Tetrahedron Letters,Vol.26,No.12,pp 1493-1496,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

STABLE VINYL CATIONS 4:

CARBON-13 NMR SPECTROSCOPIC OBSERVATION OF AN α-FERROCENYL-VINYL CATION

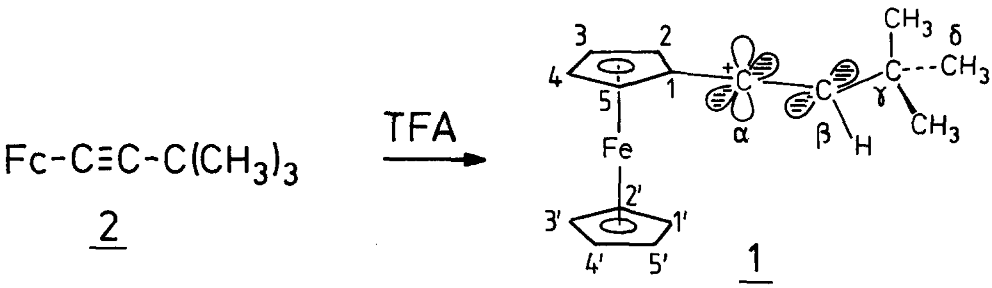
Ernst-Wilhelm Koch, Hans-Ullrich Siehl* and Michael Hanack*

Institute of Organic Chemistry, University of Tübingen
Morgenstelle 18,D-7400 Tübingen,Germany

Abstract ^{13}C-chemical shift data of α-ferrocenyl-ß-t-butyl-vinyl cation are compared with model compounds to give proof of hybridization and structure.

Vinyl cations are well established reactive intermediates[1] which have been observed only recently by ^{13}C NMR spectroscopy.[2,3,4] Early attempts to generate vinyl cations by protonation of alkynes under strong acidic conditions have failed to give stable species in solution because of rapid sequential inter- and intramolecular reactions.[5,6,7] The protonation of ferrocenyl substituted alkynes with trifluoracetic acid (TFA) however led to species that were assigned vinyl cation structures from their ^{1}H NMR spectra[8,9,10]. Very recently an organometallic stabilized vinyl cation was isolated as a zwitterion in crystalline form and characterized by IR and ^{1}H NMR spectroscopy but no X-ray data were reported[11]. Proton NMR and IR spectroscopic data in general do not give sufficient information about the structure and charge distribution of carbocations. Especially for vinyl cations ^{13}C NMR spectrocopic data are essential for an unequivocal characterization of the exact nature of the C_{α}-C_{β}-bond[12].

Bulky substituents at the ring or at the ß-position increase the stability of ferrocenyl vinylcations which otherwise are captured very rapidly by the solvent to form α-trifluoracetoxy carbocations[10]. We anticipated the lifetime of the α-ferrocenyl-ß-t-butyl-vinylcation 1[9] generated by protonation of 3,3-dimethyl-1-ferrocenyl-butin-1 2 in TFA / SO_2ClF to be sufficient to obtain ^{13}C-NMR spectra using contemporary instrumentation.



The 100.6 MHz ^{13}C NMR spectrum of 1 was measured in TFA/SO_2ClF at -50 °C. Only eight peaks are observed (Figure 1) thus only one isomer is present which is most likely the sterically less congested cation with the t-butyl group in the exo position.

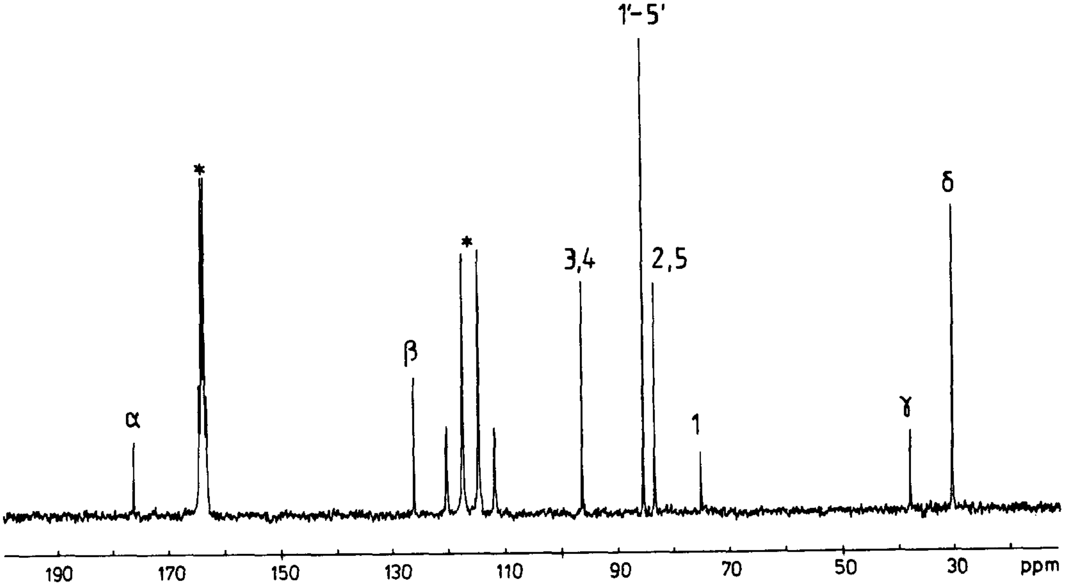
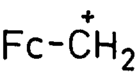


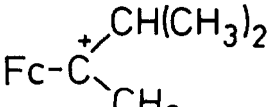
Figure 1: 100.6 MHz ^{13}C NMR spectrum of cation 1 in TFA/SO_2ClF at -50°C. (TFA peaks are marked *).

Assignments were made from specific ^{1}H-decoupled ^{13}C NMR spectra and are given in Table 1. The ^{13}C NMR data of 1 can be compared with model compounds 2-5.

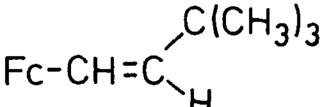


$\mathrm{Fc}\text{-}\overset{+}{C}H_2$

3



4



5

Table 1 ^{13}C NMR chemical shifts (ppm) of cation 1 and model compounds 2-5.

	C-α	C-β	C-γ	C-δ	C-1	C-2,5	C-3,4	C-1'-5'	Ref.
1	177.14	126.63	38.11	30.27	74.68	83.06	96.12	85.15	
2	76.37	94.65	27.90	31.26	66.59	71.14	68.01	69.77	14
3	88.6				111.8	85.5	95.6	83.3	13
4	178.0	21.7^a 40.8^b	19.3^c 26.3^c		100.1	76.9 77.9	94.5 94.9	81.2	13
5	121.33	139.18	33.82	29.28	84.33	66.37	68.13	69.04	14

a) β-CH_3, b) β-CH, c) nonequivalent γ-CH_3.

The signal for the cationic carbon in 1 (177.14 ppm) is similarly deshielded as in comparable dialkyklsubstituted sp^2-hybridized α-ferrocenyl carbocations as, for example, in the 1,2-dimethyl-1-ferrocenylpropyl-cation 4 (178.0 ppm). The shift of C_β (126.63 ppm) indicates sp^2-hybridization for this carbon, compared to sp^3-hybridized β-carbons in other α-ferrocenyl cations (20- 40 ppm) and to the sp-hybridized β-carbon in the ferrocenylalkyne 2 (94.65 ppm). The C_β-signal in 1 is 15 ppm upfield compared to the C_β-signal in 3,3-dimethyl-1-ferrocenylbuten-1 5 caused by the shielding effect of the adjacent sp-hybridized C^+-carbon in 1.

The signal for C_1 (74.68 ppm) in 1 is 10 ppm shielded compared to alkene 5 and 25 ppm compared to cation 4. This is another evidence for sp-hybridization of the C^+ carbon in 1 causing this shielding. The shift of C_1 in 1 is only 8 ppm to lower field compared to ferrocenylacetylene 2.

Significant charge delocalization into the ferrocenyl moiety is evident from the downfield shift of the peaks for $C_{2,5}$, $C_{3,4}$ and $C_{1'-5'}$. The signals for C_2 and C_5 in 1 are at lower field than in all other secondary and tertiary α-ferrocenyl carbocations. C_3 and C_4 in 1 have almost the same shift than the corresponding carbons in the primary ferrocenylmethylcation 3 and the signal for $C_{1'-5'}$ in 1 is even 2 ppm more downfield.

The spectroscopic data are in accord with a linear sp-hybridized vinyl cation structure for 1. Rotation around the C^+-C_1-bond is blocked due to efficient interaction of the cationic carbon with the ferrocenyl system either via p-π-conjugation which results in partial double bond character of the C^+-C^1-bond or by direct C^+- Fe interaction[15]. Cation 1 is thus the first stable vinyl cation generated directly by protonation of an alkyne which was characterized unequivocally by ^{13}C-NMR spectroscopy giving convincing support to the ^{1}H NMR studies of 1 and related cations by Abram and Watts.[8,9,10]

This work was supported by the Deutsche Forschungsgemeinschaft

References

1) P.J.Stang, Z.Rappoport, M.Hanack and L.R.Subramanian: Vinyl Cations, 1979, Academic Press,New York
2) H.-U.Siehl and H.Mayr, J.Am. Chem.Soc. 104,909,(1982)
3) H.-U.Siehl and E.-W.Koch, J.Org.Chem. 49,575,(1984)
4) H.-U.Siehl, J.C.S.Chem.Commun. 1984,635
5) G.A.Olah ,J.S.Staral,R.J.Spear and G.Liang, J.Amer.Chem.Soc. 97,5489,(1975)
6) G.A.Olah and H.Mayr, J.Am. Chem.Soc. 98, 7333, (1976); 100, 6544, (1978)
7) G.Capozzi,V.Lucchini,F.Marcuzzi and G.Melloni, Tetrahedron Lett. 1976,717
8) T.S.Abram and W.E.Watts, J.C.S.Chem.Commun. 1974,857
9) T.S.Abram and W.E.Watts,J.Organomet.Chem. 87,C39,(1975)
10) T.S.Abram and W.E.Watts, J.C.S.Perkin I 1977,1522
11) L.I.Zakharkin and V.V.Kobak, J.Organomet. 270,229,(1984)
12) M.Hanack and H.-U.Siehl, J.Am. Chem.Soc. 102,2686, (1980)
13) S.Braun,T.S.Abram and W.E.Watts, J.Organomet.Chem. 97,429,(1975)
14) E.-W-Koch Diplomarbeit Tübingen 1981
15) U.T.Mueller-Westerhoff,A.Nazzal,W.Prössdorf,J.J.Mayerle and R.L.Collins, Angew.Chem.,Int.Ed.Engl.1982,293;Angew.Chem.Suppl.1982,686 and references cited.

(Received in Germany 14 January 1985)