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An Olefin-Insertion Reaction into a Fluorocarbon-Aluminium Compound and a π-Bonded Olefin-Aluminium System[1]

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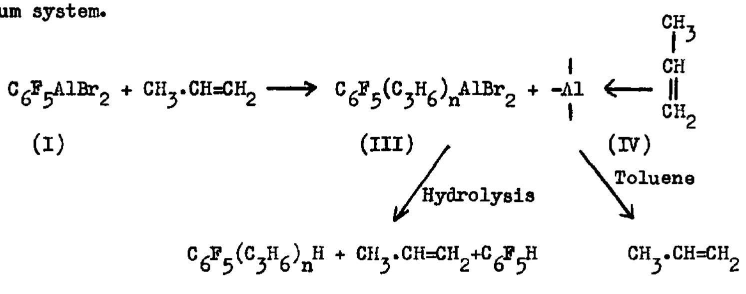
Pentafluorophenylaluminium dibromide (I) and bis(pentafluorophenyl)aluminium bromide II are the first fluorocarbon derivatives of, formally, tricovalent aluminium to be characterised[2,3] and, consequently, olefin insertion reactions with fluorocarbon-aluminium compounds have not been reported. The latter compounds are normally unstable with respect to migration of fluorine from carbon to aluminium[4,5] but (I) and (II) are stabilised by bromine bridging leading to co-ordinative saturation of the aluminium.

Some reactions of (I) and (II) have already been described[2] but we now report that (I) will undergo an olefin insertion reaction with propene, resulting in insertion of the olefin between the Al and the C_6F_5 group. Also, the product contained propene apparently π-bonded to aluminium and, to our knowledge, this is the first reported case of an isolable π-bonded olefin-aluminium system.



$$C_6F_5AlBr_2 + CH_3.CH{=}CH_2 \longrightarrow C_6F_5(C_3H_6)_nAlBr_2 + {-}Al \leftarrow \begin{matrix} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{matrix}$$

$$C_6F_5(C_3H_6)_nAlBr_2 \xrightarrow{\text{Hydrolysis}} C_6F_5(C_3H_6)_nH + CH_3.CH{=}CH_2 + C_6F_5H$$

$$(IV) \xrightarrow{\text{Toluene}} CH_3.CH{=}CH_2$$

$$C_6F_5AlBr_2 + CH_3.CH{=}CH_2 \not\longrightarrow C_6F_5AlBr(C_3H_6)_nBr$$

(VI)

Like aluminium tribromide, neat (I) in contact with propene leads to rapid polymerisation of the olefin to a high molecular weight polymer but it was not possible to distinguish between an insertion process leading to (III) or (V). However, in other experiments equimolar amounts of propene and (I) in hexane, contained in a sealed evacuated Carius tube, were warmed to 50°. Then the solvent was removed to a vacuum system and shown not to contain propene, while the residual material eventually solidified. Careful hydrolysis of this solid in a vacuum system gave a polymer (V) which contained $\sim$10% fluorine but no bromine and the I.R. spectrum confirmed the presence of pentafluorophenyl. Therefore the polymer was produced via (III) and not (VI). During the hydrolysis of the solid product, volatile material was evolved consisting of pentafluorobenzene and propene (confirmed by its mass-spectrum) and, indeed, propene was also obtained on addition of toluene or benzene to the solid.

It is difficult to account for the displacement of propene by π-donors except from a π-bonded system as represented by (IV). However, it is not yet clear which other groups are attached to the aluminium in (IV) because the olefin could be attached to (I), which the hydrolysis shows is still present in the product, or the growing polymer (III). In fact, (IV) is probably an intermediate to (III).

Further work is proceeding on these systems.

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