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Preliminary communication

SYNTHESIS AND REACTIONS OF η^5-$C_5H_5Fe(CO)_2(ACETYLENE)^+$ BF_4^- COMPLEXES

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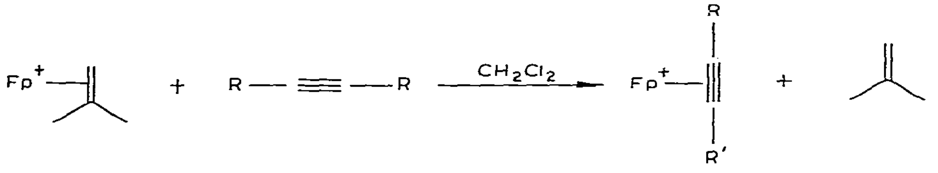
Summary

Dicarbonylcyclopentadienyliron(acetylene)-tetrafluoroborate complexes of diphenylacetylene and hexyne-3 have been isolated from the exchange reaction of the acetylene with $CpFe(CO)_2$(isobutylene) tetrafluoroborate. With phenylacetylene the sole product formed in the exchange reaction is 2-phenylnaphthalene. Methyl propiolate yields the condensation products VI, VII and VIII.

Although a large number of η^5-$C_5H_5Fe(CO)_2(olefin)^+ X^-$ [$Fp(olefin)^+X^-$] salts have been prepared [1], the corresponding acetylene complexes are virtually unknown. Only one such substance, the propyne complex (Ia) has been reported [2] and moreover the method employed for its synthesis lacks generality. Despite the comparative ease of decomposition of Ia through ligand displacement, we now have found that the disubstituted acetylene complexes Ib and Ic are readily formed by slow decomposition of Fp(isobutylene)BF_4 in refluxing methylene chloride in the presence of 1.3 molar equivalents of acetylene (eq. 1).



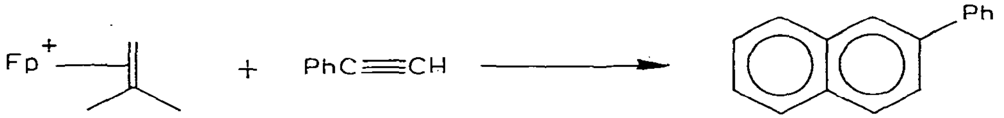
(1)

(Ia, R = H, R' = Me;
Ib, R = R' = Et;
Ic, R = R' = Ph)

Both the hexyne complex Ib (IR (CH_2Cl_2): 2050, 2090 cm^{-1}, NMR: δ 2.80 (q, CH_2), 1.45 (t, CH_3), 5.69 ppm (s, Cp); Anal. Found: C, 45.06; H, 4.40.

$C_{13}H_{15}BF_4FeO_2$ calcd.: C, 45.10; H, 4.30%) as well as the tolane complex Ic (IR (CH_2Cl_2): 2050, 2102 cm^{-1}; NMR (CD_3NO_2): δ 6.0 (s, Cp), 7.7—8.0 ppm (m, Ph)) are yellow, crystalline, air stable solids which are readily isolated from these reactions by precipitation with dry ether (Yields: Ib 86%, Ic 53%). Surprisingly, the hexyne cation undergoes ligand displacement by nitromethane only slowly at room temperature*.

By contrast, phenylacetylene does not afford a complex on treatment with Fp(isobutylene)BF_4. Instead, the single product, obtained in low yield from this reaction, is 2-phenylnaphthalene (II) (eq. 2), identified by melting point, IR, NMR and mass spectral data**.

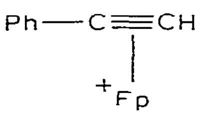


(2)

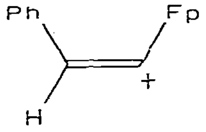
(II)

The reaction is mildly catalytic in Fp(isobutylene)BF_4, since treatment of phenylacetylene with 10 molar % of the salt in refluxing methylene chloride results in complete consumption of the isobutylene complex within 3.5 h, and recovery of 45% of phenylacetylene together with a 16% yield of II based on the acetylene. When the reaction is carried out with 1-deuteriophenylacetylene, II is found to be specifically labelled at C(1) and C(3). Thus, the singlet low field resonance at δ 8.2 ppm in the proton NMR spectrum of II, assignable to C(1), is missing from II-d_2. Furthermore the ^{13}C NMR broad band decoupled spectrum*** of II-d_2 shows only three of the four quaternary and eight of the ten tertiary ^{13}C resonances of II. The missing signals at 139.0, 126.2 and 126.0 may be assigned to C(2) and to C(1,3) respectively [4].

These results exclude processes which provide a pathway for exchange of the acetylenic proton and hence render unlikely a mechanism involving uncatalyzed conversion of the acetylene complex III to the vinylidene complex IV. Evidence for the formation of the latter species by protonation of FpC≡CPh has recently been provided by Davison and Solar [5].



(III)



(IV)

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*The propyne complex (Ia) in nitromethane solution is converted to $[Fp(CH_3NO_2)]BF_4$ within minutes at 0°C, while the hexyne (Ib) complex shows no significant change after 30 minutes at 35°C. The tolane complex decomposes in these solutions on attempted recrystallization.

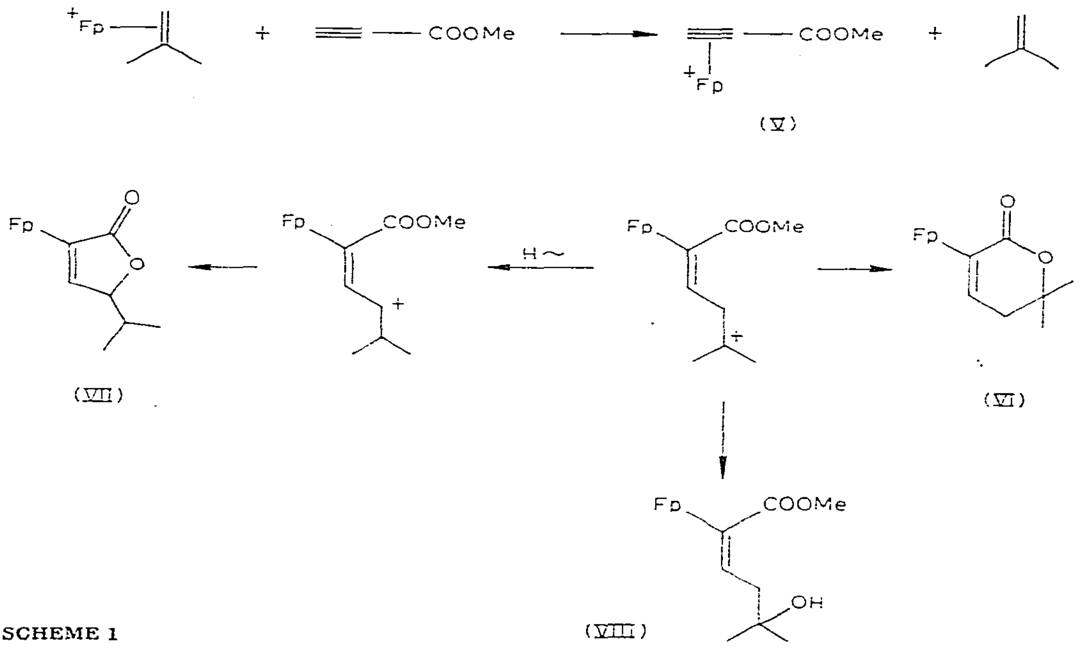
**M.p. 102—103°C, lit. [3] 105—106°C. IR and NMR spectral data were taken from Sadtler Standard Spectra (Sadtler Research Laboratories, Philadelphia, PA).

***Determined on a Bruker WH-90 spectrometer (NSF GU 3852, GP 37156).

The isomerization of η^2-acetylene-metal complexes to vinylidene complexes has been postulated for the reactions of *trans*-[Pt(Cl)MeL$_2$] complexes with monosubstituted acetylenes and AgPF$_6$ [6], and rearrangement of PhC≡CH to isolable vinylidene complexes of Mn [7], Re [8] and Fe [9] has recently been reported. Similarly the reaction of phenylacetylene with Fp(THF)BF$_4$ is observed to give products apparently derived from IV [5], and the hydration products of Ia are best accounted for in terms of its partial isomerization to the related vinylidene complex [2]. However, at least some and possibly all of these reactions may proceed by acid- or base-catalyzed isomerization of an acetylene-metal complex.

Like III, the related terminal acetylene complex V, generated by the reaction of methyl propiolate with Fp(isobutylene)BF$_4$ in refluxing methylene chloride, exhibits strong electrophilic character. This is demonstrated by the formation of the lactones VI (IR (CH$_2$Cl$_2$) 1680 cm^{-1}, NMR (CS$_2$) 6.64 (t, 1, *J* 4 Hz, CH=), 4.83 (s, 5, Cp), 2.29 (d, 2, *J* 4 Hz, CH$_2$), 1.37 (s, 6, CMe$_2$)) and VII (IR (CH$_2$Cl$_2$) 1720 cm^{-1}, NMR (CS$_2$) 7.07 (d, 1, *J* 1.5 Hz, CH=), 4.95 (s, 5, Cp), 4.53 (dd, 1, *J* 1.5, 5 Hz, OCH), 1.75 (m, 1, CH), 0.90 (d, 6, *J* 5 Hz, CHMe$_2$)) (Anal. Found: C, 56.22; H, 5.06. Calculated for mixture of lactones C$_{14}$H$_{14}$FeO$_4$: C, 55.71; H, 4.68%) along with smaller amounts of the hydroxy ester VIII (IR (CHCl$_3$): 1685 cm^{-1}, NMR (CS$_2$): 5.47 (t, 1, *J* 7.5 Hz, CH=), 4.87 (s, 5, Cp), 3.62 (s, 3, OCH$_3$), 2.58 ((br)s, 1, OH), (d, 2, *J* 7.5 Hz), 1.09 (s, 6, CMe$_2$)). These products are formed even under conditions in which isobutylene is removed from the reaction by purging with nitrogen. Plausible pathways for the formation of these products, involving *trans* addition of isobutylene to complex V are in Scheme 1.

Further investigations of the chemistry of these acetylenic complexes are in progress.



SCHEME 1

Acknowledgement

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