Direct Synthesis of Tris(dimethylamino)silane

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In late 1974, taking advantage of the recent development of more active forms of copper-activated silicon masses at Union Carbide, Bernard Kanner proposed that a newly hired chemist be assigned to investigate direct reactions of silicon with organic compounds other than the halides and alcohols that were then known to react. When William Herdle arrived for work in Tarrytown in late 1975 with a Ph. D. in organic chemistry, he (perhaps naively) accepted Kanner's proposal that dimethylamine ought to react in a copper-catalyzed high-temperature gas-solid reaction. Upon learning some small part of the enormous body of knowledge about fluidized bed reactors and building a quartz laboratory reactor with the assistance of Jeff Mui, Herdle set out to demonstrate that reaction. The first experiments were conducted using active mass prepared at the Sistersville plant and shipped to Tarrytown. This mass was reactive toward methyl chloride, but when subjected to dimethylamine at conditions similar to those used for the methyl chloride reaction, it produced entirely products of dimethylamine cracking. Herdle discovered that if the mass was reacted first with HCl or methyl chloride to re-activate it, and then with dimethylamine, small amounts of aminosilanes were produced in addition to the cracking products. Soon he learned that at lower temperatures, around 250°C, the dimethylamine reaction could be made to proceed smoothly and to produce almost entirely tris(dimethylamino)silane, later referred to internally as "tris".

A patent was easily obtained, particularly in view of prior literature references claiming that the dimethylamine reaction with silicon could not be made to proceed. However, it was never exploited commercially, despite the considerable efforts of subsequent researchers working under Kanner to develop a general route to silanes from "tris", replacing trichlorosilane in most cases.