SYNTHESIS AND SOME REACTIONS OF THE STABLE VINYL CATION STABILIZED BY THE 3-η^5-CYCLOPENTADIENYL-η^5-(3)-1,2-DICARBOLLYLIRON(II)-1 GROUP

L.I. ZAKHARKIN* and V.V. KOBAK

Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, 28 Vavilova St., Moscow (U.S.S.R.)

(Received March 22nd, 1984)

Summary

An individual vinyl cation in the form of a zwitterion stabilized by the 3-η^5-$C_5H_5Fe^{II}$-η^5-(3)-1,2-$C_2B_9\overline{H}_{10}$-1 group has been produced for the first time, and its reactions with nucleophilic agents have been studied. Deprotonation yielding an acetylene derivative is the main reaction in the interaction of the vinyl cation with MeLi, $NaBH_4$ and C_5H_5N.
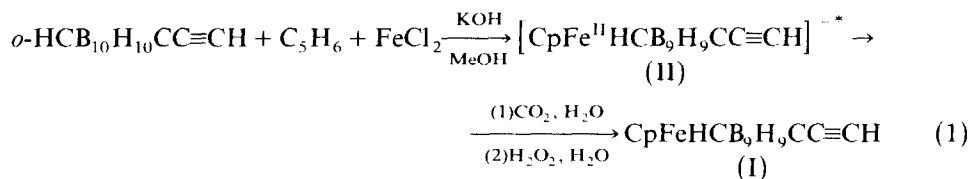
Introduction

It has been proved in the last few years that vinyl cations are active intermediates in a large number of reactions of unsaturated compounds [1]. The direct spectroscopy of vinyl cations has been described in two papers that can be relied on. Abram and Watts obtained ferrocenyl group-stabilized vinyl cations by protonation of the corresponding acetylenes in a CF_3COOH solution, and studied their ^1H NMR spectra [2]. Siehl and Mayr described the ^{13}C NMR spectra of vinyl cations stabilized by double-bond conjugation (of vinyl-substituted vinyl cations) [3]. Earlier, we found that the vinyl cation bonded to the 3-η^5-$C_5H_5Fe^{II}$-η^5-(3)-1,2-$C_2B_9\overline{H}_{10}$-1 group is stabilized to such a degree that it becomes possible to isolate usually unstable carbocations [4,5]. In the present paper we report the synthesis and properties of a vinyl cation stabilized by this group (cf. ref. 5).

Results and discussion

One of the major methods of generating vinyl cations is the protonation of actylenes [1]. This method was used in the present work. To this end, 1-ethynyl-3-η^5-cyclopentadienyl-η^5-(3)-1,2-dicarbollyliron(III) (I) was obtained from the known 1-ethynyl-*o*-carborane *, cyclopentadiene and ferrochloride in a methanol solution of potassium hydroxide, by a previously described method [7].

---

* *o*-carborane = 1,2-dicarbaclosododecacarborane(12) = 1,2-$C_2B_{10}H_{12}$ = *o*-$HCB_{10}H_{10}CH$.

$$o\text{-}HCB_{10}H_{10}CC{\equiv}CH + C_5H_6 + FeCl_2 \xrightarrow[\text{MeOH}]{\text{KOH}} \left[CpFe^{II}HCB_9H_9CC{\equiv}CH\right]^{-*} \rightarrow$$
$$(II)$$

$$\xrightarrow[\text{(2)}H_2O_2,\ H_2O]{\text{(1)}CO_2,\ H_2O} CpFeHCB_9H_9CC{\equiv}CH \qquad (1)$$
$$(I)$$

Oxidation by H_2O_2 is necessary to transform the 1-ethynyl-3-η^5-cyclopentadienyl-η^5-(3)-1,2-dicarbollyliron(II) (II) anion into the electroneutral Fe^{III}-form [1]. The yield of complex I equals 36%. Together with this compound, the methyl vinyl ether $CpFeHCB_9H_9CC(OMe){=}CH_2$ (IV) and the ketone $CpFeHCB_9H_9CCOCH_3$ (III) are formed in low yield due to nucleophilic addition of MeO^- and OH^- anions to the $C{\equiv}C$ bond. The acetylene derivative I is a paramagnetic, dark-green substance, stable in air. The structures of complexes I, III and IV were confirmed by spectrometry. The paramagnetic acetylene complex I was transformed by treating it with excess $NaBH_4$ in ethanol, and then with Me_4NBr in water, into the diamagnetic tetramethylammonium salt $[CpFe^{II}HCB_9H_9CC{\equiv}CH]NMe_4$ (V):

$$I \xrightarrow[\text{(2) }Me_4NBr,\ H_2O]{\text{(1) }NaBH_4,\ EtOH} \left[CpFe^{II}HCB_9H_9CC{\equiv}CH\right]NMe_4$$
$$(V)$$
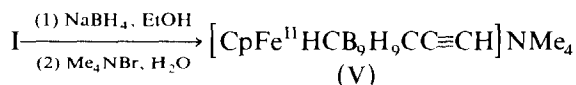
The acetylene derivative V is a diamagnetic, crystalline substance of a yellowish-brown hue. It is stable in air in the solid state and oxidizes slowly in solution. The structure of complex V was confirmed by IR spectroscopy. A 73% yield of vinyl cation VI in an isolated state was obtained by protonation of the acetylene group of complex V by 12 N H_2SO_4 in a double-phase C_6H_6/H_2O system:

$$V \xrightarrow[C_6H_6/H_2O]{H^+}$$

(VI, ● C or CH ,
O BH)
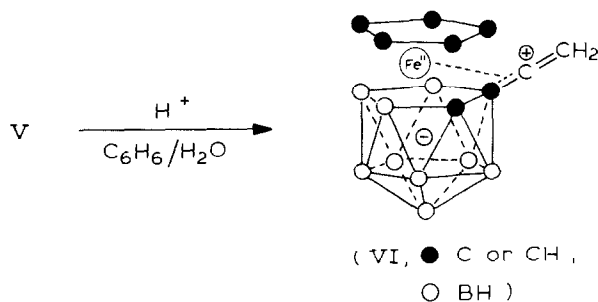
Vinyl cation VI is a diamagnetic, crystalline, dark-red substance. Like previously obtained aliphatic carbocations that were stabilized by the $CpFe^{II}HCB_9H_9\overline{C}$ group [4,5], it is a zwitterion. It is stable in air in the crystalline state and slowly decomposes in solution. In the IR spectrum of vinyl cation VI, the vinyl group has a $C{=}C$ bond absorption band at 1735 cm^{-1}. Such a sharp increase in absorption band compared to the average 1600–1650 cm^{-1} is evidently explained by a change in the force coefficient of the group, brought about by a positive charge. The same was true for the transformation of acylhaloids (for instance, CH_3COF, $\nu(CO)$ 1848 cm^{-1}) to acylium cations (for instance, CH_3CO^+ SbF_6^-, $\nu(CO)$ 2294 cm^{-1}) [8]. On the other hand, a larger absorption band of the vinyl cation group as compared to olefins may

---

* $CpFe^{II}HCB_9H_9\overline{C} = 3\text{-}\eta^5\text{-}C_5H_5Fe^{II}\text{-}\eta^5\text{-}(3)\text{-}1,2\text{-}C_2B_9\overline{H}_{10}\text{-}1.$
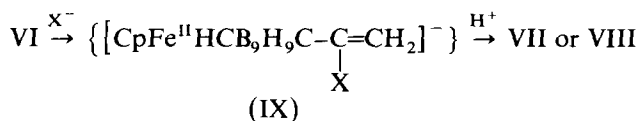
be due to an increase of up to 180° in the valency angle between carborane C and the $CH_2=C^+$ group. In the ^{1}H NMR spectrum of vinyl cation VI, the $CH_2=C^+$ group signal appears as an AB-quartet at δ 4.80 and 6.00 ppm (J(HH) 7 Hz). This can probably be explained by the linear geometry of the vinyl cation group (carborane $C-C_{sp}^+=C_{sp^2}$) according to ref. 9. The stable, isolated vinyl cation VI indicates that the $3\text{-}\eta^5\text{-}C_5H_5Fe^{II}\text{-}\eta^5\text{-}(3)\text{-}1,2\text{-}C_2B_9\overline{H}_{10}\text{-}1$ group radically stabilizes its vinyl cation centre. The fact that vinyl cation VI is sufficiently stable provided us the opportunity to study some of its reactions. It was found that vinyl cation VI attracts HCl and HBr along the vinyl cation group, yielding the stable carbon zwitterions VII and VIII whose Cl and Br atoms are in the immediate vicinity of the carbocationic centre.

$$VI + HX \xrightarrow[C_6H_6/H_2O]{20\,°C} CpFe^{II}HCB_9H_9\overset{-}{C}\text{-}\overset{+}{C}\underset{X}{\overset{CH_3}{<}}$$
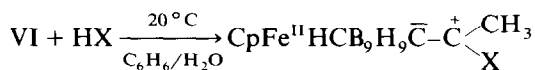
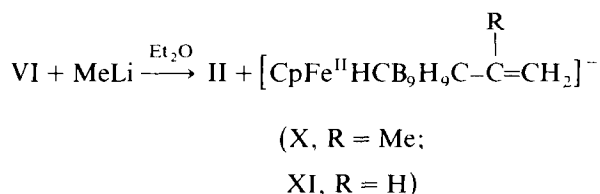$$(VII, X = Cl;$$

$$VIII, X = Br)$$

Cations VII and VIII were obtained in an isolated state. They are diamagnetic, dark red, crystalline substances, stable in air but less stable in solution. The methylhalogen-substituted cation structure was confirmed by the ^{1}H NMR spectra, which recorded the methyl group as a singlet at δ 1.87 ppm for the VII chloro derivative and at δ 2.09 ppm for the bromo derivative (VIII). As seen from ref. 2, the ferrocenyl vinyl cations yielded by protonation of ferrocenylacetylenes in a CF_3COOH solution easily attract a solvent molecule. This yields ferrocenyl carbocations whose cation carbon is bonded to the CF_3COOH group. According to Abram and Watts [2], the ferrocenyl vinyl cation CF_3COO^- reaction is a two-stage process: (1) nucleophilic addition of CF_3COO^- to the cation carbon; (2) protonation of the resulting enol ether. These data point out that acetylene protonation (VI) with the formation of vinyl cation VI is faster than the interaction of vinyl cation VI with halohydrogen acids which yields methylhalogen cations VII and VIII. For example, it takes 18 h for vinyl cation VI to react with 36% HCl, and 96 h with 48% HBr. The low reactivity of vinyl cation VI as regards aqueous solutions of HCl and HBr is evidence of formidable delocalization of the positive charge in the cation. We believe that the addition of HX to vinyl cation VI is a two-step process. The first step is slow addition of the halide anion to the carbocation site, yielding a halovinyl derivative IX, which, as a second step, is then rapidly protonated to yield cation VII or VIII.

$$VI \overset{X^-}{\to} \left\{ [CpFe^{II}HCB_9H_9C\text{-}\underset{X}{\overset{|}{C}}=CH_2]^- \right\} \overset{H^+}{\to} VII \text{ or } VIII$$

$$(IX)$$

$$(X = Cl, Br)$$

This mechanism obviously explains why HBr is more difficult to add to vinyl cation VI than HCl. First of all, Br^- is a weaker base than Cl^-, therefore reacting slower with a strong acid, which is the vinyl cation. Secondly, Br^-, which has a larger volume, is slower in forming a bond with the carbocation site which is linked to the larger ferrocarborane cage than Cl^-, which is smaller in volume.

The effect of nucleophilic reagents on vinyl cations has yet to be studied. Abram and Watts [2] mentioned the fact that when ferrocenyl vinyl cations were treated with excess aqueous $NaHCO_3$, the reaction proceeded along two directions. Depending on the cation structure, both the products of ferrocenylacetylene deprotonation and the products of nucleophilic addition (ferrocenyl ketones) are yielded. We studied the reaction of vinyl cation VI with such nucleophiles as MeLi, $NaBH_4$ and pyridine. When vinyl cation VI was treated with MeLi in an ether solution, Me group addition with isopropenyl derivative formation (X) was found to be insignificant. Mainly, it was $CH_2=C^+$ group deprotonation to the acetylene derivative II that took place. Together with these products, an insignificant amount of vinyl derivative XI was also obtained:

$$VI + MeLi \xrightarrow{Et_2O} II + \left[CpFe^{II}HCB_9H_9C-\overset{\overset{\displaystyle R}{\displaystyle |}}{C}=CH_2 \right]^-$$

$$(X, R = Me;$$

$$XI, R = H)$$

To identify the reaction products, the H_2O_2 reaction mixture was oxidized to electroneutral Fe^{III} derivatives, which were then compared, using TLC, to the known $CpFe^{III}HCB_9H_9C-C(R)=CH_2$ (R = Me, H) [4].

Vinyl cation VI reacts with $NaBH_4$ in the same way as with MeLi. The main product is the acetylene derivative II, and, in a smaller amount, the vinyl derivative XI:

$$VI + NaBH_4 \xrightarrow{CH_3CN} II + XI$$

The reaction products were identified as before. Treating vinyl cation VI with pyridine also yields mainly acetylene, which is a product of deprotonation, and a small amount of vinyl derivative XI. It should be mentioned that the pyridine reaction is noticeably slower. Whereas it took only a few minutes for the reaction of vinyl cation VI with MeLi and $NaBH_4$ to occur, it took 72–96 h for the same reaction to take place with pyridine. According to the data obtained, vinyl cation VI, in contrast to the primary and secondary carbocations $CpFe^{II}HCB_9H_9\overline{C}-\overset{+}{C}HR$ (R = H, Me), which are easily added to nucleophilic reagents [4,5], mainly deprotonates under these conditions, yielding the corresponding acetylene derivative. This forms the basis for the conjecture that hydrogen atoms of the $CH_2=C^+$ group take an acid character. In other words, it is along the hydrogen atoms of the vinyl cation group that strong nucleophilic reagents attack. The $CpFe^{II}HCB_9H_9\overline{C}$-group stabilized vinyl cation is so stable that it has no analogue either in organic, or in organo-elemental chemistry.

Experimental

Reagents and materials

Freshly distilled cyclopentadiene was used. Ether was distilled over benzophenone ketyl just before the reactions. KOH was used in the form of tablets containing 85% alkali. Column chromatography was performed on silica gel with a particle size of

100–160 μm (Chemapol). TLC was performed on Silufol plates. The ketone $CpFeHCB_9H_9C\text{–}COCH_3$, as well as the vinyl and isopropenyl derivatives of ferrocarborane $CpFeHCB_9H_9C\text{–}C(R)=CH_2$ (R = Me, H), were obtained for identification according to the methods of refs. 5–7. All substances were recrystallized by solvent distillation in a vacuum at 30°C.

Apparatus

IR spectra were obtained on a UR-20 double-ray spectrometer. Samples were pressed into tablets with KBr. NMR spectra were obtained on a RYa.2309 spectrometer in benzene; work frequency 90 MHz. Chemical shifts were measured on the δ scale in ppm. Benzene was used as the internal standard. Mass spectra were obtained on an MS-30 apparatus.

$CpFeHCB_9H_9C\text{–}C\equiv CH$ (I). 55 g (0.84 mol) of KOH was carefully added in portions while mixing to 11.25 g (66.86 mmol) of 1-ethynyl-*o*-carborane in 75 ml of CH_3OH. After a violent exothermic reaction, the mixture was refluxed for 4 h while stirring. After it was cooled down to 20°C, 17.68 g (267.46 mmol) of cyclopentadiene was added and the mixture stirred for 5 min. Then, while stirring thoroughly, 21.2 g (167.16 mmol) of water-free $FeCl_2$ in 50 ml of CH_3OH was added and the mixture boiled while mixing for 12 h in argon. After the mixture had been cooled down to 20°C, it was diluted with 250 ml of water and filtered. The precipitate on the filter was washed in water (6 × 50 ml). All filtrates were concentrated in vacuo at 40–50°C, treated with CO_2 up to pH 8–9 and filtered. 10 ml of 30% H_2O_2 was then carefully added to the filtrate. The dark-green precipitate obtained was filtered, washed in water, and dried. The uncleaned product was subjected to chromatography on a 3 × 40 cm column, with C_6H_6/heptane(1/1) and C_6H_6 as the eluant. Three products were obtained. Recrystallization in C_6H_6/heptane yielded 6.65 g (35.9%) of dark green crystals, m.p. 165–166°C. Found: C, 38.69; H, 5.82; B, 35.19. $C_9H_{16}B_9Fe$ calcd.: C, 38.97; H, 5.81; B, 35.08%. IR spectrum: 3300 ($C\equiv C\text{–}H$), 3120 (Cp), 3035 (CH carborane), 2500–2650 cm^{-1} (BH).

Complex III. 0.89 g (4.5%) of dark purple crystals, m.p. 177–178°C (from C_6H_6/heptane) (see ref. 7). Complex IV. 0.07 g (0.36%) of purple crystals, m.p. 158–160°C (from C_6H_6/heptane). IR spectrum: 3110 (Cp), 3060 (CH carborane), 2940, 2865 (CH_3) 2400–2600 (BH), 1665 cm^{-1} (C=C). Mass spectrum: m/e 311 ($M^+ - {}^{12}C_{10}{}^{1}H_{20}{}^{11}B_9{}^{56}Fe^{16}O$).

$[CpFe^{II}HCB_9H_9C\text{–}C\equiv CH]NMe_4$ (V). To 1.67 g (6.02 mmol) of a solution of complex I in 150 ml of EtOH, was added excess $NaBH_4$ in small portions. After the release of hydrogen and a change in colour from green to yellowish-brown, the mixture was evaporated in vacuo until dry, and the residue dissolved in 50 ml of water and filtered. The filtrate was treated with excess aqueous Me_4NBr solution. The residue obtained was filtered, washed in water and dried in vacuo. 2.01 g (95%) of complex V was obtained in the form of yellowish-brown crystals, m.p. 277–278°C (from CH_3OH/toluene). Found: C, 44.58; H, 8.40; B, 27.86. $C_{13}H_{28}B_9FeN$ calcd.: C, 44.52; H, 8.03; B, 27.68%. IR spectrum: 3280 ($C\equiv C\text{–}H$) 3100 (Cp), 3040 (CH carborane), 2400–2600 (BH), 1990 cm^{-1} (C≡C).

$CpFe^{II}HCB_9H_9\overset{-}{C}\text{–}\overset{+}{C}=CH_2$ (VI). 0.52 g (1.48 mmol) of complex V was suspended in 30 ml of C_6H_6 and vigorously shaken with 30 ml of 12 N H_2SO_4 until the main product completely dissolved. The organic phase was separated, washed in water several times up to pH 7.0, and dried over $MgSO_4$. After chromatography

performed on a 3×15 cm column with C_6H_6 as the eluant, 0.3 g (73%) of dark red crystals of the vinyl cation was obtained, T_{decomp} 180–190 °C (from C_6H_6/heptane). Found: C, 39.28; H, 6.05; B, 35.14; Fe, 19.39. $C_9H_{17}B_9Fe$ calcd.: C, 38.83; H, 6.16; B, 34.95; Fe, 20.06%. IR spectrum: 3125 (Cp), 3040 (CH carborane), 3080, 2980 (=CH_2), 2450–2660 (BH), 1735 ($\overset{+}{C}$=C) cm^{-1}. ^{1}H NMR spectrum: ABq 4.80 (J(HH) 7.0 Hz), 6.00 (J 7.0 Hz), s 4.42 ppm (Cp).

$CpFe^{II}HCB_9H_9\overset{-}{C}-\overset{+}{C}ClCH_3$ (VII). A mixture of 0.24 g (0.86 mmol) of vinyl cation VI and 30 ml of C_6H_6 with 30 ml of concentrated HCl was stirred vigourously for 4 h and left overnight. The organic layer was separated, washed in water, and dried over $MgSO_4$. Following chromatography on a 3×40 cm column with C_6H_6 petroleum ether as the eluant (1/1), 0.13 g (48%) of dark red crystals of zwitterion VII was obtained. T_{decomp} 217–219 °C (from C_6H_6/heptane). Found: C, 33.92; H, 5.56; Cl, 10.88; Fe, 17.95. $C_9H_{18}B_9ClFe$ calcd.: C, 34.33; H, 5.96; Cl, 11.26; Fe, 17.73%. IR spectrum: 3140, 3120 (Cp), 3050 (CH carborane), 2400–2600 (BH). ^{1}H NMR spectrum: s 1.87 (CH_3), s 4.40 ppm (Cp).

$CpFe^{II}HCB_9H_9\overset{-}{C}-\overset{+}{C}BrCH_3$ (VIII). Similar to the above procedure, 0.05 g (17%) of dark red crystals of zwitterion VIII was obtained from 0.23 g (0.83 mmol) of vinyl cation VI, 30 ml C_6H_6 and 30 ml of 48% aqueous HBr in 96 h. T_{decomp} 200 °C (from C_6H_6/heptane). Found: C, 30.04; H, 5.13; B, 27.13; Br, 22.19; Fe, 15.42. $C_9H_{18}B_9BrFe$ calcd.: C, 30.09; H, 5.05; B, 27.08; Br, 22.14; Fe, 15.54%. IR spectrum: 3150, 3130 (Cp), 3055 (CH carborane), 2400–2600 cm^{-1} (BH). ^{1}H NMR spectrum: s 2.09 (CH_3), s 4.42 (Cp).

Reaction of vinyl cation VI with MeLi. 1.45 mmol of methyllithium in 10 ml of ether was added dropwise while stirring to 0.31 g (1.11 mmol) of vinyl cation VI in 75 ml of ether in dry argon. After stirring for 30 min, ether was distilled off in vacuo, the residue was treated with 50 ml of water and CO_2 up to pH 8–9, then 1 ml of 30% H_2O_2 was added. The product was benzene-extracted (3×25 ml). The extracts were washed in water (3×50 ml) and dried over $MgSO_4$. Chromatography on a 2×5 cm column with C_6H_6 as the eluant yielded 0.28 g of a dark green, crystalline product, which, according to TLC (eluant: C_6H_6/heptane, 1/2; seven treatments), was a mixture of three products: complex I (main component) and $CpFeHCB_9H_9C-C(R)=CH_2$ (R = Me, H) (in a distinctly smaller amount). The IR spectrum confirmed TLC data.

Reaction of vinyl cation VI with NaBH$_4$. Similar to the method described above, 0.12 g (0.43 mmol) of vinyl cation VI and a slight excess of $NaBH_4$ in 30 ml of CH_3CN yielded 0.1 g of a dark green product, which, according to TLC data, was a mixture of complex I and a small amount of $CpFeHCB_9H_9C-CH=CH_2$.

Reaction of vinyl cation VI with pyridine. Similar to the method described above, 0.16 g (0.57 mmol) of vinyl cation VI in 10 ml of pyridine yielded in 72–96 h 0.09 g of a dark green product, which, according to TLC data, was a mixture of complex I and a small amount of $CpFeHCB_9H_9C-CH=CH_2$.

References

1 In: P.J. Stang, Z. Rappoport, M. Hanack and L.R. Subramanian, Vinyl Cations, 1979, Academic Press, New York.

2 T.S. Abram and W.E. Watts, J. Chem. Soc., Perkin Trans. I, (1977) 1522.

3 H.V. Siehl and H. Mayr, J. Am. Chem. Soc., 104 (1982) 909

4 L.I. Zakharkin and V.V. Kobak, Izv. Akad. Nauk Ser. Khim., (1980) 2671.

5 L.I. Zakharkin, V.V. Kobak, A.I. Yanovsky and Yu.T. Struchkov, Tetrahedron, 38(1982) 3515.

6 L.I. Zakharkin and V.V. Kobak, Izv. Akad. Nauk Ser. Khim., (1982), 1919.

7 L.I. Zakharkin, V.V. Kobak, A.I. Yanovsky and Yu.T. Struchkov, J. Organomet. Chem., 228(1982) 119.

8 In: D. Bethel and V. Gold, Carbonium Ions: an Introduction, 1967, Academic Press, London, New York.

9 A.C. Hopkinson, K. Yates and I.G. Csizmadia, J. Chem. Phys., 55 (1971) 3835.