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Preliminary communication

SYNTHESIS OF ORGANOIRON COMPLEXES CONTAINING THE η^1-1-(1,3-ALKADIENYL) LIGAND

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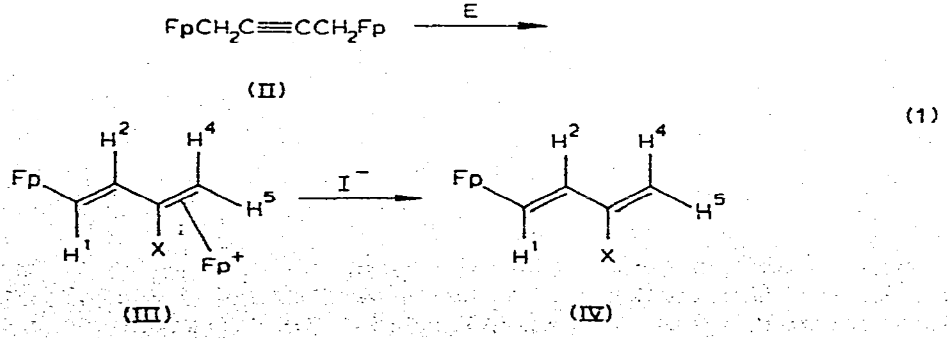
Summary

The synthesis and spectroscopic properties of organoiron complexes of the type [FpCH=CHCX=CH$_2$]Fp$^+$ and FpCH=CHCX=CH$_2$ (X = H, Me, Et, CH(OMe)$_2$; Fp = η^5-C$_5$H$_5$(CO)$_2$Fe) are described.

Although complexes containing the η^1-1-(1,3-butadienyl) moiety are thought to be important intermediates in the oligomerization of alkynes, little is known of the chemistry of these substances [1]. Undoubtedly this is attributable to the high reactivity of these transient complexes and the lack of synthetic procedures for the preparation of suitable model compounds. Until the initiation of the



(II)

(III)

(IV)

(1)

(a) E = MeOSO$_2$F ; X = Me
(b) E = EtOSO$_2$F ; X = Et
(c) E = $^+$CH(OMe)$_2$; X = CH(OMe)$_2$

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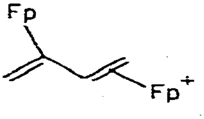
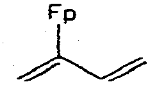
work to be described here, the only reported organoiron complex containing the η^1-1-(1,3-butadienyl) ligand was FpCH=CHCH=CHFp (Fp = η^5-$C_5H_5(CO)_2Fe$).

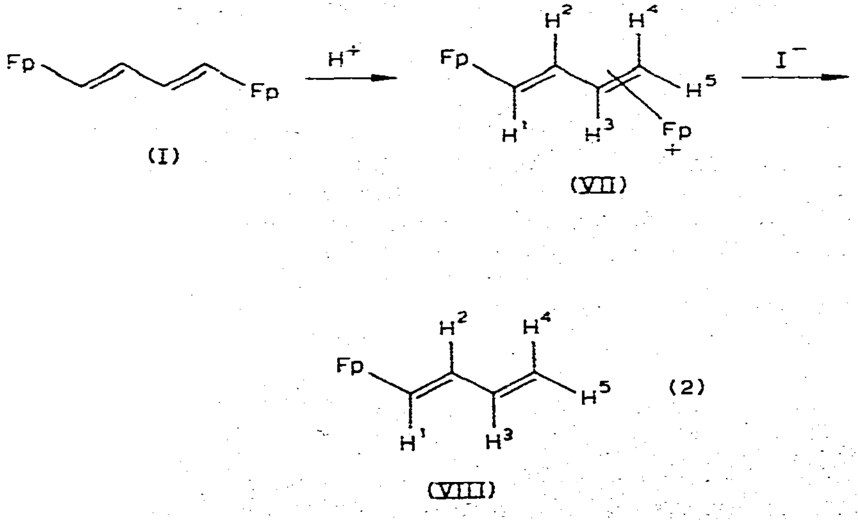


(V)



(VI)

We now report a novel and useful synthesis of Fp complexes containing η^1-1-(1,3-butadienyl) ligands (eq. 1). Treatment of a methylene chloride solution of II with methyl fluorosulfonate afforded after 2 h at 30°C a deep red solution from which the cationic complex IIIa was precipitated by the slow addition of diethyl ether. The ethyl derivative IIIb was prepared in an analogous manner except that the product was a red oil contaminated with an equimolar amount of the protonated product V. The dimethoxymethyl adduct IIIc also was obtained as a somewhat impure red oil. The parent complex VII (X = H) was obtained as a red solid by the careful protonation of I. The binuclear complexes IIIa—IIIc and VII were readily converted by sodium iodide in acetone to the neutral complexes IVa—IVc and VIII which were purified by column chromatography on alumina.



(I) (VII) (VIII)

(2)

An analysis of the PMR spectra of the new complexes* leaves no doubt as to the formulation of these complexes as containing the *trans*-η^1-1-(1,3-butadienyl) ligands rather than the η^1-2-(1,3-butadienyl) ligand (V and VI) which is obtained when II is protonated [3]. In particular, $J_{1,2}$ of III, IV, VII and VIII is 15—20 Hz, characteristic of *trans*-vicinal hydrogens of the butadiene moiety [4]. The most striking feature of the PMR spectra of IIIa, IIIc** and VII is the unusually low

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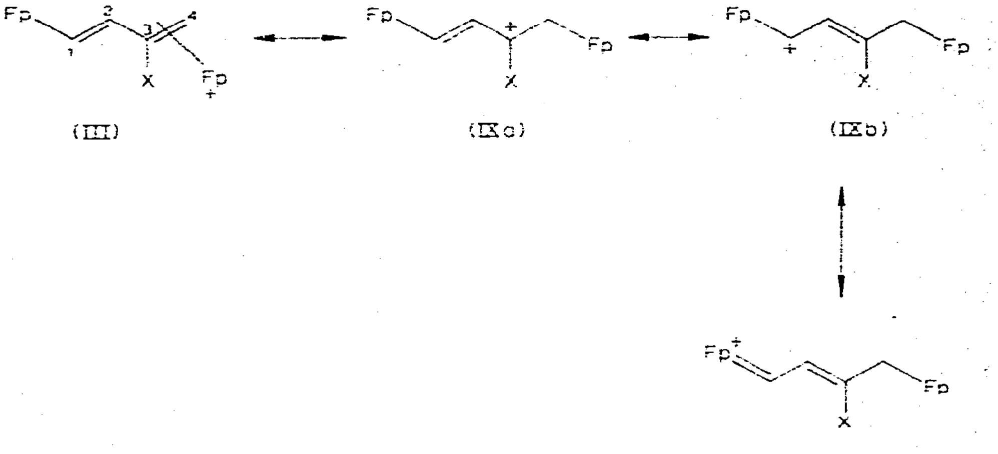
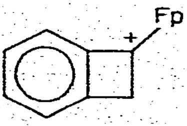
*Satisfactory iron analyses were obtained for the neutral mononuclear complexes IVa, IVc and VIII.
**The PMR spectrum of IIIb was not obtained.

field resonances of ^{1}H which is observed at τ 0.34, 1.10 and 0.69 ppm, respectively. These chemical shifts are to be compared with τ 3.08, 2.72 and 3.48 ppm for the analogous protons of IVa, IVb and VIII. In the IR spectra of IIIa and VII the diene absorptions are observed as intense bands at 1510—1535 cm^{-1}. The binuclear complexes also exhibit a strong absorption near 500 nm in the visible; hence their color is red to maroon in contrast to the orange-yellow of V and most other Fp(alkene)$^+$ complexes.

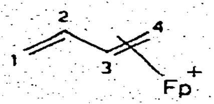


(III) (IXa) (IXb) (IXc)

The spectroscopic properties of III and VII suggested that the carbenoid canonical forms IXb and IXc are significant contributors to the structure of III. The ^{13}C NMR spectra of the binuclear complexes IIIa and VII were obtained to estimate the importance of IXb and IXc. In the spectra of both IIIa and VII, the chemical shift of C(1) was 179 ppm downfield from TMS. This is considerably downfield from C(1) (125 ppm) of the butadiene complex XI, but not as extreme as the chemical shift (352 ppm) of the ligating carbon of the benzocyclobutenylidene complex X. The C(4) resonances (40 and 42 ppm) of IIIa and VII were upfield from C(4) (52 ppm) of XI [5]. Thus the ^{13}C chemical shifts appear to support the contention that the carbenoid canonical forms do make at least a small contribution to the structure of these compounds.



(X)



(XI)

The neutral mononuclear complexes IV and VIII are well behaved compounds exhibiting the expected chemical properties.

Studies of these compounds are in progress.

Acknowledgement

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