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Preliminary communication

THE REACTIVITY OF CYCLOPENTADIENYLCARBONYLIRON ACETYLIDES WITH ELECTROPHILES: THE ISOLATION OF A 1,3-DIMETALLO-STABILIZED CYCLOBUTENIUM ION AND A CATIONIC "VINYLIDENE"

A. DAVISON and J.P. SOLAR

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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Summary

The reactions of cyclopentadienylcarbonyliron acetylides with protic acids generate cationic "vinylidene" intermediates. These intermediates can be trapped with nucleophiles and, in one case, isolated as a tetrafluoroborate salt.

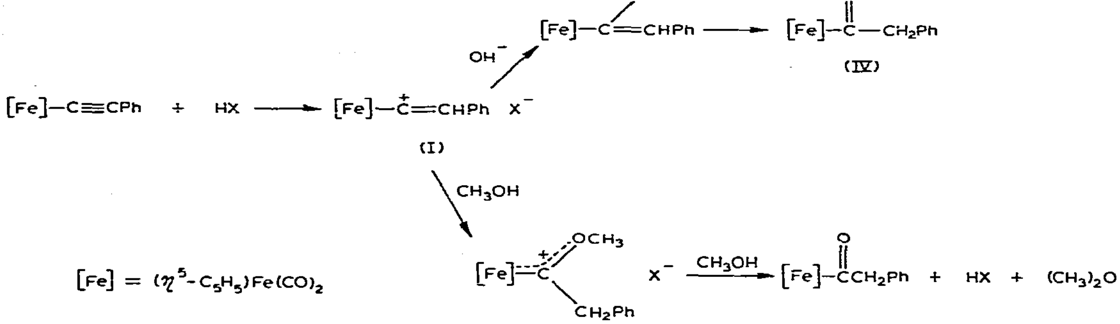
Chisholm and Clark have proposed a metal-stabilized vinylcarbonium ion, M—C$^+$=CHR (I), as the reactive intermediate in the reactions of platinum π-acetylene complexes [1]. This intermediate has also been postulated in the formation of alkoxycarbene [2] and α-chlorovinyl [3] complexes from platinum(II) acetylides.

We have studied the reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}CPh$ (II) and $(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)C{\equiv}CPh$ (III) [4] with the aim of preparing cationic vinylidene carbene complexes (or vinylcarbonium ions) (I) and studying their reactivity. We report here that the reactions of these acetylides with protic acids indicate that such an intermediate is formed and, in the case of III, it can be isolated as an unstable salt.

Salah and Bruce have described the acid-catalyzed addition of water to II which gives $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)CH_2Ph$ (IV) [5]. We have found that the reaction of II with $HBF_4\cdot$dimethyl ether complex in anhydrous methanol also leads to formation of IV in 30% yield. Both reactions probably proceed via I, as shown in Scheme 1.

The addition of hydroxide ion to a "metal-stabilized vinyl cation" to give an acyl has been proposed by Jolly and Pettit [6]. Although $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-substituted alkoxycarbene complexes are unknown, nucleophilic attack by methanol on an electron-deficient carbeneplatinum complex has been shown to produce an acylplatinum compound [7].

SCHEME 1



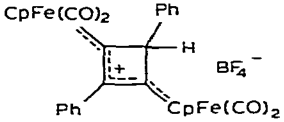
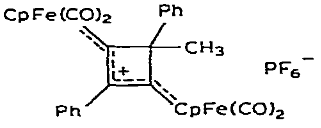
We have attempted to isolate a salt of the intermediate carbonium ion $(\eta^5\text{-}C_5H_5)Fe(CO)_2C^+\text{=}CHPh$ by treating II with $HBF_4 \cdot O(CH_3)_2$ in CH_2Cl_2 at −78°C. The reaction proceeds rapidly; however, addition of diethyl ether precipitates V as a yellow-orange microcrystalline powder in 86% yield. Spectroscopic and analytical data for this compound are given in Tables 1 and 2, respectively. The presence of two $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ moieties in this molecule is clearly demonstrated by the observation of four bands in the terminal carbonyl region of its infrared spectrum. The NMR spectrum of V is indicative of two equivalent cyclopentadienyl rings and a unique proton whose signal is found at δ 5.53 ppm. These data are consistent with structure V.

Oth et al. have shown that reaction of an ynamine, $RC{\equiv}CNR'_2$, with HCl or HBF_4 leads to a cyclized product analogous to V [8] (eq. 1).

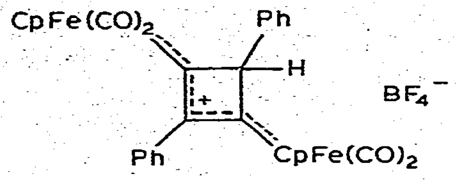
The formation of V can be explained by analogy to the ynamine reactivity (Scheme 2).

TABLE 1

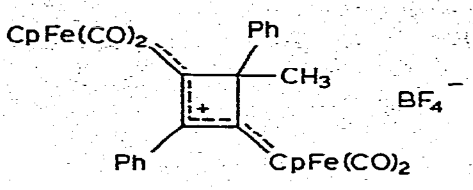
SPECTROSCOPIC DATA

Compound	IR ν(CO) (cm^{-1})	NMR (δ, ppm)
	2052s, 2041s, 2010s, 1997s[a]	5.17(s, 10H), 5.53 (s, 1H) 7.50, 7.52(s, 10H)[c]
	2055s, 2044vs, 2008vs, 2008vs, 1999(sh)[b]	1.90(s, 3H), 5.20(s, 10H) 7.40—7.65(m, 10H)[d]
$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(OCH_3)CH_2Ph]BF_4$	1940s[a]	4.00, 4.61(AB, J 12 Hz, 2H), 4.22(s, 3H), 5.05(d, J 1.5 Hz, 5H), 7.25—7.85 (m, 20H)[e]
$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CCHPh]BF_4$	2030s, 1665m (C=C)[a]	

[a] Nujol mull. [b] CH_2Cl_2. [c] $CDCl_3$. [d] DMSO-d_6. [e] Acetone-d_6.



(V)

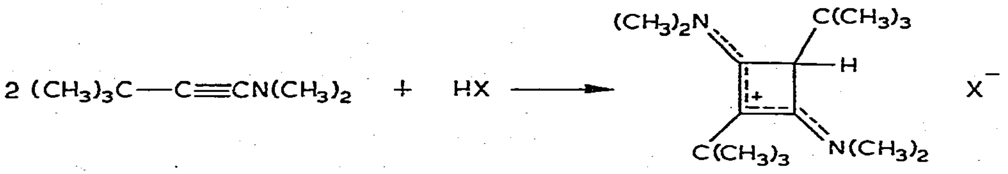


(VI)

TABLE 2

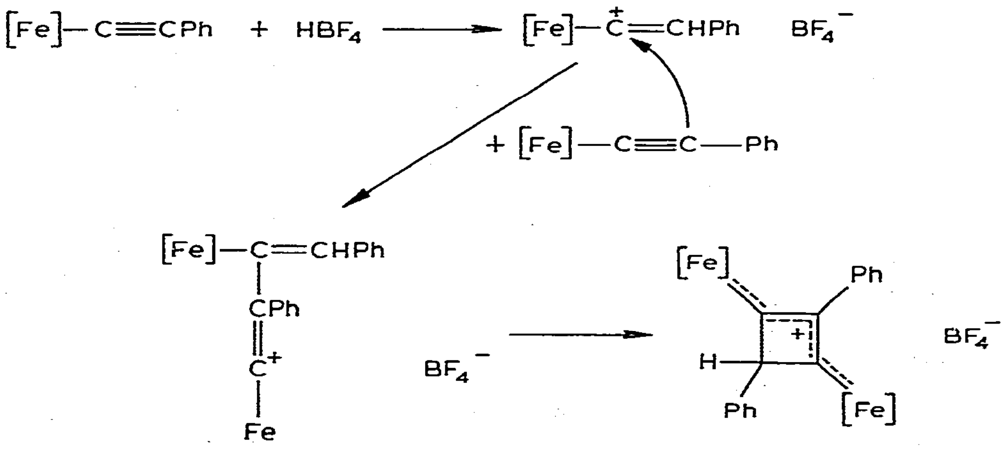
ANALYTICAL DATA (found (calcd.) (%))

Compound	C	H	Other	M.p. (°C)
$C_{30}H_{21}O_4BF_4Fe_2$ (V)	55.69 (55.96)	3.40 (3.29)	F 12.13 (11.80)	149—150 (dec)
$C_{31}H_{23}O_4PF_6Fe_2$ (VI)	52.20 (52.00)	3.37 (3.24)	P 4.44 (4.34)	167.5—170 (dec)
$C_{33}H_{30}O_2PBF_4Fe$ (VIII)	61.95 (62.69)	5.16 (4.78)	P 4.92 (4.90)	154.0—154.7



(1)

SCHEME 2

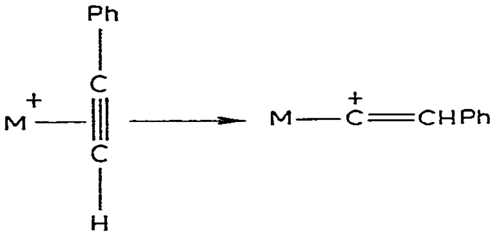


$[Fe] = (\eta^5\text{-}C_5H_5)Fe(CO)_2$

The protonation gives a vinyl cation, (a powerful electrophile) which, in the absence of a competing nucleophile, reacts with a second molecule of acetylide (a nucleophile) to give V.

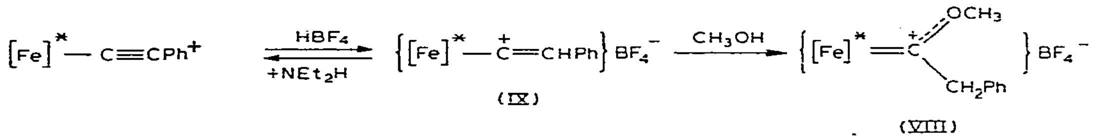
We have also demonstrated that alkylation of acetylide II follows the same pathway. Reaction of II with methylfluorosulfonate in CH_2Cl_2 gives, after metathesis with NH_4PF_6, a 51% yield of orange crystalline VI. Spectroscopic and analytical results (Tables 1 and 2) are consistent with a structure analogous to that proposed for V.

We have also explored the preparation of the vinylcarbonium ion by the rearrangement of a terminal acetylene. Reaction of phenylacetylene and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ [9] in CH_2Cl_2 produces V. Some decomposition to $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]BF_4$ also occurs. This reaction, which implies the rearrangement of the π-complex to the carbonium ion, is in contrast to the reaction of II with HCl gas, which gives $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and phenylacetylene [4]. Rearrangements of terminal acetylenes to give stable vinylidene complexes have been recently reported [10].



We have also studied the reactions of the acetylide III with protic acids. Reaction of a THF solution of III with dilute aqueous HBF_4 gives $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)CH_2Ph$ (VII) [11] in 61% yield. The reaction of III with $HBF_4\cdot O(CH_3)_2$ in methanol gives yellow $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(OCH_3)CH_2Ph]BF_4$, (VIII) in 82% yield. The infrared and NMR spectra of VIII are consistent with what has been recorded for other $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$-alkoxycarbenes [12]. These results suggest the formation of a vinylcarbonium ion from acetylide III.

Our preliminary results indicate that, in contrast to what was observed in the case of II, a vinylcarbonium ion may be isolated from III by reaction with excess $HBF_4\cdot O(CH_3)_2$ in CH_2Cl_2 or in toluene. The resulting unstable pink solid (IX) has a single carbonyl stretch at 2030 cm^{-1} and an infrared band at 1665 cm^{-1} assignable to a C=C stretch. Reaction of IX with methanol gives a 73% yield of the alkoxycarbene complex VIII. Furthermore, addition of a base, diethylamine, deprotonates IX to the starting acetylide III (eq. 2).



(2)

$[Fe]^* = (\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$

These data suggest that VIII is a "cationic vinylidene" complex or "metal-stabilized vinylcarbonium ion". Further studies on the reactivity of these compounds are in progress.

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