Hydroalumination of Nitriles and Isonitriles

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Hydroalumination of H_5C_6-C≡N with di(*tert*-butyl)aluminum hydride **1** or the corresponding diethyl compound **2** yielded the products *t*Bu_2Al-N=C(C_6H_5)H **3** and Et_2Al-N=C(C_6H_5)H **4**, respectively, both of which form dimers possessing Al_2N_2 heterocycles with two exocyclic C=N double bonds. NMR spectroscopic data indicate the occurrence of *cis*/*trans* isomers in solutions of compound **4**. The dimerization of the imide *via* Al-N interactions was prevented by employing the hydride $[(Me_3Si)_2HC]_2AlH$ **6** bearing the bulky bis(trimethylsilyl)methyl substituents. Its reaction with benzonitrile yielded the compound R_2Al-N=C(C_6H_5)H(N≡C-C_6H_5) **7** [R = $CH(SiMe_3)_2$], in which the coordinative saturation of the aluminum atoms was achieved by adduct formation with one molecule of the starting nitrile. In these cases the C≡N triple bond inserted completely into the Al-H bond of the hydride. In contrast, the reaction of *tert*-butyl isonitrile afforded the product *t*Bu_2Al-C(H)=N-C_6H_5 **8** by the insertion of its terminal carbon atom into the Al-H bond. Hence, it has a geminal arrangement of the aluminum and hydrogen atoms. Dimerization of **8** yielded a six-membered heterocycle. Hydroalumination does not occur upon treatment of the hydride **1** with trimethylsilylnitrile. Instead, the Si-CN bond was cleaved, and the aluminum cyanide (*t*Bu_2Al-C≡N)$_4$ **9** was isolated in a high yield.

Key words: Aluminum, Hydroalumination, Nitriles, Isonitriles