Introduction

Like some of the other group 13 trihalides (not Al, In, and Tl), gallium trichloride has a (bridged dimer) molecular lattice as shown (Figure 1).

\[ \text{GaCl}_3 \]

The dimer molecules are arranged in sheets. The low intermolecular forces are responsible for the low mp (77.9 °C, the lowest of the Al, Ga, In, and Tl trihalides).\(^1\)

GaCl\(_3\) is evidently a weaker acid than AlCl\(_3\). Its application in organic synthesis has been known for a long time e.g. in the Fridel–Crafts synthesis of benzophenone from benzene and benzoyl chloride GaCl\(_3\) results in a faster reaction than AlCl\(_3\),\(^2\) the reaction of benzene with alkyl halides is also quicker with gallium.\(^3\)

Preparation

GaCl\(_3\) is available commercially or can be prepared by burning gallium in a stream of Cl\(_2\)\(^4,5\) or by the action of HCl or SOCl\(_2\) (> ca 200 °C) Ga\(_2\)O\(_3\).\(^4,6\) The pure anhydrous compound can be obtained by redistillation in a steam of Cl\(_2\) (or Cl\(_2\)/N\(_2\)) followed by vacuum sublimation or by zone refining.\(^7\)

Abstracts

(A) In the presence of GaCl\(_3\), silyl enol ethers are ethynylated at the \(\alpha\)-carbon atom with chlorotrimethylsilylethylene to give \(\alpha\)-ethynylated aryl ketones possessing \(\alpha\)-protons without isomerization to conjugated allenyl ketones.\(^7\)

(B) Trimethylsilylethylene and silyl enol ether were reacted with GaCl\(_3\) in methylcyclohexane at r.t. and after treatment with THF and 6 M H\(_2\)SO\(_4\), \(\alpha\)-ethenyl ketone was obtained in high yield. Employment of GaCl\(_3\) was essential, and no reaction occurred with AlCl\(_3\), InCl\(_3\), or other Lewis acids of group 13 elements.\(^8\)

(C) Treatment of alkynes with allyl trimethyl silanes in the presence of GaCl\(_3\) gives 1,4-dienes via allylgallation.\(^9\)
(D) Treatment of aryl halides with alkenyl gallium dichloride, prepared from GaCl₃ and alkenyl magnesium bromide, in the presence of a catalytic amount of palladium provided cross-coupling product in good yield.¹⁰

(E) GaCl₃ catalyzes the tandem ring opening of epoxides and cyclization with alkynes to generate naphthalene derivatives with complete regiocontrol.¹¹

(F) In the presence of GaCl₃, silyl enol ethers derived from substituted ketoesters or malonates are ethenylated at the carbon atom with trimethylsilylthiophene in high yields. Ethenylmalonates can also be synthesized by this method.¹²

(G) A gallium hydride reagent, HGaCl₂, was found to act as a radical mediator, like Bu₃SNH. Treatment of alkyl halides with HGaCl₂, generated from GaCl₃ and sodium bis-(2-methoxy-ethoxy)aluminium hydride, provided the corresponding reduced products in excellent yields. Radical cyclization of halo-acetals was also successful with both a stoichiometric amount of gallium reagent but also a catalytic amount of GaCl₃ combined with a stoichiometric amount of AlH₃ as a hydride source.¹³

(H) Alkenyl Fischer chromium carbene complexes react with various kinds of simple imines to produce 3-pyrroline derivatives in the presence of a catalytic amount of GaCl₃.¹⁴

(I) The allylgallium reagent which may be prepared by mixing GaCl₃ and an equimolar amount of allylmagnesium chloride, allylated carbonyl compounds in good yields in aqueous media and organic solvents.¹⁵

(J) (Trimethylsilyl)acetylene upon treatment with GaCl₃ in CH₂Cl₂ and methylcyclohexane, trimerized rapidly giving acrylic conjugated trienes.¹⁶

References

(2) Id, Z. Electrochemistry 1935, 41, 509.
(3) Ulrich, H. Angew. Chem. 1942, 55, 37.