

A Simple High-Yield Synthesis of Gallium(I) Tetrachlorogallate(III) and the Reaction of Digallium Tetrachloride Tetrahydrofuran Solvate with 1,2-Diols

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Gallium(I) tetrachlorogallate(III) $\text{Ga}[\text{GaCl}_4]$ was prepared in quantitative yield by thermal decomposition of dichlorogallane $[\text{HGaCl}_2]_2$, which is readily available from Et_3SiH and $[\text{GaCl}_3]_2$. The reaction of catechol with solutions of this gallium(I) tetrachlorogallate(III) in tetrahydrofuran leads to the evolution of hydrogen gas and affords a dinuclear gallium(III) complex with penta-coordinate metal atoms chelated and bridged by mono-deprotonated catechol ligands. In the crystalline phase tetrahydrofuran molecules are hydrogen-bonded to the hydroxy groups: $[\text{Ga}(1,2\text{-OC}_6\text{H}_4\text{OH})\text{Cl}_2(\text{C}_4\text{H}_8\text{O})]_2$. The reaction with pinacol also gives hydrogen and the analogous product $[\text{Ga}(\text{OCMe}_2\text{CMe}_2\text{OH})\text{Cl}_2(\text{C}_4\text{H}_8\text{O})]_2$. The structures of the two compounds have been determined by X-ray diffraction. A mechanism of the new reaction has been proposed which involves oxidative addition of the diol to the solvate $(\text{THF})\text{Cl}_2\text{Ga-GaCl}_2(\text{THF})$ present in the tetrahydrofuran solution to give a gallium hydride intermediate.