Organohalogenometalates

Reacting a metallane R_3M of Al, Ga, or In with an alkali halide such as $M'X$ in a polar solvent like MeCN at room temperature yields formal adducts, the Triorganohalogenomatelates:

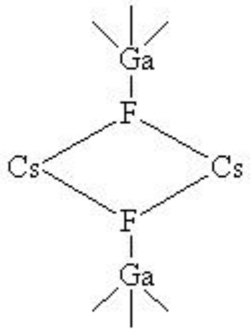
$R_3M + M'X \rightarrow M'[R_3MX]$

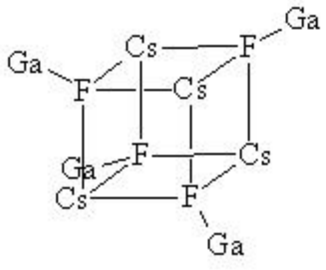
Starting from an Organometalhalide $R_{3-x}MX_x$ and a fluorid source $M'F$, the addition reaction is accompanied by a substitution of the X ligands:

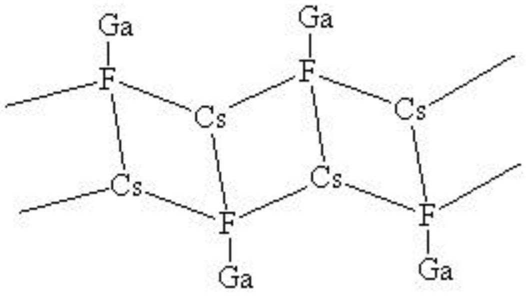
$R_{3-x}MX_x + (x+1)\ M'F \rightarrow M'[R_{3-x}MF_{x+1}] + x\ M'X$

The reactivity of these substrates towards nucleophilic and oxidizing reagents like molecular oxygen is drastically decreased compared to the free metallanes. Since the metallane can be set free under special conditions, the metalates are useful in their storage. Furthermore in varying the ligands one can vary the meltingpoint of the compounds and the metalates are used in low-temperature waste heat storage.

While Organofluorometalates with two or three fluoride ligands build up polymeric structures in the solid state, all but two triorganofluorometalates form discrete molecules. The dominating structural motifs are $(M'F)_2$ four membered rings. The fluoride ions are further coordinating one metallane unit. Depending on the sterical and electronical properties of the organic ligands the rings may undergo further oligomerisation to cubane type cores or ladder structures for example (figure 1).







A striking feature of the metalates containing organic substituents with p-systems is a significant interaction of these ligands to the alkali cations. In this way the four membered ring in $[Cs\{(PhCH_2)_3GaF\}]_2$ is shielded for further oligomerisation as seen in figure 2.

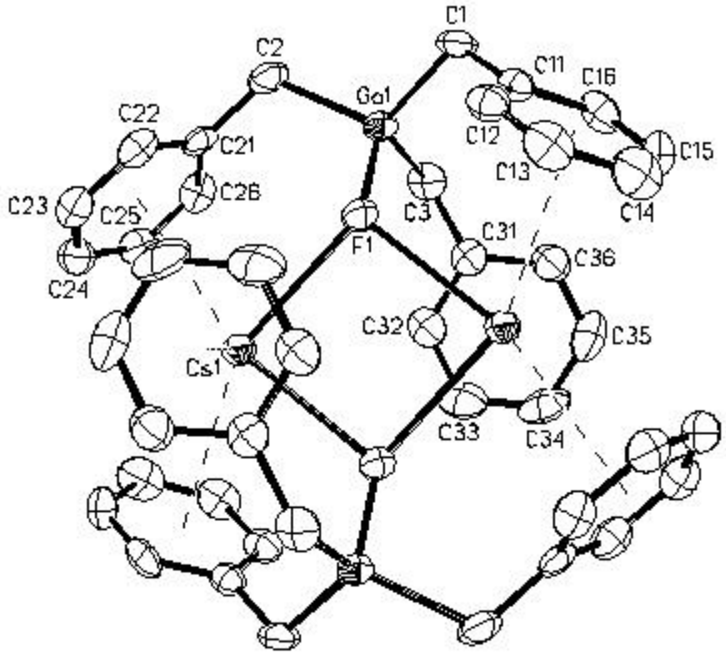


figure 2

Searching for the first monomeric unit -or "molecular CsF"- we have been successful in consequently following this principle by using toluene as now neutral ligand for the Cs cations (figure 3):

$In\{N(SiMe_3)_2\}_3 + CsF \rightarrow [Cs(toluene)_3(FIn\{N(SiMe_3)_2\}_3)]$

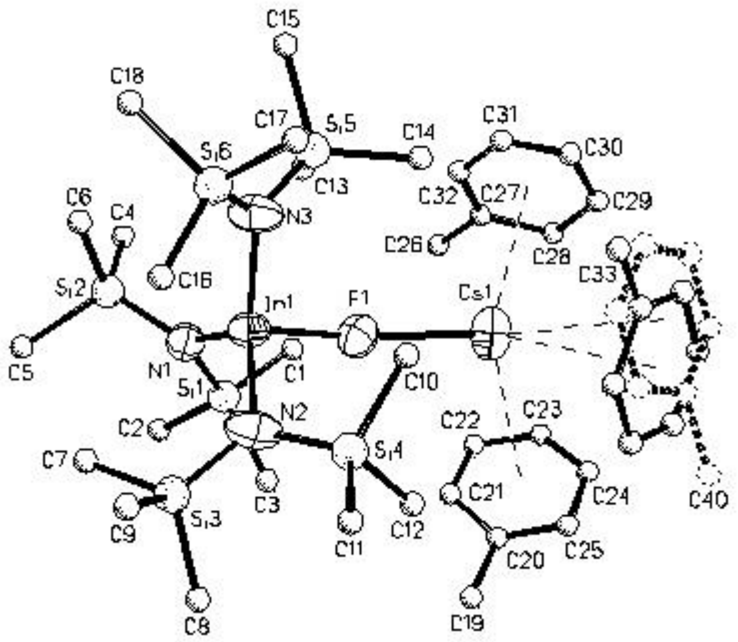


figure 3

Literature:

For a general survey to organometallic group 13 fluorine compounds see:
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For Organohalogenometalates see:
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