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Preliminary communication

ALUMINUM TRIHALIDE INTERACTIONS WITH POLYOLEFIN TRICARBONYLIRON COMPOUNDS

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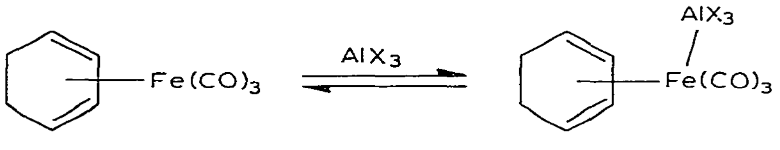
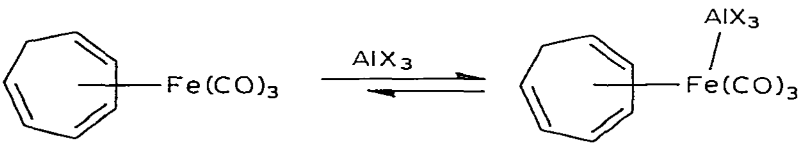
Summary

IR studies show that in solution aluminum 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 aluminum 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 aluminum trihalides to produce polycyclic ketones [1,2]. It was therefore of interest to examine the nature of the interaction of aluminum halides with these organometallic complexes, and here we report preliminary results of such studies.



(I) (Ia)



(II) (IIa)

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*Publication accidentally delayed.

TABLE 1

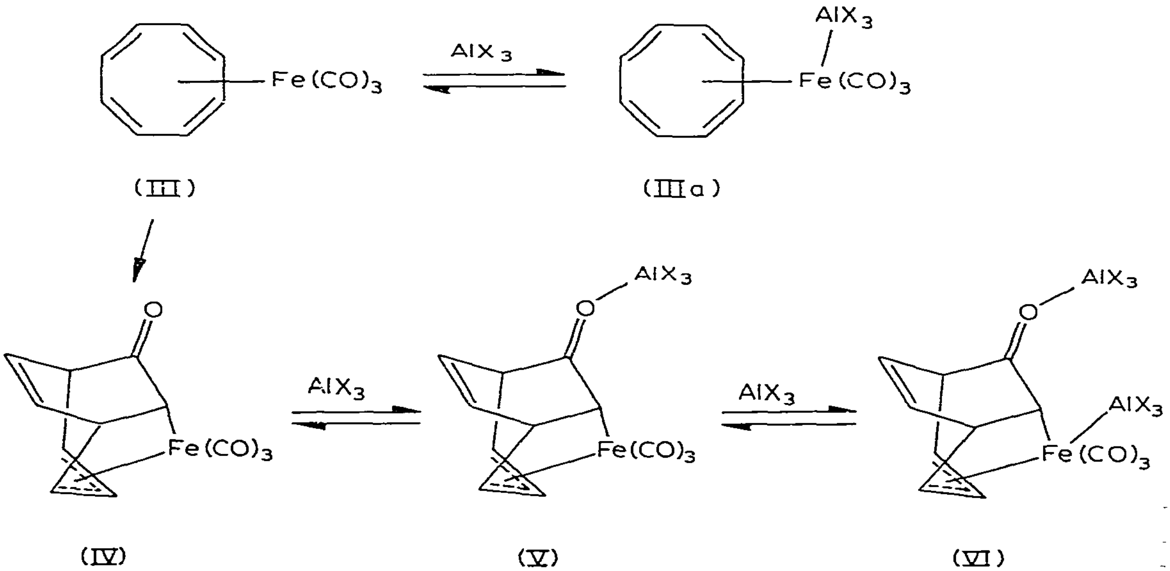
THE CO STRETCHING FREQUENCIES FOR INVESTIGATED COMPLEXES IN CH_2Cl_2 SOLUTIONS

Formula	ν(CO)(cm^{-1})	ν(CO)(cm^{-1}) in the presence of AlX_3	$\Delta\nu$(CO)(cm^{-1}) mean	
			M—CO	>C=O
$C_6H_8Fe(CO)_3$ (I)	2042s, 1962s	2121s, 2069s (Ia, X = Cl)	+97	
		2122s, 2070s (Ia, X = Br)	+98	
$C_7H_8Fe(CO)_3$ (II)	2048s, 1970s	2114s, 2669s (IIa, X = Cl)	+88	
		2114s, 2067s (IIa, X = Br)	+87	
$C_8H_8Fe(CO)_3$ (III)	2050s, 1978s	2110s, 2064s (IIIa, X = Br)	+77	
$(C_9H_8O)Fe(CO)_3$ (IV)	2068s, 2002s, 1660m	2095s, 2035s, 1520m (V, X = Cl)	+31	−140
		2127s, 2088s, 1610m (VI, X = Cl)	+77	−50
		2094s, 2039s, 1520m (V, X = Br)	+41	−140
		2130s, 2095s, 1610m (VI, X = Cl)	+83	−50

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 aluminum halide—carbonyl oxygen interaction as is found in other systems [3,4] and these data suggest the generation of an aluminum halide adduct with coordination at the iron atom $(C_6H_8)(CO)_3Fe \rightarrow AlX_3$ [4,*].

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,

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



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

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 aluminum 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 to 1520 cm^{-1}. This shift of 140 cm^{-1} is comparable to the shifts observed in aluminum 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 1) 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 quantitative 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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