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Preliminary communication

CATIONIC IRON COMPLEXES CONTAINING THE η^2-BUTATRIENE LIGAND

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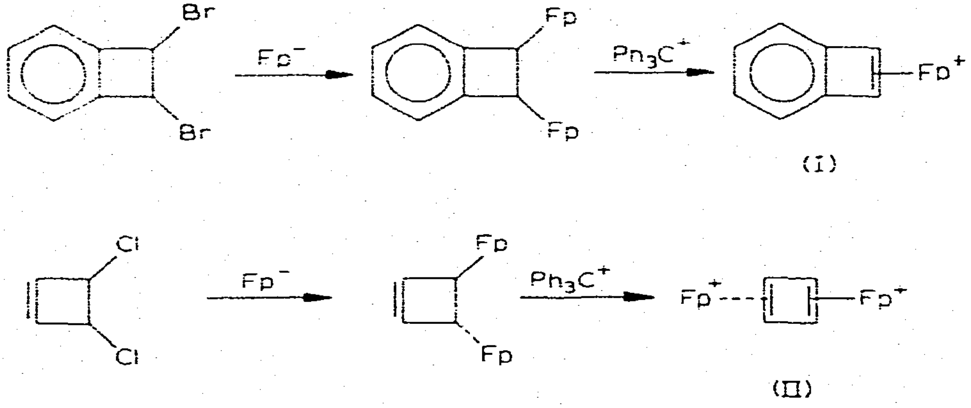
Summary

Cationic iron complexes of the type Fp(alkene)$^+$ (Fp = η^5-$C_5H_5(CO)_2Fe$) containing an unsubstituted η^2-butatriene ligand are synthesized and characterized by spectroscopic and analytical data.

Cationic iron complexes of the type Fp(alkene)$^+$ (Fp = η^5-$C_5H_5(CO)_2Fe$) containing highly reactive and/or unstable alkenes as *dihapto* ligands are not preparable by standard synthetic methods [1]. Recently, we reported the synthesis of complexes (I and II, Scheme 1) containing the η^2-cyclobutadienoid ligands via the oxidation of binuclear complexes in which the iron groups formally are σ-bonded to the cyclobutadienoid ligands [2–5]. These neutral complexes were derived, in turn, from dihalo-cyclobutenes or -benzocyclobutenes [6]. Since the dihalides of many highly reactive alkenes are known, it was thought that the reaction sequences as illustrated in Scheme 1 might be a general and useful method for the generation of novel Fp(alkene)$^+$ complexes. We have embarked on a research program to determine the generality of this approach and to explore the



SCHEME 1

TABLE 1

PMR (τ, ppm) AND IR (cm^{-1}) SPECTRAL DATA AND ANALYTICAL DATA FOR NEW COMPOUNDS

Complex	PMR	IR	Analysis
IV	4.04 (s, 10, C_5H_5), 6.10 (s, 4, C_4H_4)^a	2090, 2065 (C≡O)^b	$C_{18}H_{14}F_{12}Fe_2O_4P_2$ calcd.: C, 31.03; H, 2.01. Found: C, 30.84; H, 2.04%.
V	4.35 (s, 5, C_5H_5), 4.77 (s, 5, C_5H_5) 5.31 (s, 2, CH_2), 7.72 (s, 2, CH_2)^{a,c}	2067, 2015 1960 (C≡O)^b	$C_{18}H_{14}ClF_6Fe_2O_4P$ calcd.: Fe, 19.05. Found: Fe, 18.80%.
VI	4.08 (s, 1, =CH), 4.59 (s, 1, =CH) 4.81 (brs, 2, =CH_2), 5.10 (s, 5, C_5H_5)	2010, 1965^f (C≡O)	
VII	5.36 (s, 5, C_5H_5), 5.55 (s, 5, C_5H_5), 6.01 (dd, 2, AB J 10Hz, CH_2), 6.58 (s, 6, CH_3), 7.76 (d, 1, H^1), 8.27 (d, 1, J 3.0Hz, H^1)^{d,g}	2000, 1951 1933, (C≡O), 1685 (C=O)^f	h
VIII	4.79 (s, 10, C_5H_5), 5.91 (s, 4, CH_2) 6.60 (q, 4, J 7Hz, CH_2), 8.68 (t, 6, CH_3)^a	2004, 1970 (C≡O)^b	$C_{22}H_{24}F_6Fe_2NO_4P$ calcd.: Fe, 17.98. Found: Fe, 17.82%.
XI	3.83 (s, 1, =CH), 4.25 (s, 1, =CH), 5.10 (s, 5, C_5H_5), 7.80 (s, 3, CH_3)	2008, 1960 (C≡O)^f 1654 (C=O)	$C_{11}H_{10}FeO_3$ calcd.: Fe, 22.70. Found: Fe, 22.67%.

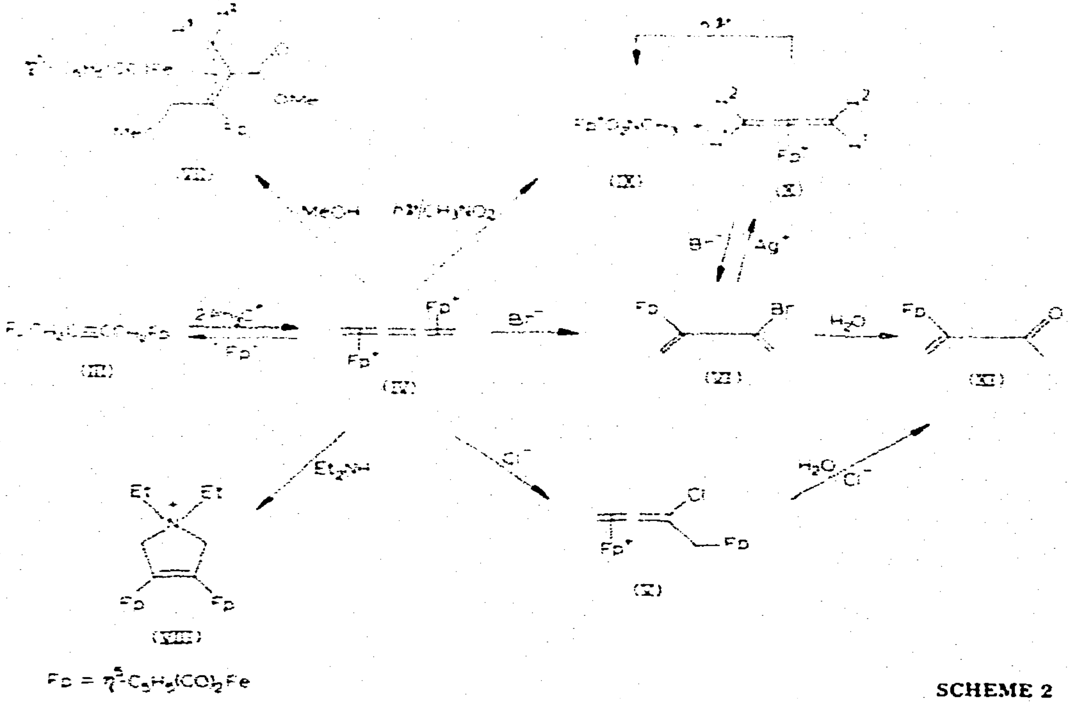
[a] CD_3NO_2. [b] KBr pellet. [c] Broad singlets. [d] CS_2. [e] Shoulder. [f] Neat. [g] In benzene-d_6, the degeneracy of the two methyl resonances is removed. [h] We have not been successful in crystallizing VII, hence an analytically pure sample of VII has not been obtained.

chemistry of the resultant cationic complexes. Herein, we report the preparation and some of the chemical properties (Scheme 2) of the first transition metal complexes (IV and X) containing the unsubstituted η^2-butatriene ligand.

Complex IV precipitates directly as a bright-yellow solid when methylene chloride solutions of 1,4-bis(η^5-cyclopentadienyldicarbonyliron)-2-butyne (III) [7, 8] and trityl hexafluorophosphate are mixed in a 1:2 ratio at −78°C and then allowed to warm to 25°C. The product, which is air stable, is readily collected by filtration. Further purification by dissolution in nitromethane followed by reprecipitation by the addition of methylene chloride gave a 36% yield of IV. The spectroscopic and analytical properties of all new compounds are given in Table 1. The PMR spectrum of IV indicates that the two iron groups and the two methylene groups are equivalent. Unfortunately, due to the low solubility of IV in appropriate solvents it has not been possible to distinguish between IV and a fluxional system involving structures such a IVa and IVb.

(IVa) (IVb)

Complex IV manifests several different modes of electrophilic reactivity that are dependent on the nature of the nucleophile. Thus, Fp⁻ reduces IV to III whereas Cl⁻ adds to IV to give V which can be isolated in crystalline form only with difficulty. Treatment of IV with excess Cl⁻ followed by chromatography of the reac-



SCHEME 2

tion mixture on activity III alumina gave the methylvinylketone complex XI. Small amounts of the neutral bromobutadienyl complex VI were isolated from the reaction between benzyltriethylammonium bromide and IV, or from the bromination of III. Complex VI is unstable thermally and difficult to obtain in pure form. Its identity was established by spectroscopic examination of a sample that was about 90% pure. The bromo group of VI is labile (vide infra) as evidenced by the rapid formation of silver bromide when VI is treated with silver hexafluorophosphate. The addition of methanol to IV gives the novel binuclear complex VII that contains an η^3-allyl ligand which is also an η^1-ligand for the second iron group. The binuclear 3-pyrrolinium complex VIII is formed by the cycloaddition of diethylamine to IV.

The iron groups of IV are labile. Thus refluxing in nitromethane or photolysis in nitromethane at 25°C effects a stepwise decomposition of IV to the nitromethane complex IX and the mononuclear η^2-2,3-butatriene complex X. When the course of the photolysis of IV in CD_3NO_2 was monitored by PMR spectroscopy there was observed a decrease in the concentration of IV concomitant with the formation of initially equimolar amounts of IX and X. Prolonged photolysis led to the complete conversion of IV and X to IX. The presence of X was inferred by a singlet resonance at τ 4.10 ppm and an AA′BB′ multiplet centered at τ 3.30 ppm in 5:4 ratio. Although attempts to separate IX and X have been unsuccessful, a mixture of the two complexes was obtained free of IV. Treatment of this mixture with benzyltriethylammonium bromide gave VI. X was also prepared in low yield by treatment of VI with silver hexafluorophosphate in methylene chloride. Although X was obtained as a solid by the addition of petroleum ether to this latter reaction mixture, the PMR spectrum of this substance showed it to be only 85–90% pure. Attempts to crystallize X gave only an oil.

The AA′BB′ multiplet exhibited by X is consonant with either a η^2-2,3- or a η^1-1,2-butatriene ligand. However, the chemical shift is clearly consistent with uncoordinated terminal double bonds* and thus supports structure X.

Acknowledgments

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*The resonances of methylene protons of a coordinated alkene in Fp(alkene)$^+$ are observed at ca. τ 6.0 ppm.