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## Preliminary communication

# ALUMINIUM TRIHALIDE INTERACTIONS WITH POLYOLEFIN TRICARBONYLIRON COMPOUNDS

B.F.G. JOHNSON, KENNETH D. KARLIN* and J. LEWIS
*University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)*

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## Summary

IR studies show that in solution aluminium trihalides form Lewis acid adducts at the iron atom in polyolefin tricarbonyliron complexes. A ketonic organometallic compound also forms a 2:1 adduct.

In earlier studies [1], we found that cyclooctatetraene(tricarbonyl)iron (III) reacts with aluminium trihalides to form the cyclic ketonic complex (IV) which, under carbon monoxide pressure, yields the tricyclic ketone, barbaralone. The reaction is general and other polyolefin(tricarbonyl)iron complexes react with aluminium trihalides to produce polycyclic ketones [1,2]. It was therefore of interest to examine the nature of the interaction of aluminium halides with these organometallic complexes, and here we report preliminary results of such studies.

TABLE 1

THE CO STRETCHING FREQUENCIES FOR INVESTIGATED COMPLEXES IN $CH_2Cl_2$ SOLUTIONS

| Fromula | $\nu$(CO)(cm$^{-1}$) | $\nu$(CO) (cm$^{-1}$) in the presence of $AlX_3$ | $\Delta\nu$(CO) (cm$^{-1}$) mean | |
|---|---|---|---|---|
| | | | M—CO | $\geq$C=C |
| $C_6H_8Fe(CO)_3$ | 2042s, 1962s | X = Cl 2121s, 2069s (Ia) | +97 | |
| (I) | | X = Br 2122s, 2070s (Ia) | +98 | |
| $C_7H_8Fe(CO)_3$ | 2048s, 1970s | X = Cl 2114s, 2669s (IIa) | +88 | |
| (II) | | X = Br 2114s, 2067s (IIa) | +87 | |
| $C_8H_5Fe(CO)_3$ | 2050s, 1978s | X = Br 2110s, 2064s (IIIa) | +77 | |
| (III) | | | | |
| $(C_9H_8O)Fe(CO)_3$ | 2068s, 2002s, 1660m | X = Cl 2095s, 2035s, 1520m (V) | +31 | —140 |
| (IV) | | 2127s, 2088s, 1610m (VI) | +77 | — 50 |
| | | X = Br 2094s, 2039s, 1520m (V) | +41 | —140 |
| | | 2130s, 2095s, 1610m (VI) | +83 | — 50 |

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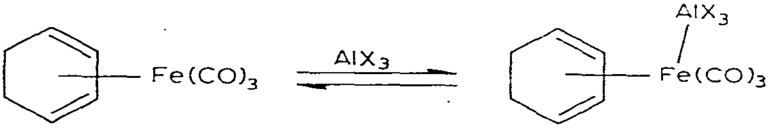
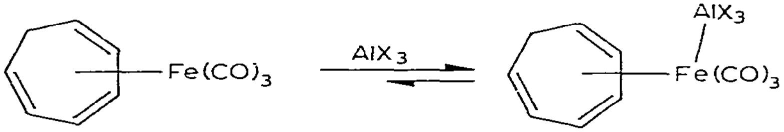
*Present address: Department of Chemistry, State University of New York at Albany, Albany, NY 12222 (U.S.A.)

When $AlX_3$ (X = Cl, Br) is added gradually to $C_6H_8Fe(CO)_3$ (I) in $CH_2Cl_2$ under nitrogen atmosphere and the reactions are monitored by IR spectroscopy, the two carbonyl bands at 2042 and 1962 $cm^{-1}$ decrease in intensity. At the same time, the two new bands grow in at higher energies (see Table 1). No bands appear at lower energy thereby ruling out the possibility of an aluminium halide-carbonyl oxygen interaction as is found in other systems [3,4] and these data suggest the generation of an aluminium halide adduct with coordination at the iron atom $(C_6H_8)(CO)_3Fe\rightarrow AlX_3$ [4]*.



(I) (Ia)

Compounds I and Ia are in equilibrium and an equimolar mixture of I and $AlBr_3$ shows an approximately equal mixture of I and Ia by IR spectroscopy. The solution is stable for several hours, but I can be quantitatively recovered on hydrolysis with dilute HCl followed by extraction into the organic phase.



(II) (IIa)

Cycloheptatriene(tricarbonyl)iron (II) forms a similar Lewis acid adduct (IIa) but in this case hydrolysis affords only about 45% recovery of II. Addition of cyclooctatetraene(tricarbonyl)iron to a large excess of $AlBr_3$ in a dilute solution leads to the formation of the aluminium halide adduct IIIa. No reaction to give barbaralone(tricarbonyl)iron (IV) is observed under these conditions. On hydrolysis, III reforms together with a small amount of $C_8H_9Fe(CO)_3X$ [6].

It was also of interest to examine aluminium halide interactions with IV in order to further understand the nature of the transformation III→IV. Addition of approximately stoichiometric quantities of $AlX_3$ to IV in $CH_2Cl_2$ gives a solution of V, characterised by a shift in the carbonyl band at 1660 $cm^{-1}$ to 1520 $cm^{-1}$. This shift of 140 $cm^{-1}$ is comparable to the shifts observed in aluminium halide complexes of organic ketones [7] as well as carbonyl-bridged transition metals [3,8]. The IR bands due to terminal Fe—CO groups also move to higher energies showing that electron density is removed from the iron atom by $AlX_3$ interaction of the ketone oxygen atom. Further addition of $AlX_3$ causes disappearance of the IR bands due to V and appearance of new bands (see Table ascribed to species VI). Here, direct $Fe\rightarrow AlX_3$ interaction results in a further shift to higher energies of the terminal Fe—CO bands. The ketonic group also moves to a higher frequency. Hydrolysis of solutions of V and/or VI results in quanti-

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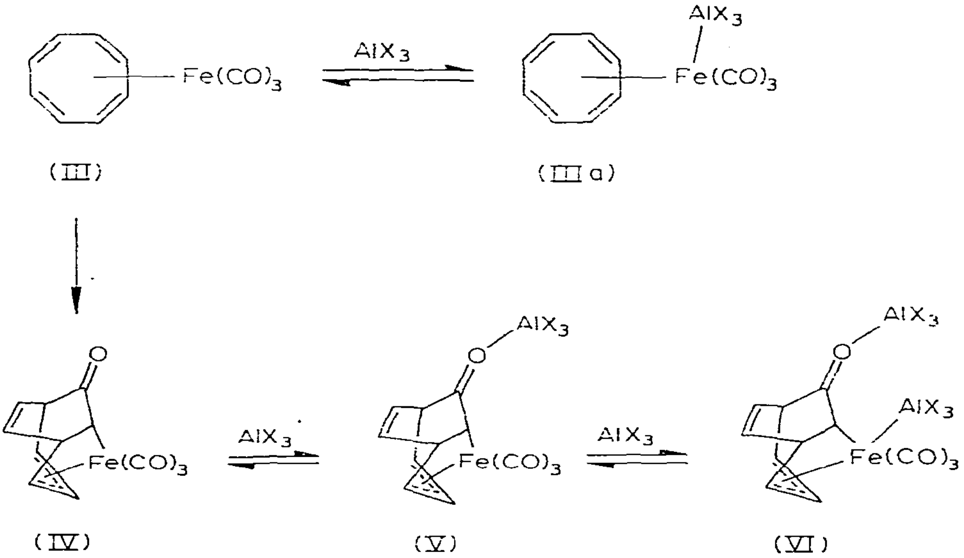
*Fe—Al interactions in organometallic chemistry have been observed [5].



tative recovery of IV. The interactions of $AlX_3$ with IV undoubtedly help drive the reaction III→IV.

We are currently extending these studies to other polyolefin transition metal carbonyl compounds, and to other Lewis acids.

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