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Preliminary communication

REACTIVITY OF IRON TRICARBONYL CYCLOHEPTATRIENIDE: SYNTHESIS OF METAL CARBONYL DITROPYLIUM COMPLEXES ($C_{14}H_{14}FeM(CO)_6$) (M = Fe, Cr, Mo, W)

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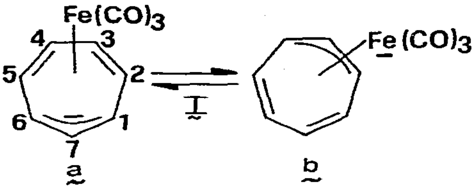
Summary

Reaction of [$C_7H_7Fe(CO)_3$] (I) with allyl halides gives as the final product $(OC)_3FeC_7H_7—C_7H_7Fe(CO)_3$, which shows a different stereochemistry from the similar mixed $(OC)_3FeC_7H_7—C_7H_7M(CO)_3$ derivatives obtained by reaction of I with $[\eta\text{-}C_7H_7M(CO)_3]^+$ (M = Cr, Mo, W).

Although the preparation of $[C_7H_7Fe(CO)_3]^-$ (I) was reported in 1971** [1,2], only few data are available on its reactions [1,3,4]. The fluxional compound I might be an equilibrium mixture of a and b forms.



With the aim of discriminating between a and b we have treated I with a number of halides of different electrophilicity. The deep red solution of the anion I*** rapidly turns yellow upon addition of allyl halides, while only a small change in colour is noticed after hours in the case of alkyl halides.

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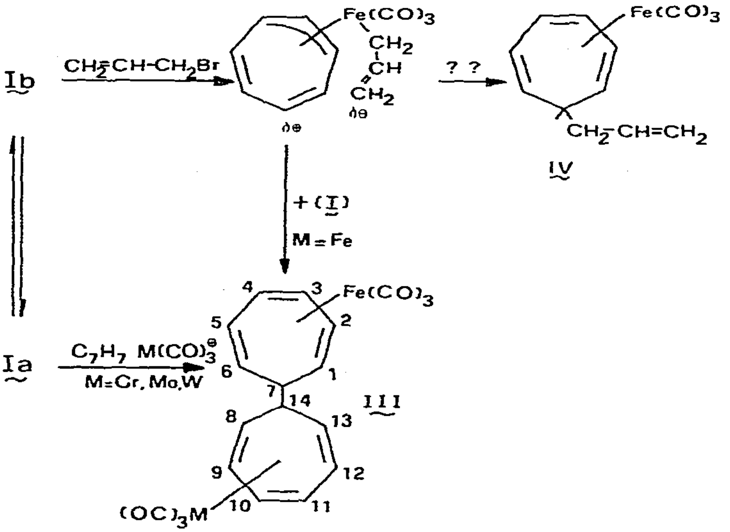
**For a recent survey of the iron, ruthenium and osmium derivatives of cyclic polyolefins see ref. 2.

***We have found that I may be conveniently prepared at room temperature by treating a THF solution of $(1\text{-}4\eta^4\text{-}C_7H_8)Fe(CO)_3$ (II) with stoichiometric amount of anhydrous t-BuOK.

In this latter case the major product of the reaction isolated by column chromatography on Florisil is (1-4η^4-C_7H_8)$Fe(CO)_3$ (II)*. With allyl halides good yields are obtained of a yellow crystalline compound, which shows the characteristic ν(CO) absorptions of an $Fe(CO)_3$ group (2059, 1990 and 1979 cm^{-1}, in n-hexane solution) and the ^{1}H NMR spectrum consistent with configuration III (M = $Fe(CO)_3$; τ 3.90-5.25 ppm H(2,3,5,6) and H(9,10,12,13) and τ 6.70-7.25 ppm H(1,4,8,11) and H(7,14). The behaviour of I towards the above reagents suggests that all the alkylations first occur on iron (configuration b) to give an unstable iron σ-alkyl derivative, with subsequent decomposition (R = alkyl) or further reaction with I (R = allyl) to the ditropylium compound III.



II is very likely formed by reaction of the very unstable ($C_7H_7Fe(CO)_3R$) intermediate with moisture, during chromatography.

Direct reaction at C(7) (configuration Ia) is likely to occur with more electrophilic reagents so that the less reactive form Ia is also involved. Preliminary results indicate that such direct reaction occurs in the reaction of I with SiR_3Cl [3], ROCOCl, and [η^7-$C_7H_7M(CO)_3$]$^-$ (M = Cr, Mo, W). Depending upon the reagents, variable yields of II are always obtained in these reactions.

The reaction of I with [η^7-$C_7H_7M(CO)_3$]$^-$ gives mixed metal carbonyl ditropylium derivatives which show a different configuration from the above diiron hexacarbonyl ditropylium complex. This is shown by the position of the signal assigned to H(7) in the ^{1}H NMR spectra: H(7) appears at τ 7.0 (M = Fe) and at τ 8.6 (M = Cr, Mo, W)**. According to Pauson and his co-

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*Trace amounts of other two compounds were obtained but were not further investigated. All the complexes here reported gave good elemental analyses.

**The other signals of the mixed iron—molybdenum hexacarbonyl ditropylium derivative appear at τ 3.95 (H(10,11)) 4.05 (H(5,6)) 4.75 (H(2,3)) 5.05 (H(9,12)) 6.00 (H(8)) 6.25 (H(13)) 7.00 (H(1,4)) 7.30 ppm (H(14)). (assignments as in the scheme). Similar ^{1}H NMR spectra have been registered for the analogous chromium and tungsten complexes.

workers [5] the two types of complexes should have (for the H(1) ↔ H(7) ring) an *endo* configuration of H(7) in the diiron complex and an *exo* configuration of H(7) in the mixed ditropylium derivatives (III).

We are now extending our studies to the relative reactivity of the two polyolefinic rings and to the selective disengagements of the metals. Further studies are in progress to see if it may be possible, to inhibit the formation of III in favour of IV, a *C*-allylated product, which could be obtained by an intramolecular allylic rearrangement.

Acknowledgments

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