

A Contribution to the Chemistry of 2,2,6,6-Tetramethylpiperidino Aluminium Compounds

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Dedicated to Prof. Dr. Dr. h. c. mult. H. W. Roesky on the occasion of his 70th birthday

tmpAlBr₂ (tmp = 2,2,6,6-tetramethylpiperidino) was prepared from AlBr₃ and tmp₂AlBr at 90 °C in the absence of a solvent, but could not be crystallised from toluene or hexane because it reacted with the solvents to form tmpH·AlBr₃ in high yield. tmpH·AlMeCl₂, obtained from the components, decomposes at elevated temperatures but no tmpAlCl₂ could be isolated. Attempts to generate the cation [tmp-Al-tmp]⁺ from tmp₂AlBr or tmp₂AlCl by halide abstraction with B(C₆F₅)₃, Ph₃C(SnCl₅) or SbCl₅ or from tmp₂AlR (R = Me, Ph) and B(C₆F₅)₃ have failed. An unexpected reaction occurred on treatment of tmp-B=P(*t*Bu)AlBr₃ with BH₃ in THF which led to the formation of [AlBr₂(thf)₄][AlBr₄]. The attempted synthesis of *t*Bu₂Al(tmp) from *t*Bu₂AlBr and Li(tmp) gave a product which, on exposure to CO₂ at dry ice temperature, yielded the salt [(*t*BuAl)₂(O₂C(tmp))₃][*t*Bu₃Al-Br-Al*t*Bu₃] in low yield. All isolated products were characterized by NMR spectroscopy and by X-ray determination of their molecular structures.

Key words: Tetramethylpiperidino Alanes, Tetramethylpiperidino Aluminiumdihalides, Dibromo-tetrakis(tetrahydrofuran)aluminium Tetrabromoaluminate, Bis(tri-*tert*-butylaluminium)bromide Anion, X-Ray Structure