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ORGANOMETALLIC COMPLEXES IN SYNTHESIS. NUCLEOPHILIC REACTIONS ON TRICARBONYLCYCLOHEXADIENYLIRON CATIONS: SOME CYCLOHEXADIENYL PHOSPHINIC, PHOSPHONIC AND SULPHONIC ACID DERIVATIVES

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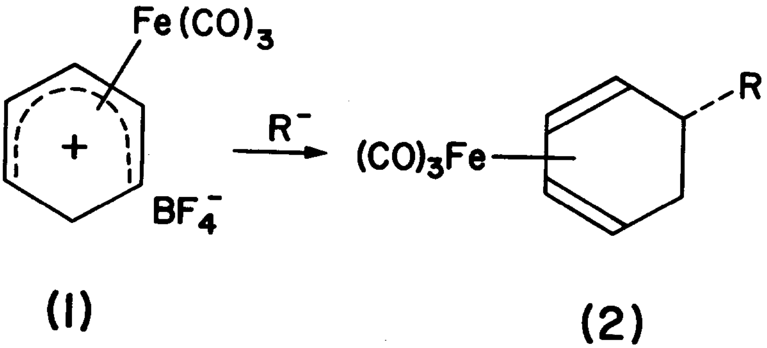
Readily available[1] tricarbonylcyclohexadienyliron tetrafluoroborate (1) is a mild alkylating agent and reacts with nucleophiles (amines, alkoxide, hydroxide, carbanions or enolates derived from carbonyl compounds) to give tricarbonylcyclohexa-2,4-dienyliron derivatives (2).[2]

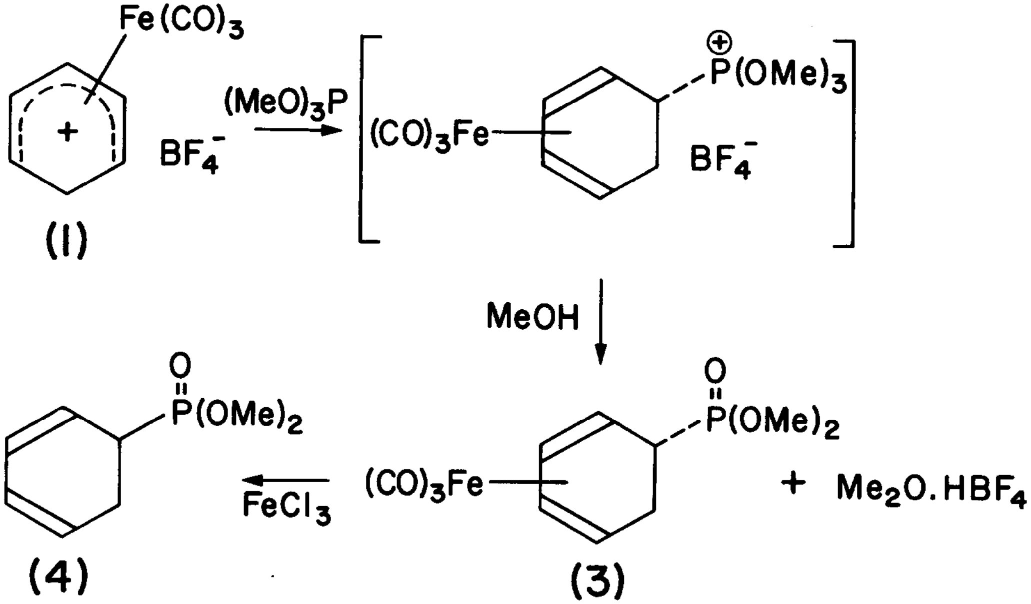


Some of these products can be used for further synthetic reactions and with those involving carbon nucleophiles, the Fe(CO)$_3$ group can be removed leading to possibilities in organic synthesis.[2(a)] A recent publication[3] describing a mild procedure for phenylating amines involves addition of a nucleophile (the amine) to an alkoxy substituted derivative of the cation (1).

Cyclohexadienyl cations (1) do not always behave identically with open-chain analogues. For example, reversal of addition of the nucleophile seems more facile with (1), amine products such as (2, R = NHR') undergoing ready reversal to (1) with acid, in contrast to a pentadienyl analogue[4] which is merely protonated.

We now report extensions to the range of nucleophiles that can be alkylated by (1) to give synthetically useful products. In particular, phosphites undergo a facile Arbusov reaction to give cyclohexa-2,4-dienylphosphonic acid derivatives. This type of compound has not been reported previously and would be difficult to synthesise by other procedures.

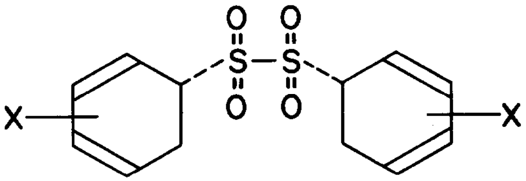
Thus, trimethylphosphite reacts rapidly with (1) at ambient temperatures to give a virtually quantitative yield of the phosphonate diester (3) as a pale yellow oil. The tricarbonyl iron group was readily removed by aqueous methanolic ferric chloride to give (4).



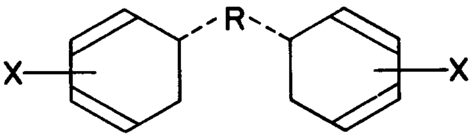
The phosphonate (3) was stable to mild acid treatment, unaffected by trityl fluoroborate, and converted into (2, R = P(O)(OMe)OH) by treatment with cyclohexylamine followed by acid.

Hypophosphorous acid in water at 65°/2 hr, gave the phosphinic acid (2, R = P(O)H(OH)) m.p. 104-105°, converted by mercuric oxide in benzene into (2, R = $P(O)(OH)_2$).

Aqueous sodium hydrogen sulphite yielded (2, R = SO_3H), characterised as the *p*-toluidine salt m.p. 159-161° (decomp). Sodium dithionite produced the disulphone (5) as a yellow oil. Sodium hydrogen carbonate acted as a base giving the ether (6, R = O) m.p. 119-120° in a manner observed with some other carbonium salts.[5] Aqueous sodium sulphide resulted in (6, R = S) m.p. 110-111°.



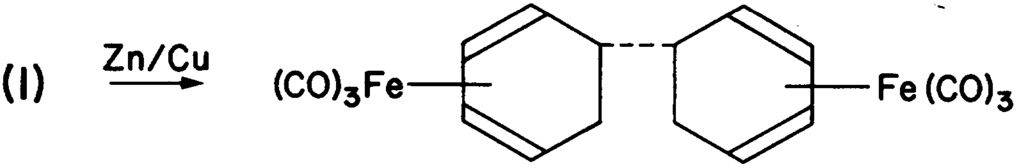
(5)



(6)

X = Fe(CO)$_3$

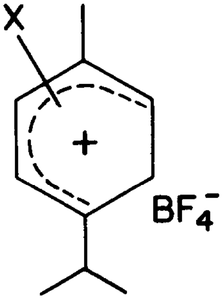
Reduction of (1) by borohydride to tricarbonylcyclohexadieneiron is well known[6] and the same product is conveniently produced by tributyltin hydride in benzene. This result contrasts with dissolving metal reduction, e.g. Zn/NaBr/dioxan/2 days, or Zn/Cu/THF/16 hr which gives the dimeric product (7) m.p. 120-122°, apparently as one isomer.



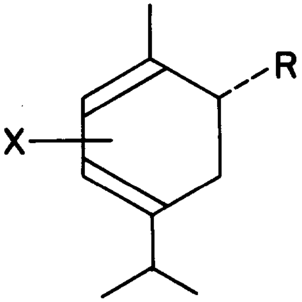
(7)

The ease of reduction of (1) is underlined by formation of (7) by the action of diisopropylamine in acetonitrile. Similar reductive dimerisations have been observed with tricarbonylchromium tropylium cations[7] and tricarbonylcycloheptadienyliron cations.[8]

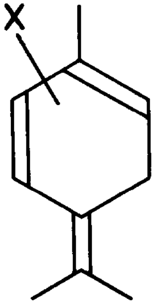
The substituted salt (8) derived from (-)-α-phellandrene[9] gave the corresponding dimethylphosphonate (9, R = $P(O)(OMe)_2$) and sulphonic acid (9, R = SO_3H) derivatives with trimethylphosphite and sodium hydrogen sulphite respectively, but weakly basic reagents (sodium hydrogen carbonate, sodium dithionite, amines, enamines) resulted in elimination of a proton from (8) to give (10) as a yellow oil.



(8)



(9)



(10)

X = $Fe(CO)_3$

The acids (2, 9, R = P(O)(OMe)OH) reacted with D.C.C. to form the expected pyrophosphates; (2, R = P(O)H(OH)) gave a stable phosphinic anhydride which was a little surprising in view of the instability of the closely related phenylphosphinic anhydride.[10] The anhydride reacted with morpholine to give the corresponding phosphinic amide (2, R = P(O)H(morpholine)).

The structures of the products are supported by analytical, n.m.r., i.r. and mass spectral data, which agree with accepted standards and interpretations. The configurations shown are assumed to result from attack opposite to $Fe(CO)_3$, by analogy with all other reactions of this type so far examined.[2(a)] This assumption is supported in the case of (3) by its inertness to trityl fluoroborate, indicating hindrance to attack at the position adjacent to the substituent.

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