Gallium(I) Chemistry

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At Last: A Stable Univalent Gallium Cation**

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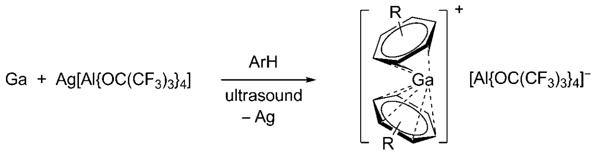
With the exception of thallium and the non-metal boron, the +1 oxidation state of the other Group 13 elements aluminum, gallium, and indium is thermodynamically unstable in aqueous solutions, leading to disproportionation into the metal and the +3 ions.[1] Solid indium(I) halides are stable under inert conditions, but disproportionate upon attempted dissolution into polar solvents.[2] In 2004, the synthesis of a stable indium(I) triflate was reported from the reaction of [Cp*In] (Cp* = C_5Me_5) with triflic acid at room temperature in toluene solution.[3] This compound is readily soluble in aromatics and ethers, forms complexes $[L_nIn]^+$ with ligands such as $(i\text{PrO})_3P$, and is resistant to disproportionation. The analogous reaction with [Cp*Ga] afforded mixtures of gallium(I) and gallium(III) compounds.[4] Indium(II) and gallium(II) halides M_2X_4 consist of the ion pair $M^+[MX_4]^-$. In aromatic solvents, the M^+ cations are solvated by η^6-coordinated arenes, but attempts to exchange the $[MX_4]^-$ anion have been unsuccessful to date.[1,2] The compound "GaI", which is actually a mixture of subvalent gallium iodides, is obtained in the reaction of gallium metal with one half of an equivalent of iodine, with $Ga_2[Ga_2I_6]$ being the main product.[5] Solutions of metastable gallium(I) halides can be prepared by co-condensation of the high-temperature species GaX in a toluene/donor matrix at −196 °C, followed by slow dissolution at −78 °C. This method allowed for the isolation of crystalline, oligomeric, solvated gallium(I) halides $(XGaL)_n$ (X = halide, donor L = ether, amine, phosphine) and numerous metalloid gallium clusters. Unfortunately, this route also requires a specialized reactor, carefully fine-tuned reaction conditions, and very well-trained personnel.[6]

This research into gallium compounds in low oxidation states has led to numerous interesting advances. The isolation and structural characterization of the compound $Na_2[Ar^*GaGaAr^*]$ ($Ar^* = 2,6\text{-}Trip_2C_6H_3$, $Trip = 2,4,6\text{-}i\text{Pr}_3C_6H_2$) improved our understanding of multiple bonding between heavier elements greatly.[7] Neutral and anionic gallium(I) compounds have been investigated as ligands for metal complexes,[8] and Schnöckel and co-workers have pioneered the synthesis of a wide range of gallium clusters that may be viewed as intermediates in disproportionation reactions leading to gallium metal.[6] Nevertheless, it could be argued that this progress may have been slowed owing to inadequate access to suitable starting materials.

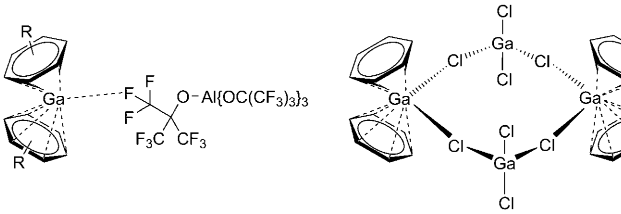
Recently, Slattery et al. have reported a simple route to stable, crystalline, univalent gallium salts.[9] Metallic gallium is oxidized by $Ag[Al\{OC(CF_3)_3\}_4]$ in toluene or fluorobenzenes using sonication as the energy source (Scheme 1). The resulting solutions containing the $[(ArH)_2Ga]^+$ cation are not subject to disproportionation reactions at room temperature. The key for this feat appears to be the use of the weakly coordinating anion $[Al\{OC(CF_3)_3\}_4]^-$.



Scheme 1. Synthesis of univalent gallium salts. R = Me, F.

The crystal structures of these compounds show that gallium(I) is in a bent sandwich environment involving two η^6-coordinated arenes, similar to Schmidbaur's $[(ArH)_2Ga][MX_4]$ (ArH = benzene, toluene, mesitylene).[10] The main difference is the absence of the strong cation···anion interactions in the former compounds that are so common in the latter examples (Scheme 2). The authors propose that, along with the absence of the reactive $[MX_4]^-$ anion, the lack of the halide bridges contributes to the stability of their compounds by shutting down a decomposition pathway.

The reaction of gallium with $Ag[Al\{OC(CF_3)_3\}_4]$ in $o\text{-}C_6H_4F_2$ led to partial decomposition of the anion to afford the more stable $[\{(CF_3)_3CO\}_3Al\text{-}F\text{-}Al\{OC(CF_3)_3\}_3]^-$ anion and



Scheme 2. Sketch of the halide bridges in $[(ArH)_2Ga][Al\{OC(CF_3)_3\}_4]$ and $[(ArH)_2Ga][MX_4]$.

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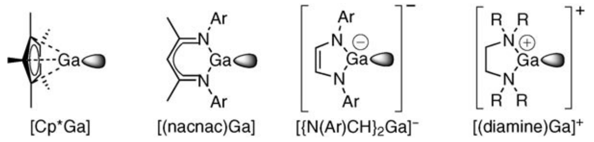
presumably GaF as a result of the strong Ga–F bond and a high Lewis acidity and fluorine affinity of the gallium(I) cation. Such decomposition reactions may be avoided by the application of other weakly coordinating anions, such as $[B(C_6F_5)_4]^-$, $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$, or $[CH_6B_{11}X_6]^-$ (X = Cl, Br, I).

The $[(ArH)_2Ga]^+$ compounds allow for the first time the exploration of the coordination chemistry of the gallium(I) cation. Coordination of triphenylphosphine gave the $[(Ph_3P)_3Ga]^+$ complex; the crystal structure has a trigonal pyramidal coordination environment at the gallium center, which is indicative of a stereochemically active lone pair. Quantum chemical calculations of the model compound $[(PH_3)_3Ga]^+$ reveal that the HOMO is the lone pair, with mostly s character. It will be interesting to see if this early result can be extended to other ligands, such as ethers, thioethers, amines, carbenes, and their polydentate analogues. Are such complexes, for example, $[(\text{diamine})Ga]^+$ (Scheme 3), still nucleophilic in similar fashion to [Cp*Ga], [(nacnac)Ga], or the NHC analogue $[\{N(Ar)CH\}_2Ga]^-$?



Scheme 3. Nucleophilic gallium(I) compounds.

Other areas to explore include the use of $[(ArH)_2Ga]^+$ cations as well-defined sources for gallium(I) compounds, such as RGa (R = alkyl, aryl), $\{(Me_3Si)_2NGa\}_n$, or even well-defined donor-stabilized gallium(I)halides L_nGaX (L = phosphine, amine, thioether; X = halide). Careful thermal or photochemical decomposition experiments of these gallium(I) compounds may lead to novel approaches to metalloid clusters. It is also quite possible that these new gallium(I) species might find applications in organic or materials chemistry.

The newly developed $[(ArH)_2Ga]^+$ synthesis is straightforward and should be reproducible in every organometallic chemistry laboratory, although access to a high-wattage ultrasonic bath is required. Similarly, the preparation of $Ag[Al\{OC(CF_3)_3\}_4]$ can easily be accomplished.[11] Overall, the contribution of Slattery et al. has provided access to well-defined gallium(I) salts and should invigorate this area of chemistry.

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