Recent Advances in Aluminum(I) Chemistry

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Aluminum makes up 8.8% of the mass in the Earth's crust and is encountered in nature only in the +III oxidation state.[1] The Héroult-Hall process, discovered independently in 1886 by P. Héroult and C. Hall, is used industrially to isolate aluminum metal. This electrolytic process involves the reduction of alumina (Al_2O_3) in molten cryolite (Na_3AlF_6).[2] The mechanism of this reaction is unknown, though recent electrochemical investigation of the mechanism utilizing a rotating ring-disc electrode indicates the possibility of an aluminum(I) intermediate.[3]

Aluminum(I) halides are thermodynamically unstable at room temperature. As an example, the enthalpy of the disproportionation of AlCl to $AlCl_3$ and aluminum metal is 420 kJ/mol. At higher temperatures, gaseous AlCl is thermodynamically favored.

$$3AlCl(g) \longrightarrow 2Al(s) + AlCl_3(s) \quad T = 298\ K$$
$$3AlCl(g) \longleftarrow 2Al(s) + AlCl_3(s) \quad T = 1000\ K$$

The first compound containing aluminum(I) was reported in 1943 by W. Klemm.[4] In this experiment, a mixture of AlF_3 and aluminum metal under vacuum was heated to produce a gas which condensed on a cold finger within the apparatus. Investigation of the residue revealed that it was a mixture of compounds, with an equimolar quantity of aluminum and fluorine. This suggests the formation of volatile AlF which decomposes to give the observed mole ratios.

In the years following, aluminum(I) halides were studied spectroscopically at high temperatures.[5] The first synthetic reaction involving an aluminum monohalide was not reported until 1986.[6] AlCl was generated at high temperatures and quenched in a solid matrix of 2-butyne at 78 K. Upon warming to room temperature, AlCl and 2-butyne reacted to form an aluminum(III) addition compound.

When a mixture of donating ligands and aryl solvents was used as the frozen matrix, the aluminum monohalides generated at high temperature were kinetically stabilized.[7,8,9] The solutions could be stored for several months at low temperature without decomposition. Crystal structures of the monohalides revealed a cyclic tetramer of aluminum atoms, with one chloride and one donor ligand bonded to each aluminum.

Reaction of aluminum(I) chloride solution with $Mg(Cp^*)_2$ ($Cp^* = h^5$-pentamethylcyclopentadienide) produces AlCp* by ligand exchange.[10] The product was determined to consist of a tetrahedron of aluminum atoms, each capped by a Cp*. Reactions of $[AlCp^*]_4$ with metals bound to labile ligands yield metal compounds with Cp*Al bound in a bridging[11] or terminal[12] fashion. The shortening of the Al-C bond length in these compounds indicate that the aluminum is oxidized from the +I oxidation state.

Donor-stabilized aluminum halide solutions are also used to make aluminum metalloid clusters. These clusters, formed by reaction of the halide solutions with lithium amides, are potential intermediates in the formation of bulk aluminum metal from aluminum(I) compounds.[13,14]

The stabilization of aluminum(I) compounds in solution and as the $[Cp^*Al]_4$ tetramer have allowed their use as aluminum sources for the synthesis of well-defined metal clusters. Future uses of these compounds include the introduction of aluminum into compounds containing main group or transition metals, as well as formation of novel organoaluminum compounds. More work can also be done on the determination of the mechanism of aluminum formation using metalloid cluster models.

References

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