Direct Observation of Vinyl Cations in Solution

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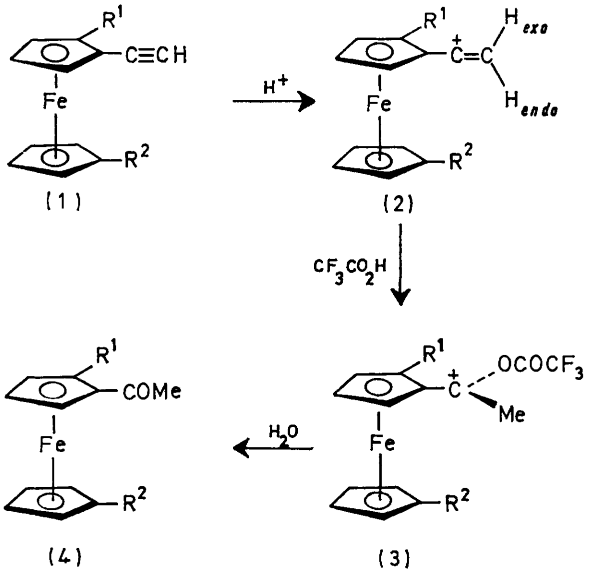
Summary In CF_3CO_2H solution, ethynylferrocenes bearing a 2-t-butyl substituent undergo protonation to give the corresponding vinyl cations which, though short-lived, can be observed by ^1H n.m.r. spectroscopy.

ALTHOUGH the intermediacy of vinyl cations in electrophilic addition reactions of alkynes and in solvolytic ionisation of substituted ethylenes is now well established,[1] species of this type have not yet been prepared in solution with lifetimes sufficiently long to permit their observation by spectral methods. In view of the excellent ability of the ferrocenyl group to stabilise an electron-deficient centre, it seemed that ^{1}H n.m.r. spectroscopic observation of ferrocenylvinyl cations in solution might be possible. This expectation has been realised.



a; $R^1 = R^2 = H$
b; $R^1 = Bu^t$; $R^2 = H$
c; $R^1 = R^2 = Bu^t$

Scheme

The alkynes (**1a**—**c**) dissolve readily in CF_3CO_2H to give purple solutions from which the corresponding ketones (**4a**—**c**) can be recovered after hydrolysis.[2] The course of these reactions (Scheme) was monitored by ^{1}H n.m.r. spectroscopy. With ethynylferrocene[3] (**1a**), the very fast rate of capture by solvent of the (presumed) first-formed cation (**2a**) prevented determination of its spectrum and only that of the product (**3a**) of further addition of CF_3CO_2H was obtained.[4] However, in the case of the ring-substituted alkynes† (**1b** and **c**) in which the reactive centre is sterically shielded by the proximate t-butyl group, the resonances of the intermediate vinyl cations (**2b** and **c**) were obtained by recording the spectra of solutions of the alkynes in cold CF_3CO_2H (−15° initially) immediately following their preparation. The signals of these cations quickly decayed and were replaced after a few minutes by those characteristic‡ of the addition products (**3b** and **c**). The ferrocenylvinyl cations (**2**) are thus more reactive towards nucleophilic addition of CF_3CO_2H than ferrocenylalkylium cations, including the parent ($FcCH_2^+$), which are stable in this solvent.

The ^{1}H n.m.r. spectra of the vinyl cations (**2b** and **c**) are in good accord with the expected[5] 'linear' geometry of the vinyl group. The cyclopentadienyl proton resonance patterns are typical of those exhibited by ferrocenylalkylium cations[6] while the associated chemical-shift values correspond quite closely to those of ($FcCH_2^+$) itself. The resonances of the vinyl protons appear in each spectrum as a clean AB quartet (τ 3·25 and 3·82; *J ca.* 12 Hz). We have previously shown [6a] that there exists an appreciable energy barrier to rotation about the ring–C^+ bond in ferrocenylalkylium ions. In the case of the vinyl cations (**2**), this restricted torsion produces differential shielding of the vinyl protons which occupy different locations (*exo* and *endo*) relative to the ferrocene system.[7]

The most compelling evidence of a 'linear' vinyl group geometry is provided by the magnitude of the geminal coupling constant which may be compared with the corresponding values[8] for keten (15·8 Hz) and 1,1-dimethylallene (9·0 Hz). For molecules of such orbital geometry, hyperconjugative interaction between the CH_2 bonds and the adjacent coplanar $p\pi$-system leads to an enhancement of the geminal coupling constant from the much lower values (*ca.* 2 Hz) normally associated with terminal alkenes.[8]

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† The method of preparation of these compounds, which have been satisfactorily characterised, will be described in a full paper.

‡ In particular, the (MeC^+) protons appear as a sharp singlet around τ 7·4 in the spectra of the cations (**3**).

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