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Preliminary communication

SIMPLE PREPARATION OF IRON STABILIZED CARBOXONIUM IONS. CONCURRENT COMPLEXATION, REARRANGEMENT AND ALCOHOL ADDITION TO TERMINAL ACETYLENES

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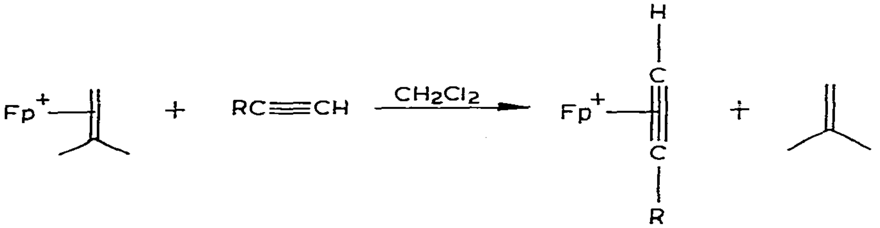
Summary

$CpFe(CO)_2[C(OEt)R]BF_4$ complexes can be prepared by reaction of $CpFe(CO)_2(isobutylene)BF_4$ with monoalkylated acetylenes in methylene chloride/ethanol solutions. Methyl propiolate yields methyl *trans*-2-ethoxyacrylate, in a reaction catalytic in $CpFe(CO)_2(isobutylene)BF_4$, and internal acetylenes can be transformed to $CpFe(CO)_2(vinyl\ ether)BF_4$ complexes.

Cationic η^2-olefin [1], η^2-acetylene [2], η^3-allyl [3], η^5-pentadienyl [4] and η^6-arene [5] transition metal complexes occupy a position of increasing synthetic importance as reagents in carbon—carbon bond forming reactions. We recently provided evidence for the formation of powerful electrophilic complexes I in the exchange reaction [6] (eq. 1).



(1)

(Ia, R = Ph;
Ib, R = COOMe)

The products formed in these reactions are readily accounted for as resulting from attack of Ia on uncomplexed phenylacetylene and of Ib on iso-

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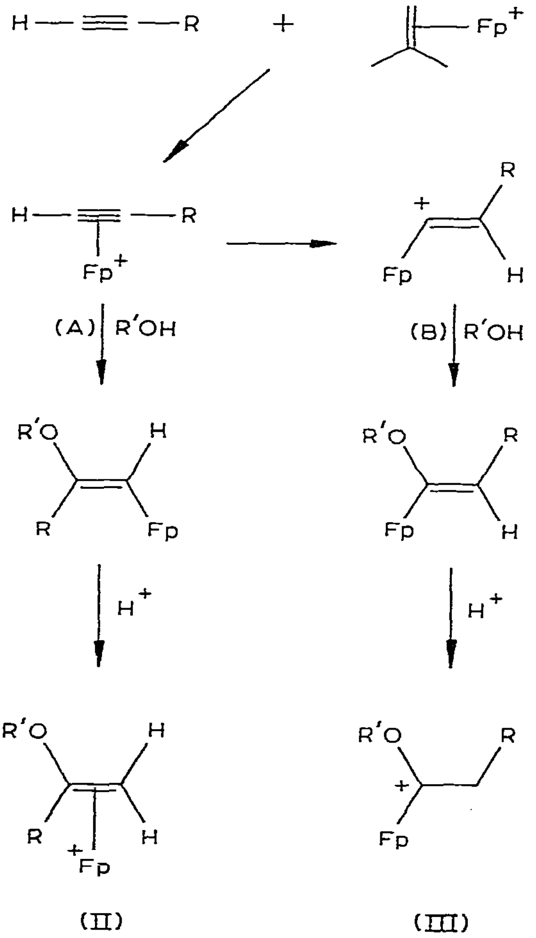
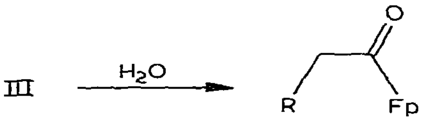
butylene. These bimolecular processes are apparently competitive with rearrangement of the acetylenic complexes to their vinylidene isomers. Nevertheless, the latter process has been well documented for a number of manganese [7], rhenium [8], platinum [9], iron [10] and ruthenium [11] complexes, and protonation of CpFe(L)(L')C≡CR (L,L' = CO, PPh_3, dppe) has been shown to yield cationic vinylidene complexes [12]. Furthermore, we had earlier found [13] that hydration of $Fp(propyne)^+BF_4^-$ led to ketonic products apparently derived from the reaction of both the acetylene complex and its vinylidene isomer, and Marten [14] has recently reported that exchange complexation of 3-butyne-1-ol with $Fp(isobutylene)BF_4$ also yields products derived from intramolecular alcohol addition to both an intermediate acetylene and vinylidene complex.

These observations prompted us to examine the reactions of alcohols with Fp^+ complexes of terminal acetylenes as a potential route to either cationic Fp(η^2-vinyl ether) complexes II, or to the carboxonium complexes III (Scheme 1, paths A,B). We now find that the exchange reaction involving



Scheme 1. a, R = n-C_3H_7; b, R = n-C_4H_9; c, R = Ph.

Fp(isobutylene)BF_4 and monoalkylated acetylenes, when carried out in the presence of ethanol, provides an efficient route to the metal-stabilized carboxonium complexes III. These reactions, whose overall course closely resembles that of cationic platinum complexes with terminal acetylenes [9], were conveniently carried out in refluxing methylene chloride solution with a mole ratio of Fp(isobutylene)BF_4, acetylene and alcohol of 1/5/1 for a period of 3—5 h*. The mixture was then filtered through 1 cm of celite in a Schlenk tube, and the product was then precipitated from solution by the slow addition of ether**. Butyne-1 gave the salt IIIa, IR(CH_2Cl_2): 2070, 2010 cm^{-1}; NMR (CD_3NO_2); δ(Cp) 5.45, in 51% yield, while pentyne-1 afforded a 71% yield of IIIb, IR (CH_2Cl_2) 2060, 2000 cm^{-1}; NMR (CD_3NO_2) δ(Cp) 5.48. Phenylacetylene yielded the stabilized cation IIIc (83%), IR (CH_2Cl_2): 2060, 2000 cm^{-1}; NMR (CD_3NO_2): δ(Cp) 5.37. Brief exposure of each of these to water results in their rapid hydrolysis and conversion to the corresponding acyl—iron complexes IV (eq. 2)



(2)

(IVa, R = C_3H_7;
IVb, R = C_4H_9;
IVc, R = Ph).

A limited number of these carboxonium-iron complexes and their phosphine analogues $CpFe(CO)(PR_3)[C(OR^1)Me]^+X^-$ have been prepared by alkylation of acyl complexes [15] IV, by alkoxide addition to vinylidene complexes [10b] or by hydride abstraction from α-alkoxyalkyliron complexes [16]. The present method makes these cations accessible from readily available starting materials by a simple and convenient one step process.

Although 3-hexyne (Va) readily undergoes exchange complexation in the presence of Fp(isobutylene)BF_4 to give VI, sequential complexation and alcohol addition to 3-hexyne could not be effected in one step as with terminal acetylenes. However, complex VI smoothly reacts with methanol, most likely by a sequence of steps analogous to those depicted in Scheme 1, path A, to give the vinyl ether complex VII, as a mixture of *cis* and *trans* isomers. This sequence may therefore provide a convenient and general route to Fp(vinyl ether)BF_4 complexes, which have been shown to serve as vinyl cation equivalents with carbon nucleophiles [17].

By contrast with Va, 3-hexyn-1-ol gives the dihydrofuran complex VIII, as yellow needles, m.p. 82°C (dec) (86%), directly on exchange complexation

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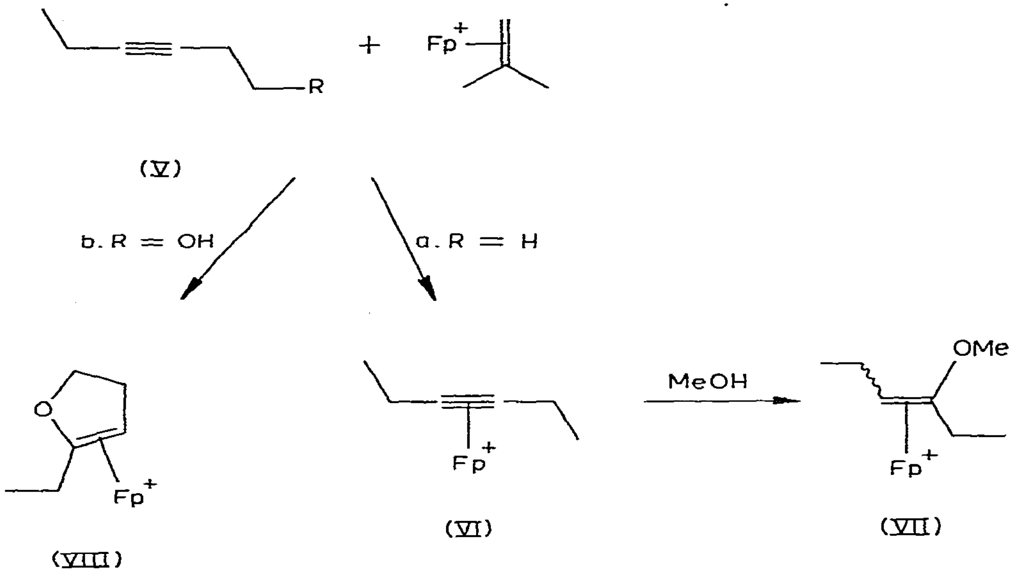
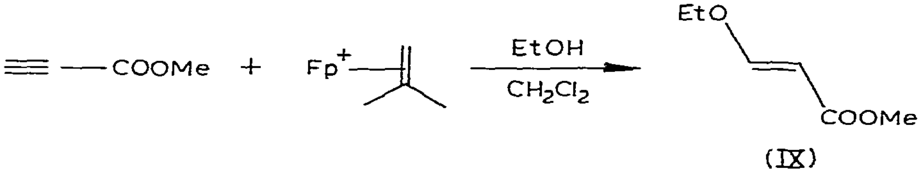
*The ratio of reactants is not necessarily optimized. Since completion of this paper, we have observed that with phenylacetylene a reactant ratio of 1/3/1 gave an 98% yield of pure product. When, however, the proportion of acetylene is lowered so that the reactant ratio is 1/1/1, product yield is decreased and the product is found to be contaminated with $Fp(EtOH)^+$.

**All new compounds were fully characterized by IR, NMR spectra and by elemental analyses. All experimental procedures were carried out in an atmosphere of nitrogen.



with Fp(isobutylene)BF_4 in close analogy to the reactions of 3-butyn-1-ol and 4-pentyn-1-ol recently reported by Marten [14].

The course of the exchange complexation, alcoholysis reaction with methyl propiolate differs substantially from the reaction of monoalkylated acetylenes. The exclusive product of this reaction is methyl *trans*-3-ethoxyacrylate (IX) [18], NMR ($CDCl_3$) δ 7.55, 5.17, $J = 12$ Hz (vinyl H). Moreover, the reaction is catalytic in Fp(isobutylene) with a turnover rate of at least four in 12 h at 40°C.



This reaction appears to proceed through alcoholysis of an initially formed propiolic ester complex, competitive with its rearrangement to a vinylidene complex (Scheme 1, path A). The final complex in this sequence, IId, would be expected to be destabilized by the electron-withdrawing ester group and undergo exchange complexation with methyl propiolate.

Further examination of these reactions and of the applications of the products in synthesis is being pursued.

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