CH<sub>2</sub>), and 8.64 and 8.79 (9 H and 9 H, 2 × s, CMe<sub>3</sub>). This compound is extremely prone to hydrolysis (in absence of solvent, or during chromatography), giving 3-(1',2-di-*t*-butylferrocenyl)-3-oxopropan-1-ol (6b), an orange liquid (Found: C, 68.7; H, 8.3. C<sub>21</sub>H<sub>30</sub>FeO<sub>2</sub> requires C, 68.1; H, 8.2%);  $\nu_{\max}$  (film) 3450 (OH) and 1664 cm<sup>-1</sup> (CO);  $\tau$ (CDCl<sub>3</sub>) 5.32 (1 H, t) and 5.44–5.64 (2 H, m) (C<sub>5</sub>H<sub>3</sub>), 5.70–6.17 (6 H, m, C<sub>5</sub>H<sub>4</sub> + CH<sub>2</sub>·OH), 6.86–7.16 (3 H, m, CO·CH<sub>2</sub> + OH), and 8.65 and 8.80 (9 H and 9 H, 2 × s, CMe<sub>3</sub>). This alcohol underwent dehydration during chromatography (Al<sub>2</sub>O<sub>3</sub>) giving 1-acryloyl-1',2-di-*t*-butylferrocene (7b), a red liquid (Found: C, 71.1; H, 7.9. C<sub>21</sub>H<sub>28</sub>FeO requires C, 71.6; H, 8.0%);  $\nu_{\max}$  (film) 1666 (CO) and 1604 cm<sup>-1</sup> (C=C);  $\tau$ (CDCl<sub>3</sub>) 2.80–4.45 (3 H, ABX, vinyl), 5.36 (1 H, t) and 5.44–5.66 (2 H, m) (C<sub>5</sub>H<sub>3</sub>), 5.74–5.97 (4 H, m, C<sub>5</sub>H<sub>4</sub>), and 8.62 and 8.79 (9 H and 9 H, 2 × s, CMe<sub>3</sub>).

(c) From the alkynol (2c), there was obtained 1-(3-methylbut-2-enoyl)-1',2-di-*t*-butylferrocene (10c), an amber liquid (Found: C, 72.7; H, 8.5. C<sub>23</sub>H<sub>32</sub>FeO requires C, 72.6; H, 8.5%);  $\nu_{\max}$  (film) 1659 (CO) and 1616 cm<sup>-1</sup> (C=C);  $\tau$ (CDCl<sub>3</sub>) 3.35–3.47 (1 H, m, vinyl), 5.40 (1 H, t) and 5.55–5.67 (2 H, m) (C<sub>5</sub>H<sub>3</sub>), 5.74–5.97 (4 H, m, C<sub>5</sub>H<sub>4</sub>), 7.85 and 8.15 (3 H and 3 H, 2 × d, Me), and 8.62 and 8.77 (9 H and 9 H, 2 × s, CMe<sub>3</sub>).

(d) From the alkynol (2d), there was obtained 1-(3-methylbut-2-enoyl)ferrocene (10d), a red solid, m.p. (from light petroleum-ether) 102–104° (lit.,<sup>13</sup> 103–104.5°);  $\tau$ (CDCl<sub>3</sub>) 3.54–3.73 (1 H, m, vinyl), 5.22 and 5.55 (2 H and 2 H, 2 × t, C<sub>5</sub>H<sub>4</sub>), 5.84 (5 H, s, C<sub>5</sub>H<sub>5</sub>), and 7.79br and 8.05br (3 H and 3 H, 2 × s, Me).

(e) From the alkynol (2e), there was obtained the ketone (10e), a red liquid;  $\nu_{\max}$  (film) 1650 (CO) and 1590 cm<sup>-1</sup> (C=C);  $\tau$ (CDCl<sub>3</sub>) 2.50–2.74 (10 H, m, Ph), 3.04 (1 H, s, vinyl), 5.19 and 5.50 (2 H and 2 H, 2 × t, C<sub>5</sub>H<sub>4</sub>), and 5.77 (5 H, s, C<sub>5</sub>H<sub>5</sub>). This compound decomposed and was not satisfactorily analysed.

(f) From the alkynol (2f), there was obtained the ketone (10f), a deep red solid, m.p. (from light petroleum-benzene)

119–121° (lit.,<sup>14</sup> 118–120°);  $\tau$ (CDCl<sub>3</sub>) 3.28 (1 H, m, vinyl), 5.19–5.60 (8 H, m, C<sub>5</sub>H<sub>4</sub>), 5.82 and 5.85 (5 H and 5 H, 2 × s, C<sub>5</sub>H<sub>5</sub>), and 7.46br (3 H, s, Me).

(g) From the alkynol (11b), there was obtained the ketone (14), red needles, m.p. (from light petroleum-ether) 210–211° (lit.,<sup>15</sup> 208–210°);  $\tau$  2.32 and 3.30 (1 H and 1 H, 2 × d, vinyl), 5.13 and 5.54 (2 H and 2 H, 2 × t, C<sub>5</sub>H<sub>4</sub>CO), 5.30–5.48 and 5.70–5.88 (2 H and 2 H, 2 × m, C<sub>5</sub>H<sub>4</sub>), and 5.83 and 5.85 (5 H and 5 H, 2 × s, C<sub>5</sub>H<sub>5</sub>).

*Reaction of 1-Ferrocenyl-3-phenylpropynol with Trifluoroacetic Acid.*—The alcohol (11a) dissolved readily in trifluoroacetic acid to give a solution containing the stable cation (12a), whose <sup>1</sup>H n.m.r. signals are given in the Table.

*3-Ferrocenyl-3-methoxy-1-phenylpropyne (19b).*—(a) A solution of trityl tetrafluoroborate (250 mg, 0.76 mmol) in dichloromethane (5 ml) was added to a solution of the alkyne (19a)<sup>1</sup> (220 mg, 0.73 mmol) in dichloromethane (25 ml). The solution became green and its electronic spectrum showed the presence of ferrocenium species ( $\lambda_{\max}$  630 nm). The solution was stirred for 5 min and then an excess of sodium methoxide in methanol was added, the colour changing slowly to orange. The solution was then washed several times with water, dried (MgSO<sub>4</sub>), and evaporated, and the residue was chromatographed (Al<sub>2</sub>O<sub>3</sub>; light petroleum) to give the alkyne (19a) (147 mg, 67% recovery) and 3-ferrocenyl-3-methoxy-1-phenylpropyne (19b) (30 mg, 12%), an amber liquid (Found: C, 72.7; H, 5.5. C<sub>20</sub>H<sub>18</sub>FeO requires C, 72.8; H, 5.5%);  $\nu_{\max}$  (film) 2230 (C≡C) and 1075 cm<sup>-1</sup> (OMe);  $\tau$ (CDCl<sub>3</sub>) 2.35–2.82 (5 H, m, Ph), 4.83 (1 H, s, CH), 5.41–5.78 (4 H, m, C<sub>5</sub>H<sub>4</sub>), 5.80 (5 H, s, C<sub>5</sub>H<sub>5</sub>), and 6.59 (3 H, s, OMe). The yield of this product was not improved by using longer reaction periods. The compound decomposes when adsorbed on SiO<sub>2</sub>, affording phenylpropiolferrocene.

(b) Trifluoroacetic acid (6 drops) was added to a solution of the alkynol (11a) (250 mg, 0.79 mmol) in methanol (15 ml). The mixture was stirred for 10 min, then diluted with aqueous sodium carbonate, and extracted with ether. The extract was washed (H<sub>2</sub>O), dried (MgSO<sub>4</sub>), and evaporated, giving the ether (19b) (243 mg, 93%), identical with the product obtained previously.

*Reaction of 1,3-Diferrocenylpropyne with Trityl Tetrafluoroborate.*—Treatment of the alkyne (19c) with trityl tetrafluoroborate in dichloromethane, as described for a previous experiment, gave a green solution containing ferrocenium species ( $\lambda_{\max}$  630 nm). Addition of sodium methoxide in methanol and work-up as before gave only starting material.

*Reaction of the Alkynol (2d) with Trityl Tetrafluoroborate.*—A solution of the alkynol (2d) (268 mg, 1.0 mmol) and trityl tetrafluoroborate (330 mg, 1.0 mmol) in alcohol-free dichloromethane (50 ml) was stirred for 5 min, then diluted with methanol, and stirred for a further 5 min. The solution was then diluted with water, and the product was extracted with dichloromethane and separated by preparative t.l.c. (SiO<sub>2</sub>). There was obtained (in order of increasing polarity): (i) (3-methylbut-3-en-1-ynyl)ferrocene (20) (15 mg, 6%), yellow-orange plates, m.p. (from pentane) 59–60°;  $\nu_{\max}$  (KBr) 2205 (C≡C) and 1612 cm<sup>-1</sup> (C=C);  $\tau$ (CDCl<sub>3</sub>) 4.64–4.84 (2 H, m, vinyl), 5.60 (2 H, t) and 5.70–5.88 (7 H, t + s) (ferrocenyl), and 8.06br (3 H, d, Me); this compound slowly polymerised; (ii) (3-methyl-3-trityloxybut-1-ynyl)ferrocene (21b) (41 mg, 8%), an unstable amber liquid;

<sup>13</sup> W. M. Horspool, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc. (C)*, 1971, 1558.

<sup>14</sup> P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1962, 3880.

<sup>15</sup> K. Schlögl and H. Egger, *Monatsh.*, 1963, 94, 376.

$\nu_{\max}$  2 218  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ );  $\tau(\text{CDCl}_3)$  2.32—2.87 (15 H, m, Ph), 5.60 (2 H, t) and 5.73—5.90 (7 H, t + s) (ferrocenyl), and 8.68 (6 H, s, Me); (iii) (3-methoxy-3-methylbut-1-ynyl)ferrocene (21a) (144 mg, 51%), yellow-orange prisms, m.p. (from pentane) 45—46° (Found: C, 68.1; H, 6.3.  $\text{C}_{16}\text{H}_{18}\text{FeO}$  requires C, 68.1; H, 6.4%);  $\nu_{\max}$  (KBr) 2 225  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ );  $\tau(\text{CDCl}_3)$  5.62 (2 H, t) and 5.75—5.90 (7 H, t + s) (ferro-

cenyl), 6.59 (3 H, s, OMe), and 8.51 (6 H, s, Me); (iv) starting material (2d) (11 mg, 4% recovery).

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