Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

1-(π-CYCLOPENTADIENYLIRON DICARBONYL)PROPYNE

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(Received December 1st, 1967)

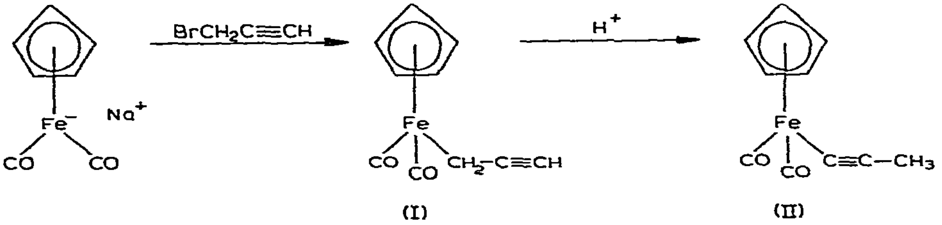
SUMMARY

Reaction of sodium π-cyclopentadienyliron dicarbonyl with 3-bromopropyne yields 3-(π-cyclopentadienyliron dicarbonyl)propyne; the latter compound undergoes facile acid catalyzed isomerization to give 1-(π-cyclopentadienyliron dicarbonyl)-propyne. Various nucleophiles, *e.g.*, acetate and water, react with the intermediate complex presumably involved in the rearrangement process.

INTRODUCTION

The linkage M–X≡Y (M = metal; X, Y = C, N or O) is one of considerable importance in coordination chemistry especially for the combinations X = C, Y = O and X = C, Y = N. It is of interest then, in the area of metal carbonyl chemistry, that despite the extensive investigations of interactions between acetylenic compounds and transition metal carbonyls those reactions designed to yield metal carbonyl acetylide complexes have been unsuccessful[1,*]. This is surprising since several groups[2] have shown that the presence of ligands capable of accepting charge from the metal atom enables stable σ-bonded acetylene derivatives of the nickel group to be prepared *e.g.*, $(Et_3P)_2Ni(C{\equiv}CH)_2$. The work of Nast *et al.*[3] indicates that in the absence of such groups the acetylenic compounds are highly unstable. We here report the discovery of a compound containing a methylacetylene group σ-bonded to iron, *viz.* 1-(π-cyclopentadienyliron dicarbonyl)propyne (II).

Reaction of sodium π-cyclopentadienyliron dicarbonyl with 3-bromopropyne yields 3-(π-cyclopentadienyliron dicarbonyl)propyne (I) as an amber liquid. The NMR spectrum of this compound consists of absorptions at τ 6.03, 5.24 and 5.11 having areas 2:5:1, respectively, which is consistent with structure (I). In addition the terminal acetylenic hydrogen absorbs at 3315 cm^{-1} in the IR region.



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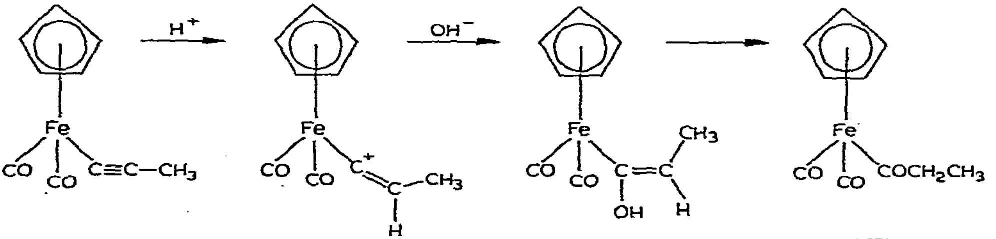
* While this work was in progress, an iridium complex containing a σ-bonded acetylene group was reported[10].

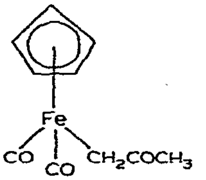
Treatment of this compound with anhydrous acids (or more efficiently by chromatography through silica gel or acid washed alumina) causes isomerization, in good yield, to 1-(π-cyclopentadienyliron dicarbonyl)propyne (II). Compound (II) is obtained as an air sensitive, yellow crystalline material (m.p. 96°) and shows two single peaks in the NMR spectrum at τ 8.21 and 5.07 having areas 3 : 5, respectively; this compound appears to be identical with that mistakenly reported by Green *et al.*[4] as the 3-propyne derivative (I). A band at 2140 cm^{-1} in the infrared spectrum is attributable to the C≡C stretching frequency. We have further obtained this compound in very small yield (*ca.* 1 %) by the reaction of sodium methylacetylide and π-cyclopentadienyliron dicarbonyl bromide in liquid ammonia.

Treatment of complex (II) with ethanolic-HCl yields propionyl-π-cyclopentadienyliron dicarbonyl (III). As indicated in the following scheme, this reaction presumably proceeds via (IV) which may be viewed as a vinylidenecarbene cationic complex; however, all attempts to trap such an intermediate with olefins, analogous to those reactions of the parent carbene complex[5], were unsuccessful. Alternatively, (IV) may be considered to be a metal stabilized vinyl cationic system. The acyl complex (III) may also be prepared by treatment of propionyl chloride with sodium cyclopentadienyliron dicarbonyl[6]. Treatment of complex (I) with ethanolic-HCl forms a mixture of the known[7] acetone complex (V) together with smaller quantities of (III), the latter presumably arising via isomerization of (I) to (II).

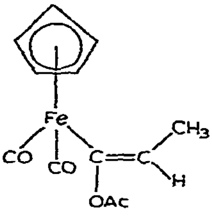


(IV)

(III)



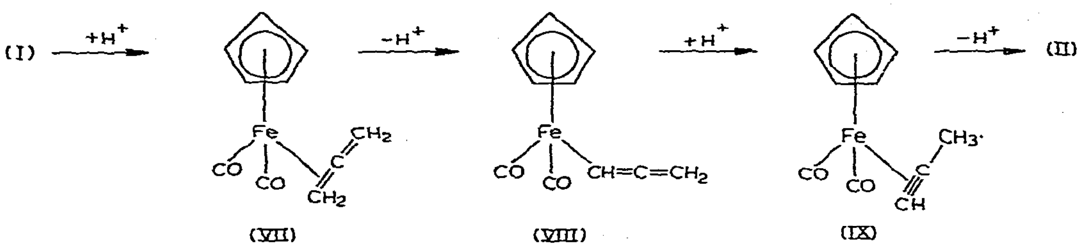
(V)



(VI)

Evidence for the carbene type intermediate (IV) is seen in the reaction of complex (II) with anhydrous acetic acid in refluxing cyclohexane which leads to the σ-bonded vinylacetate complex (VI). Complex (VI) is an amber oil which shows NMR absorptions at τ 8.59 (doublet, $J = 6.5$ cps, CH_3), τ 8.03 (singlet, $OCOCH_3$), τ 5.12 (quartet, $J = 6.5$ cps, $=CH$) and τ 5.11 (singlet, C_5H_5) with intensities of 3 : 3 : 1 : 5, respectively. Strong bands at 1731 and 1226 cm^{-1} in the IR spectrum are attributable to the acetate group. The acetate complex (VI) is rapidly hydrolyzed to the acyl complex (III) by ethanolic potassium hydroxide.

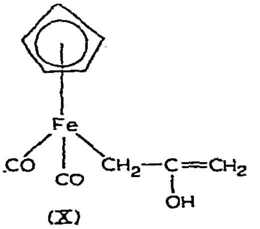
The acid catalysed rearrangement of (I) to (II) involves transfer of two protons and the facile nature of the process suggests involvement of relatively stable intermediates. A reasonable scheme would seem to be the following:



Addition of a proton to complex (I) could yield the π-allene cationic complex (VII) which upon loss of a proton would lead to the σ-allene complex (VIII). Further protonation of (VIII) is suggested to yield the π-acetylenic complex (IX) which, upon deprotonation, affords the observed product (II).

Some experimental support for this sequence comes from the fact that the π-allene cationic complex (VII) which can be formed independently through reaction of π-cyclopentadienyliron dicarbonyl chloride with allene and aluminum chloride[8], is found to react with aqueous solvents to form the acetone derivative (V); complex (V) is also the product of reaction of (I) with aqueous acids. In both reactions the allene cationic complex is trapped by water to yield complex (X), the enol derivative of (V), before isomerization to (II) can occur.

Treatment of compound (II) with HCl gas leads to the formation of π-cyclopentadienyliron dicarbonyl chloride as the only isolable organometallic product while anhydrous HBF_4 and $HSbCl_6$ cause considerable decomposition of complex (II) from which only salts of the π-cyclopentadienyl iron tricarbonyl cation could be isolated[9].



(X)

EXPERIMENTAL

Microanalyses were carried out by Dr. Alfred Bernhardt, Max-Planck Institut für Kohlenforschung, Mulheim (Ruhr), Germany. All operations were carried out under nitrogen or in a vacuum. IR spectra were recorded on a Perkin Elmer 257 in cyclohexane and carbon disulphide solutions. NMR spectra were recorded in carbon disulphide solutions on a Varian A-60.

3-(*π-Cyclopentadienyliron dicarbonyl*)*propyne* (*I*)

π-Cyclopentadienyliron dicarbonyl dimer (10 g: 27.1 mmoles) was dissolved in tetrahydrofuran (150 ml) and the solution added to an excess of 2% sodium-amalgam and stirred for 2 h. Unreacted amalgam was run off through a stopcock and the solution added, over one h to 3-bromopropyne (6.5 g; 54.6 mmoles) in tetrahydrofuran (50 ml) maintained at 0°; after the addition the mixture was stirred for one h. The solvent was evaporated and the residue extracted with pentane (200 ml) and filtered through celite. Evaporation of the pentane followed by distillation at 80° and 0.1 mm pressure gave the product as an amber oil (4.1 g; 34%). [Found: C, 55.8; H, 3.9; Fe, 25.8; mol.wt. (mass spectrum), 216. Calcd.: C, 55.6; H, 3.7; Fe, 25.9%; mol.wt., 216.] The IR spectrum showed bands at 1980 vs, 2032 vs (C≡O), 3315 w (≡C–H), 3045 w, 2988 m, 1422 s, 1140 s, 1050 s, 1015 m, 1002 m, 831 s, 804 s, 626 s. The NMR spectrum consisted of absorptions at τ 6.03 (Doublet, $J=6.5$ cps, $-CH_2-$); τ 5.24 (singlet, C_5H_5) and τ 5.11; (quartet, $J=6.5$, ≡C–H).

1-(π-Cyclopentadienyliron dicarbonyl)propyne (II)

(*a*) *By chromatography.* Compound (I) (0.5 g) was eluted with an ether/petroleum ether (80/20) solution from a silica gel column (100 g). The product was obtained as yellow crystals (0.29 g, 60%, m.p. 96°). [Found: C, 55.5; H, 3.8; Fe, 25.5; mol.wt. (mass spectrum), 216. Calcd.: C, 55.6; H, 3.7; Fe, 25.9%; mol.wt., 216.] The IR spectrum consisted of bands at 2048 vs, 1999 vs (C≡O), 2900 m, 2845 w, 2140 m (C≡C), 1370 w, 1015 w, 1001 w, 831 s. The NMR spectrum consisted of bands at τ 8.21 (singlet, $\equiv C-CH_3$) and τ 5.07 (singlet, C_5H_5).

Similar, though less efficient, rearrangement occurred during chromatography through acid washed alumina and florisil columns.

(*b*) *By acid catalysis.* Compound (I) (0.1 g) was dissolved in nitromethane (15 ml) and acetic acid (0.1 g) was added. The mixture was kept at ambient temperature and the course of the reaction followed by observation of the carbonyl absorptions in the IR spectrum. Reaction was complete after one h. Solvent was removed under high vacuum and the product (II) (0.025 g) was sublimed out of the reaction vessel and purified by recrystallization from petroleum ether. The properties of the product were identical to those described above.

Hydrolysis of 1-(π-cyclopentadienyliron dicarbonyl)propyne

Compound (II) (0.2 g) was dissolved in ethanol (30 ml) and 10% hydrochloric acid (0.1 ml) added. The solution was immediately extracted with ether (3×25 ml) and the ether extract washed with water (3×25 ml) and dried over $MgSO_4$. The residue was purified by chromatography on a florisil column to yield propionyl-π-cyclopentadienyliron dicarbonyl, (III) (0.19 g).

Hydrolysis of 3-(π-cyclopentadienyliron dicarbonyl)propyne

Compound (I) (0.13 g) was treated with HCl in ethanol in a manner identical to that just described for compound (II). Chromatography of the product on florisil afforded the propionyl complex (III) [0.13 g, ether/petroleum ether (50/50) as eluate] followed by the acetone derivative (V) (0.1 g, 100% ether as the eluate).

ACKNOWLEDGEMENT

The authors thank the National Science Foundation, the Robert A. Welch Foundation and the U.S. Army Research Office (Durham) for financial support.

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