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Preliminary communication

REACTION OF HALIDES WITH TRICARBONYLCYCLOHEXADIENYLIRON CATION: PREPARATION OF TRICARBONYL(5-*exo*-FLUOROCYCLOHEXA-1,3-DIENE)IRON

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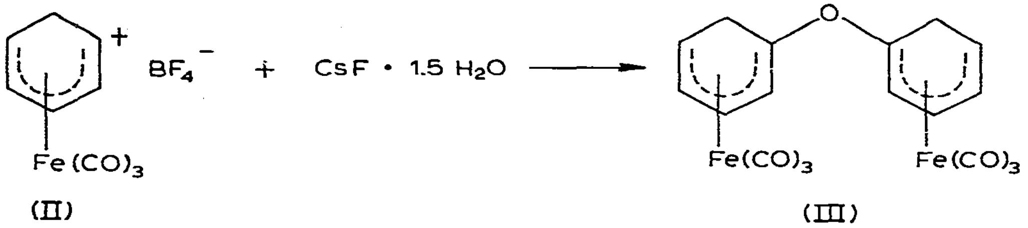
Summary

Tricarbonyl(5-*exo*-fluorocyclohexa-1,3-diene)iron has been prepared by reaction of tricarbonyl(cyclohexadienyl)iron cation with KF in the presence of 18-crown-6. Reactions of chloride and bromide salts of potassium also give unstable 5-substituted compounds while the iodo salt reacts to form a mixture of the ring and metal substituted products.

In continuation of our studies of 5-substituted tricarbonyl(cyclohexa-1,3-diene)iron complexes, we were interested in preparing tricarbonyl(5-*exo*-fluorocyclohexa-1,3-diene)iron (I). Reported attempts to prepare I are limited, and ended in failure [1, 2]. Nametkin and co-workers found that tricarbonyl-5,5-oxydicyclohexadiene-1,3-yliron (III) resulted from the reaction of hydrated cesium fluoride with the cyclohexadienyl unit II.



Fluoride ions encumbered by solvation shells are known to be poor nucleophiles and it is therefore not too surprising that the above attempt failed. However, it seemed that "naked" fluoride ions, derived from potassium fluoride and 18-crown-6 [3] would offer fluoride ions with sufficient nucleophilicity to

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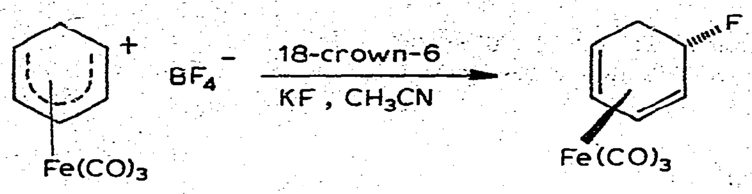
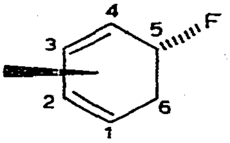


(II) (I)

form I. Thus addition of II to a stirred solution of potassium fluoride/18-crown-6 in acetonitrile resulted in formation of one major product within 15–30 minutes. Isolation by preparative TLC showed this to be I in 70% yield. Detailed spectroscopic data presented in Table 1 confirms the assignment of I.

TABLE 1

SPECTROSCOPIC PROPERTIES OF I



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^{13}C NMR (proton decoupled) $CDCl_3$ (δ, ppm)

55.5 (d *J*(CF) 1.9 Hz, C^1); 84.7 (C^2); 84.1 (C^3);
60.7 (d *J*(CF) 3.9 Hz, C^4); 75.6 (d *J*(CF) 11 Hz, C^5);
31.7 (d *J*(CF) 14.7 Hz, C^6); 210.9 ($\underline{C}{\equiv}O$):

^1H NMR $CDCl_3$ (δ, ppm)

5.43 (2H, m, $H^{2,3}$); 3.88 (1H, m, *J*(HF) 10 Hz, H^5);
2.9 (2H, m, $H^{1,4}$); 2.22 (1H, m, H^6 *endo*);
1.45 (1H, m, H^6 *exo*)

IR (cyclohexane)

$\nu(C{\equiv}O)$ 2045, 1971 cm^{-1}

Mass Spectrum

m/e 238 Parent; 220 (–HF), 210 (–CO), 208 (–CO + H_2),
182 (–2CO), 180 (–2CO + H_2), 154 (–3CO), 152 (–3CO + H_2)

Unlike for the case of fluoride ion, we found that II readily reacted with either sodium or potassium salts of chloride, bromide or iodide ions, the latter having previously been reported [4].

Reactions of II with either stoichiometric or excess potassium chloride or bromide were followed by infrared spectroscopy in acetonitrile. Only does ring attack occur in both cases as evidenced by carbonyl absorptions (IV, X = Cl 2040, 1960 cm^{-1}; X = Br 2061, 1965 cm^{-1}). No other products were observed. Removal of solvent in vacuo gave solid products, but these were found to be unstable and could not be further purified. The ^1H NMR spectra of both solutions were those typical of 5-substituted tricarbonyl(cyclohexa-1,3-diene)iron complexes*. In both cases, the mass spectra failed to show parent ions, but exhibited prominent peaks of *m/e* 219, 191, 163 and 135 corresponding to loss of halogen followed by sequential loss of three CO groups.

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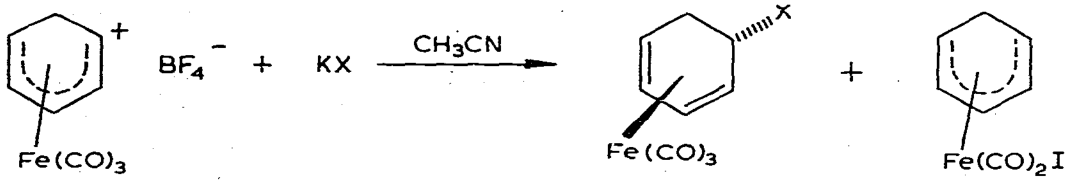
*Ring attack by I^- has also been observed for $C_6H_7Os(\overset{+}{CO})_3$ [5] and for $C_7H_9Os(\overset{+}{CO})_3$ [6].

The reaction of potassium iodide in acetonitrile was also followed. Partial gas evolution occurred, and the infrared showed formation of two products in approximately equal concentrations as II is consumed. The position of the carbonyl bands were consistent with the ring adduct V (2035, 1970 cm^{-1}) as well as the previously reported [4] metal adduct VI (2041, 1992 cm^{-1}). The low yield previously obtained [4] (less than 50%) for VI may thus be explained by presently observed concommitant formation of V [6].



(IV) X = Cl, Br
(V) X = I
(VI)

The results presented show that 5-halo-substituted tricarbonylcyclohexadieneiron compounds can be formed, and that the fluoro derivative is stable. The chloro, bromo and iodo derivatives are decreasingly stable, and in the case of iodine metal substitution also occurs.

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