# Stable Carbocations. Part 13.[1] Intra-ionic Cyclisation Reactions of Ferrocenyl- and Phenyl-stabilised Vinyl Cations

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Ferrocenylvinyl cations bearing triarylmethyl, ferrocenylmethyl, ferrocenylcarbonyl, or cycloheptatrienyl groups attached to the vinylic β-carbon atom, and the phenylvinyl cation formed by protonation of 3-ferrocenyl-1-phenyl-propyne undergo intra-ionic cyclisation to give a variety of novel mono-, bi-, and tri-cyclic derivatives.

OF the various reaction pathways open to vinyl cations in solution, a few examples have been reported of intra-ionic capture by a neighbouring π-system, *e.g.* ene (1),[2] yne (2),[3] and arene (3)[4] groups. We now describe a series of cyclisation reactions involving intra-ionic addition of ferrocenyl- and phenyl-stabilised vinyl cations to aryl, ferrocenyl, and cycloheptatrienyl groups. In these reactions,[5] the vinyl cations were generated both by addition of a carbenium ion to an alkynylferrocene and by protonation of alk-1-ynyl- and -2-ynyl-ferrocenes. The methods of synthesis of these acetylenic ferrocenes have been described elsewhere.[6]
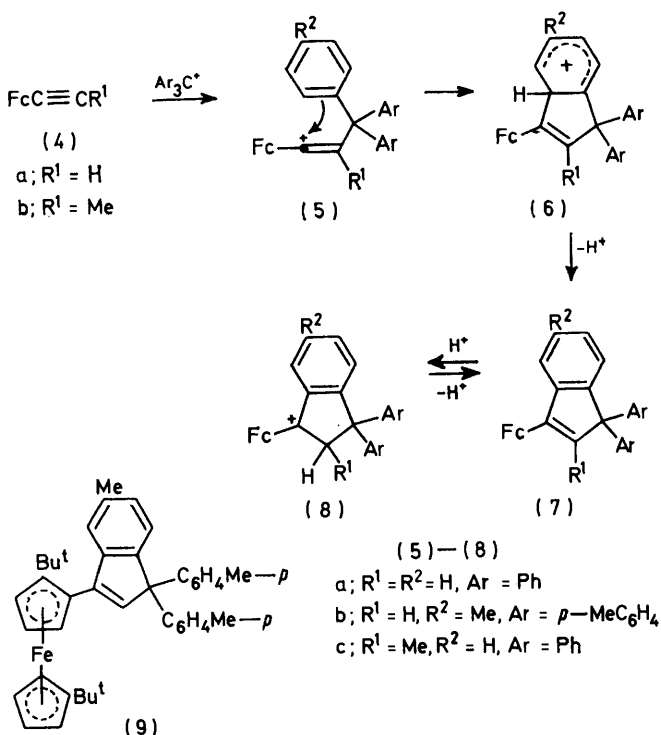
(1)   (2)   (3)
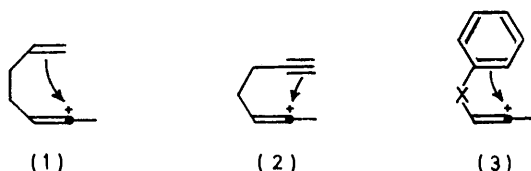
Brief treatment of ethynylferrocene (4a) in dichloro-methane solution with trityl tetrafluoroborate gave the indene derivative (7a) (57%). Similar reactions of the same alkyne with the tris-(*p*-tolyl)carbenium ion, of 1-ferrocenylpropyne (4b) with the trityl cation, and of (1',2-di-t-butylferrocenyl)ethyne with the tris-(*p*-tolyl)carbenium ion, gave the analogous products (7b), (7c), and (9), although in lower yields (20—35%). No cyclisation product was obtained, however, from the reaction of the alkyne (4b) with the tris-(*p*-tolyl)carbenium ion.

The [1]H n.m.r. spectra of the indenes (7a—c) and (9) and of the indanyl cations (8a—c), obtained by protonation of the indenes in trifluoroacetic acid, conclusively established the structures indicated (Tables 1 and 2). For example, the spectrum of the cation (8b) contained an eleven-proton aryl multiplet, a C_5H_5 singlet, a CH_2 AB quartet (J 21 Hz), and three Me singlets. Restricted rotation around the ring-C^+ bond, well established for ferrocenylalkylium ions,[7] renders non-equivalent the protons of the CH_2 group and the *p*-methyl groups of the two geminal tolyl substituents. When solutions of the indanyl cations were quenched (aqueous sodium hydrogen carbonate), the corresponding indenes were re-formed quantitatively.

The probable mechanism for these reactions is shown

in Scheme 1. Electrophilic addition of the triarylcar-benium ion to the alkyne triple bond affords a ferrocenyl-stabilised vinyl cation[1] (5) which then cyclises to a phenonium ion (6) and thence by deprotonation gives the product (7). An alternative course involving *ipso*-addition of the vinyl C^+ atom to an aryl ring followed by

$FcC \equiv CR^1$

(4)

a; R^1 = H
b; R^1 = Me

(5)   (6)

(8)   (7)

(5)—(8)

a; $R^1 = R^2 = H$, Ar = Ph
b; $R^1 = H, R^2 = Me$, Ar = p—MeC_6H_4
c; $R^1 = Me, R^2 = H$, Ar = Ph

(9)

SCHEME 1

rearrangement (1,2-CAr_2 shift) of the resulting spiro-phenonium ion and deprotonation is considered less likely in view of the greater strain associated with form-ation of this spirocyclic intermediate.

In an attempt to follow the transformation (4) $\longrightarrow$ (8) by [1]H n.m.r. spectroscopy, the behaviour of the alkyne (10a) in trifluoroacetic acid was studied. However, by methods which earlier had proved successful for observ-
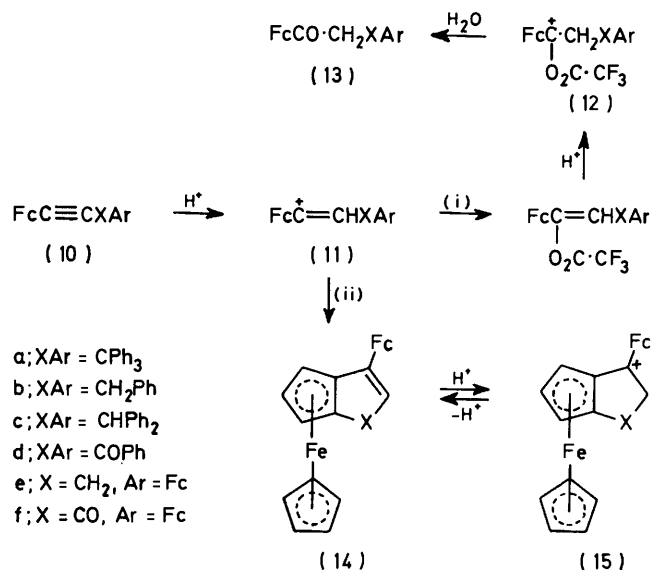
[1] Part 12, T. S. Abram and W. E. Watts, preceding paper.

[2] T. C. Clarke and R. G. Bergman, *J. Amer. Chem. Soc.*, 1972, **94**, 3627.

[3] M. J. Chandy and M. Hanack, *Tetrahedron Letters*, 1975, 4515.

[4] G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc. (C)*, 1970, 2621; F. Marcuzzi and G. Melloni, *Tetrahedron Letters*, 1975, 2771.

[5] Preliminary communications, T. S. Abram and W. E. Watts, *J. Organometallic Chem.*, (a) 1975, **87**, C39; (b) 1976, **105**, C16.

[6] T. S. Abram and W. E. Watts, *Synthesis and Reactivity in Inorganic and Metal-organic Chem.*, 1976, **6**, 31.

[7] T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

ation of a variety of ferrocenylvinyl cations,[1] the first-formed species (11a) was not detected; the spectrum obtained corresponded exactly to that of the indanyl cation (8a) recorded earlier. Consequently, the cyclis-

FcCO·CH$_2$XAr $\xleftarrow{\text{H}_2\text{O}}$ Fc$\overset{+}{\text{C}}$·CH$_2$XAr
(13)   O$_2$C·CF$_3$
           (12)

FcC≡CXAr $\xrightarrow{\text{H}^+}$ Fc$\overset{+}{\text{C}}$=CHXAr $\xrightarrow{(i)}$ FcC=CHXAr
(10)   (11)   O$_2$C·CF$_3$

a; XAr = CPh$_3$
b; XAr = CH$_2$Ph
c; XAr = CHPh$_2$
d; XAr = COPh
e; X = CH$_2$, Ar = Fc
f; X = CO, Ar = Fc

(14)   (15)

SCHEME 2

ation, deprotonation, and reprotonation steps in the sequence (5) ⟶ (8) must occur extremely rapidly in trifluoroacetic acid at 33 °C.

In order to discover the scope of this cyclisation reaction, the properties of a series of other alkynylferrocenes (10b—f) in trifluoroacetic acid were investigated
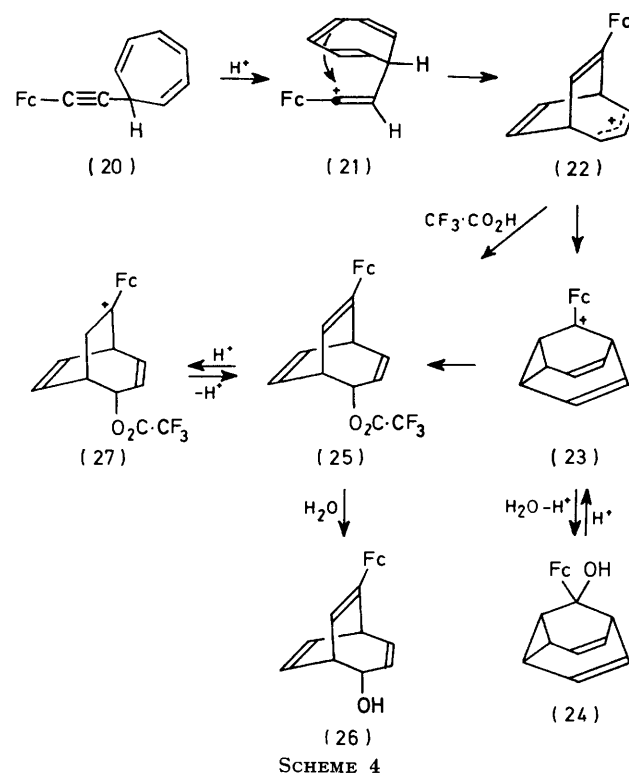
PhC≡C·CH$_2$Fc $\xrightarrow{\text{H}^+}$ Ph$\overset{+}{\text{C}}$=CH·CH$_2$Fc $\xrightarrow{-\text{H}^+}$

(16)   (17)

(18)

(19)
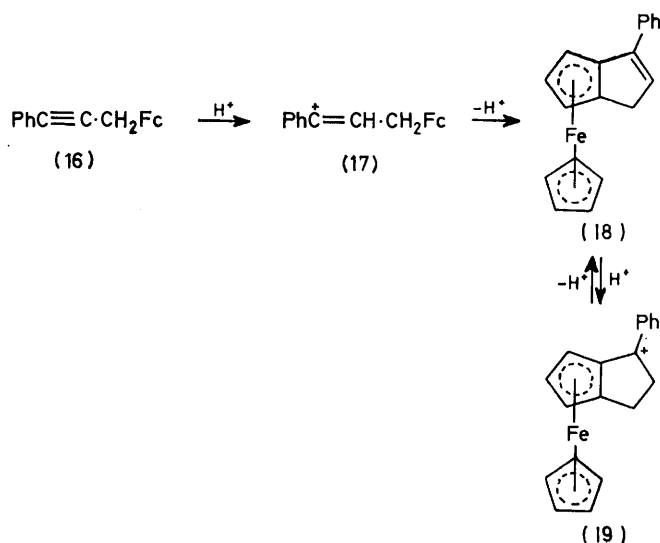
SCHEME 3

spectroscopically (^{1}H n.m.r.). Unlike the behaviour of the trityl derivative (10a), the vinyl cations (11b—d) formed from the benzyl (10b), diphenylmethyl (10c), and benzoyl (10d) derivatives did not cyclise but instead were

* Such species give characteristic broadened ^{1}H n.m.r. spectra.[1]

captured by solvent [Scheme 2; path(i)] to give trifluoro-acetoxycarbenium ions (12b—d).* The reactive centres of these vinyl cations [cf. (11a) ≡ (5a)] are less effectively shielded from solvent addition [1] and the conformational mobility of the XAr groups reduces the likelihood of intra-ionic cyclisation. Additionally, the phenyl ring of the cation (11d) is deactivated towards electrophilic attack by the carbonyl substituent. Hydrolysis (aqueous sodium hydrogen carbonate) of solutions of the cations (12b—d) gave the corresponding ketones (13b—d); the the β-diketone (13d) exists predominantly as the enol tautomer(s).

Similar treatment of the ferrocenylmethyl (10e) and ferrocenylcarbonyl (10f) derivatives, however, gave vinyl cations (11e and f) which underwent immediate and quantitative cyclisation [Scheme 2; path (ii)] to the di-ferrocenylalkylium ions (15e and f). The success of these reactions further illustrates[8] the much greater

Fc—C≡C— (20) $\xrightarrow{\text{H}^+}$ (21) ⟶ (22)

$\xrightarrow{\text{CF}_3\text{·CO}_2\text{H}}$

(27) ⇌$^{\text{H}^+}_{-\text{H}^+}$ (25) ← (23)

H$_2$O↓   H$_2$O−H$^+$↕H$^+$

(26)   (24)

SCHEME 4

reactivity towards an electrophile of a ferrocenyl group than that of a phenyl group [cf. behaviour of (11b) and (11e), and of (11d) and (11f)]. The deprotonation products (14e and f) were obtained as before by hydrolysis of solutions of the cations (15e and f). The phenylvinyl cation (17), generated in trifluoroacetic acid by protonation of the prop-2-ynylferrocene (16), also underwent immediate cyclisation (Scheme 3) to the carbenium ion (19), which afforded the alkene (18) on deprotonation.

In these reactions in trifluoroacetic acid, the first-formed vinyl cations (11a—c, e, and f) and (17) were not

[8] M. Rosenblum, J. O. Santer, and W. G. Howells, J. Amer. Chem. Soc., 1963, 85, 1450.

detected spectroscopically (^{1}H n.m.r.) owing to fast solvent capture or cyclisation.* However, the spectra of the cationic products (15e and f) and (19) and those of the hydrolysis products (13b—d), (14e and f), and (18) con-

followed by slower esterification of the hydroxy-function.[9]

The structures of the alcohols (24) and (26) and the related cations (23) and (27) were indicated by com-

TABLE 1

^{1}H N.m.r. spectra (τ values) of cyclisation products [a,b]

| Compound | Ferrocenyl protons | | Aryl protons | Vinyl protons | Other protons |
	C$_5$H$_3$ and/or C$_5$H$_4$	C$_5$H$_5$ [c]			
(7a)	5.31, 5.68 (2 × t)	5.91	2.02—2.21 (1 H), 2.36—2.95 (13 H)	3.27 (s)	
(7b)	5.36, 5.75 (2 × t)	5.94	2.28—2.39 (1 H), 2.68—3.11 (10 H)	3.31 (s)	7.58 (3 H), 7.77 (6 H) (2 × s, Me)
(7c)	5.39, 5.67 (2 × t)	5.87	1.82—2.11 (1 H), 2.5—3.0 (13 H)		8.07 (s, Me)
(9)	5.66—6.0		2.66—3.08 (10 H), 3.27—3.37 (1 H)	3.19 (s)	7.71 (6 H), 7.77 (3 H) (2 × s, Me), 8.80, 8.91 (2 × s, Bu^t)
(14e)	5.25—6.0	5.91, 6.05		3.77—3.9	6.75—6.99 (CH$_2$)
(14f)	5.03—5.57 (3 × m)	5.76, 5.88		4.40 (s)	
(18)	5.5—5.6, 5.9—6.0 (2 × m)	6.04	2.14—2.74	3.51br (t)	6.5—6.9 (CH$_2$)

[a] Solvent CDCl$_3$; Me$_4$Si as internal reference. [b] Integrated relative intensities of signals agreed with the proton assignments; multiplets unless indicated otherwise. [c] Singlet resonance.

clusively established the structures shown (Tables 1 and 2).

Intra-ionic cyclisation also occurred [5b] on treatment of 7-(ferrocenylethynyl)cycloheptatriene (20) with trifluoroacetic acid. The ^{1}H n.m.r. spectrum of the resulting solution showed the presence of the alkylium ions (23) and (27) in the ratio ca. 2 : 1, respectively (Scheme 4). On hydrolysis of this solution, there was obtained a mix-

parison of their ^{1}H n.m.r. spectra (Experimental section) with those of tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-ol,[10] its 9-methyl derivative,[11] 2-methylbicyclo[3.2.2]nona-3,6,8-trien-2-ol,[11b] and 9-hydroxytricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl cation.[11] The magnetic equivalence of (inter alia) the bridgehead protons of the alcohol (24) and of the cation (23) shows that these structures, as expected,[10a,11a] possess a fluxional homotropilidene ring system. The

TABLE 2

^{1}H N.m.r. spectra (τ values) of indanyl and related cations [a,b]

| Cation | Ferrocenyl protons | | Aryl protons | Other protons |
	C$_5$H$_3$ and/or C$_5$H$_4$	C$_5$H$_5$ [c]		
(8a)	3.5—3.7, 4.1—4.22, 4.5—4.65 (3 × m)	5.70	1.8—3.0	6.42, 7.03 (2 × d, CH$_2$, J 21 Hz)
(8b)	3.55—3.75, 4.1—4.25, 4.55—4.7 (3 × m)	5.70	2.0—3.2	6.42, 7.09 (2 × d, CH$_2$, J 21 Hz), 7.46, 7.58, 7.70 (3 × s, Me)
(8c)	3.55—3.9, 4.05—4.2, 4.6—4.8 (3 × m)	5.85	1.9—3.2	6.31 (q, CH), 8.94 (d, Me)
(15e)	4.1—4.4, 4.8—5.05 (2 × m)	5.53, 5.61		6.86—7.37 (CH$_2$·CH$_2$)
(15f)	3.55—4.95	5.29, 5.40		5.73, 6.25 (2 × d, CH$_2$, J 24 Hz)
(19)	3.68 (t), 3.91 (d), 4.57 (d)	5.52	1.9—2.7	6.5—6.9, 7.35—7.6 (CH$_2$·CH$_2$)

[a] Solvent CF$_3$·CO$_2$H; Me$_4$Si as internal reference. [b,c] As for Table 1.

ture of the tricyclononadienol (24), the trifluoroacetate (25), and the trienol (26), which was separated by preparative t.l.c. (SiO$_2$). Reduction (lithium aluminium hydride–ether) of the ester (25) gave a quantitative yield of the alcohol (26). In trifluoroacetic acid, the dienol (24) and the trienol (26) were reconverted into the corresponding carbenium ions (23) and (27). In the latter case, immediate protonation of the ferrocenylvinyl group was

structures assigned to the bicyclic products (25) and (26) were further supported by the conversion (aqueous sodium carbonate followed by lithium aluminium hydride) of the cation (23), generated unambiguously from the alcohol (24) in trifluoroacetic acid, into a mixture of regenerated dienol (24) (81%) and trienol (26) (5%), identical with the product of the original reaction and resulting from cyclopropyl ring-opening.† Similar

* The vinyl cation (11d) is relatively stable in trifluoroacetic acid solution [τ 1.47—2.41 (6 H, m, Ph + vinyl), 3.21 and 5.20 (2 H and 2 H, 2 × t, C$_5$H$_4$), and 4.46 (5 H, s, C$_5$H$_5$)] and is only slowly captured by solvent (ca. 1 h at 33 °C).

† Simple 1-ferrocenylcyclopropylalkylium ions undergo similar ring-opening reactions when solutions in trifluoroacetic acid are hydrolysed.[9]

[9] W. E. Watts, J.C.S. Perkin I, 1976, 804.
[10] (a) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, G. Klumpp, R. M. Rubin, and M. Saunders, Tetrahedron, 1967, 23, 3943; (b) M. J. Goldstein and B. G. Odell, J. Amer. Chem. Soc., 1967, 89, 6356.
[11] (a) P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, J. Amer. Chem. Soc., 1970, 92, 3478; (b) P. Ahlberg, Chem. Scripta, 1972, 2, 231.

treatment of the cation (27), prepared from the alcohol (26) in trifluoroacetic acid, gave only regenerated trienol (26).

A possible mechanism of formation of these products is given in Scheme 4. The vinyl cation (21), formed by protonation of the alkyne (20), cyclises to the 'anti-bicycloaromatic '[12] cation (22), which then collapses by two independent pathways, each generating a tertiary ferrocenylalkylium ion. Intra-ionic addition of the ferrocenylvinyl group to the allylic system leads directly to the cation (23),* while, in a competing reaction, capture of trifluoroacetate by the allylic system and protonation of the ferrocenylvinyl group generates the bicyclic cation (27). In support of this mechanism, addition of tropylium tetrafluoroborate to ethynylferrocene (4a) in dichloromethane followed by hydrolysis of the mixture gave the dienol (24), albeit in low yield. The absence of the trienol (26) in the product of this reaction is understandable since the intermediate cation (22), formed via the vinyl cation (21) in a non-nucleophilic medium, is diverted exclusively to the cation (23) and thence to product.

EXPERIMENTAL

For general details, see Part 4.[7] With the exception of the compound given below, the methods of preparation of all the alkynes used in this study have been described previously.[6]

3-*Ferrocenyl*-1-*phenylpropyne* (16).—Ethynylbenzene (5.1 g, 50 mmol) was added to a solution of methyl-lithium (40 mmol) in ether (100 ml). The mixture was stirred for 0.5 h, (ferrocenylmethyl)trimethylammonium iodide (3.5 g, 9 mmol) was added, and the slurry was stirred for 0.25 h. The ether solvent was distilled off and continuously was replaced by dry dioxan (100 ml). The solution was stirred under reflux for 24 h, then poured into water, and extracted with ether. The extracts were washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was dissolved in light petroleum and chromatographed (Al_2O_3). Light petroleum eluted the alkyne (16) (1.96 g, 74%), a yellow solid, m.p. (from pentane–ether) 77—78° (lit.,[13] 77—79°); τ(CDCl₃) 2.35—2.8 (5 H, m, Ph), 5.65—6.0 (9 H, m + s, Fc), and 6.55 (2 H, s, CH₂).

Reactions of Alkynes with Triarylmethyl Tetrafluoroborates.—A solution of the triarylmethyl tetrafluoroborate (1.5 mmol) in dichloromethane (5 ml) was added to a solution of the alkyne (1.4 mmol) in dichloromethane (20 ml). The mixture was stirred at room temperature for 5 min, then washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. The residue was separated by preparative t.l.c. (SiO_2; light petroleum–ether). The ¹H n.m.r. signals of the indene products are in Table 1.

(a) From the alkyne (4a) and trityl tetrafluoroborate there was obtained 3-*ferrocenyl*-1,1-*diphenylindene* (7a) (57%), orange-yellow needles, m.p. (from pentane–ether) 104—105° (Found: C, 82.1; H, 5.4. C₃₁H₂₄Fe requires C, 82.3; H, 5.3%); $\nu_{max.}$ (KBr) 1 596 cm⁻¹ (C=C).

(b) From the alkyne (4a) and tris-(p-tolyl)methyl tetrafluoroborate there was obtained 3-*ferrocenyl*-5-*methyl*-1,1-*di*-p-*tolylindene* (7b) (35%), orange-yellow plates, m.p.

* The stability of this cation in trifluoroacetic acid at 33 °C is remarkable; the 9-methyl analogue [11] rearranges above — 116 °C.

[12] M. J. Goldstein, *J. Amer. Chem. Soc.*, 1967, **89**, 6357.

(from pentane) 180—181° (Found: C, 82.8; H, 6.1. C₃₄H₃₀Fe requires C, 82.6; H, 6.1%); $\nu_{max.}$ (KBr) 1600 cm⁻¹ (C=C).

(c) From the alkyne (4b) and trityl tetrafluoroborate there was obtained 3-*ferrocenyl*-2-*methyl*-1,1-*diphenylindene* (7c) (20%), orange-yellow needles, m.p. (from light petroleum) 67—69° (Found: C, 82.5; H, 5.2 C₃₂H₂₆Fe requires C, 82.4; H, 5.6%); $\nu_{max.}$ (KBr) 1 592 cm⁻¹ (C=C).

(d) From (1′,2-di-t-butylferrocenyl)ethyne and tris-(p-tolyl)methyl tetrafluoroborate there was obtained 3-(1′,2-*di*-t-*butylferrocenyl*)-5-*methyl*-1,1-*di*-p-*tolylindene* (9) (28%), yellow plates, m.p. (from pentane) 204—205° (Found: C, 83.1; H, 7.8. C₄₂H₄₆Fe requires C, 83.2; H, 7.6%); $\nu_{max.}$ (KBr) 1 605 cm⁻¹ (C=C).

(e) From the alkyne (4b) and tris-(p-tolyl)methyl tetrafluoroborate there was obtained a complex mixture of unstable products which was not investigated.

Protonation of Indenes (7).—The indene derivatives (7a—c) dissolved in trifluoroacetic acid giving solutions of the corresponding indanyl cations (8a—c) whose ¹H n.m.r. signals are in Table 2. When these solutions were quenched with an excess of saturated aqueous sodium hydrogen carbonate, the original indenes were re-formed quantitatively.

Cyclisation of Alkynylferrocenes (10a, e, *and* f).—The alkyne (200—500 mg) was dissolved in trifluoroacetic acid and the ¹H n.m.r. spectrum was recorded immediately. The resonances of the resulting carbenium ions (8a) and (15e and f) are in Table 2. After ca. 10 min, the solution was quenched with an excess of saturated aqueous sodium hydrogen carbonate, and the product was isolated conventionally by extraction with ether and purified by preparative t.l.c. (SiO_2). The ¹H n.m.r. signals of these products are in Table 1.

(a) From the alkyne (10a) there was obtained the indene (7a) (85%), identical with the compound already described.

(b) From the alkyne (10e) there was obtained cyclopenta-dienyl-(3-*ferrocenylpentalenyl*)iron (14e) (88%), orange-yellow prisms, m.p. (from pentane–ether) 143—145° (Found: C, 67.6; H, 5.1. C₂₃H₂₀Fe₂ requires C, 67.7; H, 4.9%); $\nu_{max.}$ (KBr) 1 592 cm⁻¹ (C=C).

(c) From the propynone (10f) there was obtained cyclopentadienyl-(3-*ferrocenyl*-1-*oxopentalenyl*)iron (14f) (58%), dark maroon needles, m.p. (from pentane) 200—204° (decomp.) (Found: C, 65.6; H, 4.4. C₂₃H₁₈Fe₂O requires C, 65.5; H, 4.3%); $\nu_{max.}$ (KBr) 1 675 (CO) and 1 565 cm⁻¹ (C=C).

Hydration of Alkynylferrocenes (10b, c, *and* d).—Solutions of the alkynes in trifluoroacetic acid were treated with saturated aqueous sodium hydrogen carbonate and the products were isolated as in the previous experiments.

(a) From the alkyne (10b) there was obtained the ketone (13b) (95%), orange-yellow prisms, m.p. (from light petroleum–ether) 83—84° (lit.,[14] 85.5—86°); τ(CDCl₃) 2.73br (5 H, s, Ph), 5.24 and 5.54 (2 H and 2 H, 2 × t, C₅H₄), 5.94 (5 H, s, C₅H₅), and 6.97 (4 H, s, CH₂·CH₂).

(b) From the alkyne (10c) there was obtained a complex mixture of unstable products together with the ketone (13c) which was not obtained pure.

(c) From the propynone (10d) there was obtained the β-diketone (13d) (85%), red needles, m.p. (from pentane) 103—105° (lit.,[15] 105—107°); the ¹H n.m.r. spectrum showed that this compound exists predominantly as the enol tautomer(s);

[13] P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1963, 2990.
[14] T. A. Mashburn, C. E. Cain, and C. R. Hauser, *J. Org. Chem.*, 1960, **25**, 1982.
[15] C. R. Hauser and J. C. Lindsay, *J. Org. Chem.*, 1957, **22**, 482.

τ(CDCl$_3$) —6.50br (1 H, s, OH; D$_2$O-exchangeable), 1.85—2.6 (5 H, m, Ph), 3.61 (1 H, s, vinyl), 5.10 and 5.45 (2 H and 2 H, 2 × t, C$_5$H$_4$), and 5.80 (5 H, s, C$_5$H$_5$).

Cyclisation of 3-Ferrocenyl-1-phenylpropyne (16).—The ^{1}H n.m.r. spectrum of a freshly prepared solution of the alkyne (16) in trifluoroacetic acid showed the immediate formation of the cation (19) (Table 2). This solution was quenched with an excess of saturated aqueous sodium hydrogen carbonate and the product was isolated and purified as in previous experiments to give *cyclopentadienyl-(3-phenylpentalenyl)iron* (18) (83%), an amber liquid (Found: C, 75.9; H, 5.3. C$_{19}$H$_{16}$Fe requires C, 76.0; H, 5.3%); $\nu_{max.}$ (film) 1 594 cm^{-1} (C=C); for ^{1}H n.m.r. data see Table 1.

Cyclisation of 7-(Ferrocenylethynyl)cycloheptatriene (20).—A solution of the alkyne (20) in trifluoroacetic acid was quenched with an excess of saturated aqueous sodium carbonate and the products were isolated and separated as in previous experiments to give (i) 9-*ferrocenyltricyclo*-[3.3.1.0^{2,8}]*nona*-3,6-*dien*-9-*ol* (24) (38%), yellow prisms, m.p. (from light petroleum–ether) 119—121° (Found: C, 71.5; H, 5.7. C$_{19}$H$_{18}$FeO requires C, 71.7; H, 5.7%); $\nu_{max.}$ (KBr) 3 565 (OH) and 1 546 cm^{-1} (C=C); τ(CDCl$_3$) 4.18br and 4.53br (1 H and 1 H, 2 × t, H-3 and -7), 5.7—5.95 (13 H, s + m, ferrocenyl + H-2, -4, -6, and -8), 7.41br (2 H, t, H-1 and -5), and 7.98 (1 H, s, OH; D$_2$O-exchangeable); (ii) 6-*ferrocenylbicyclo*[3.2.2]*nona*-3,6,8-*trien*-2-*yl trifluoroacetate* (25) (12%), an unstable yellow liquid; $\nu_{max.}$ (film) 1 778 (CO), 1 633 and 1 545 cm^{-1} (C=C); τ(CDCl$_3$) 3.24br (2 H, t), 3.5—4.8 (2 H, m), and 4.84—4.99 (1 H, m) (vinyl), 5.79—6.15 (10 H, s + m, ferrocenyl + CH·O$_2$C·CF$_3$), and 6.2—6.6 (2 H, m, bridgehead protons); (iii) 6-*ferrocenylbicyclo*-[3.2.2.]*nona*-3,6,8-*trien*-2-*ol* (26) (9%), yellow prisms, m.p. (from light petroleum–ether) 158—160° (Found: C, 71.5; H, 6.2%; *M*, 318. C$_{19}$H$_{18}$FeO requires C, 71.7; H, 5.7%; *M*, 318); $\nu_{max.}$ (KBr) 3 590 (OH), 1 633, and 1 545 cm^{-1} (C=C); τ(CDCl$_3$) 3.0—3.98 and 4.83—4.98 (4 H and 1 H, 2 × m, vinyl), 5.67—6.07 (10 H, s + m, ferrocenyl + CH·OH), 6.2—6.62 (2 H, m, bridgehead protons), and 8.40br (1 H, s, OH; D$_2$O-exchangeable).

Comparison of the authentic ^{1}H n.m.r. spectra of the cations (23) and (27) (next experiments) with that of the alkyne (20) in trifluoroacetic acid showed that this solution contained the cations (23) and (27) in the ratio *ca.* 2 : 1 respectively.

Reduction (lithium aluminium hydride–ether) of the ester (25) gave a quantitative yield of the trienol (26), identical with the compound obtained from the quenching experiment.

Generation and Quenching of the Cation (23).—The alcohol (24) was dissolved in trifluoroacetic acid giving quantitatively the cation (23); τ(CF$_3$·CO$_2$H) 3.82 and 4.99 (2 H and 2 H, 2 × t, C$_5$H$_4$), 4.00 and 4.35 (1 H and 1 H, 2 × t, H-3 and -7), 5.05—5.5 (9 H, s + m, C$_5$H$_5$ + H-2, -4, -6, and -8), and 6.53br (2 H, t, H-1 and -5). This solution was quenched (aqueous sodium carbonate) and the products were extracted with ether and treated with an excess of lithium aluminium hydride in ether (to convert trifluoroacetate into alcohol). The resulting product mixture was separated by preparative t.l.c. (SiO$_2$) giving the dienol (24) (81%) and the trienol (26) (5%), identical (i.r. and ^{1}H n.m.r. data) with the compound described in the previous experiment.

Generation and Quenching of the Bicyclic Cation (27).—The ester (25) was dissolved in trifluoroacetic acid giving a quantitative yield of the cation (27); τ(CF$_3$·CO$_2$H) 2.5—2.9 (1 H), 3.05—3.4 (2 H), and 3.5—3.6 (1 H) (3 × m, vinyl), 3.65—3.85 (2 H), 4.85—4.95 (1 H), and 5.2—5.3 (1 H) (3 × m, C$_5$H$_4$), 4.35—5.1 (3 H, m, CH·O$_2$C·CF$_3$ + bridgehead protons), 5.22 (5 H, s, C$_5$H$_5$), and 5.65—6.05 (2 H, m, CH$_2$). The same cation was formed slowly when the alcohol (26) was dissolved in trifluoroacetic acid. When these solutions were quenched (aqueous sodium carbonate), a mixture containing only the ester (25) and the alcohol (26) was obtained.

Reaction of Ethynylferrocene (4a) *with Tropylium Tetrafluoroborate*.—Tropylium tetrafluoroborate (200 mg, 1.1 mmol) was added to a solution of the alkyne (4a) (100 mg, 0.48 mmol) in dichloromethane (100 ml) and the mixture was stirred and heated under reflux for 1 h. The solution was then washed (aqueous sodium hydrogen carbonate then water), dried (MgSO$_4$), and evaporated. The residue contained a complex mixture of products including the dienol (24) (8 mg, 5%), identified by comparison with an authentic sample. No trace of the trienol (26) was found in this mixture.