

Module 3 : Organometallic chemistry of p-block elements

Lecture 3 : Organometallic compounds of gallium and indium

Objectives

In this lecture you will learn the following

- Chemistry of gallium and indium.
- How to stabilize M—M multiple bonds.

Organometallic compounds of gallium and indium

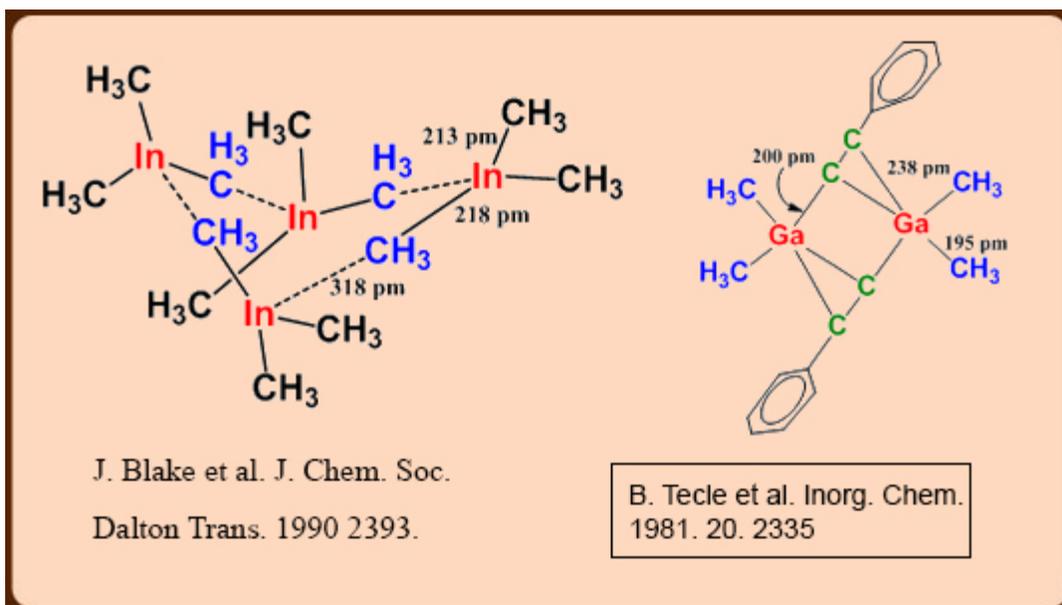


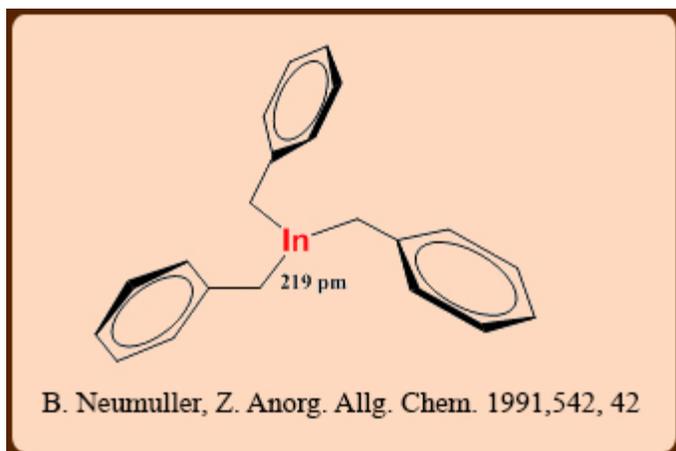
Trialkylgallium compounds are mild Lewis acids, so the corresponding metathesis reaction in ether produces the complex $(\text{C}_2\text{H}_5)_2\text{OGa}(\text{C}_2\text{H}_5)_3$. Similarly excess use of $\text{C}_2\text{H}_5\text{Li}$ leads to the salt, $\text{Li}[\text{Ga}(\text{C}_2\text{H}_5)_4]$.



Alkylindium and alkylthallium compounds may be prepared similar to gallium analogs. InMe_3 is monomeric in the gas phase and in the solid the bond lengths indicate that association is very weak. Partial hydrolysis of TlMe_3 yields the linear $(\text{MeTlMe})^+$ ion, which is isoelectronic and isostructural with HgMe_2 .

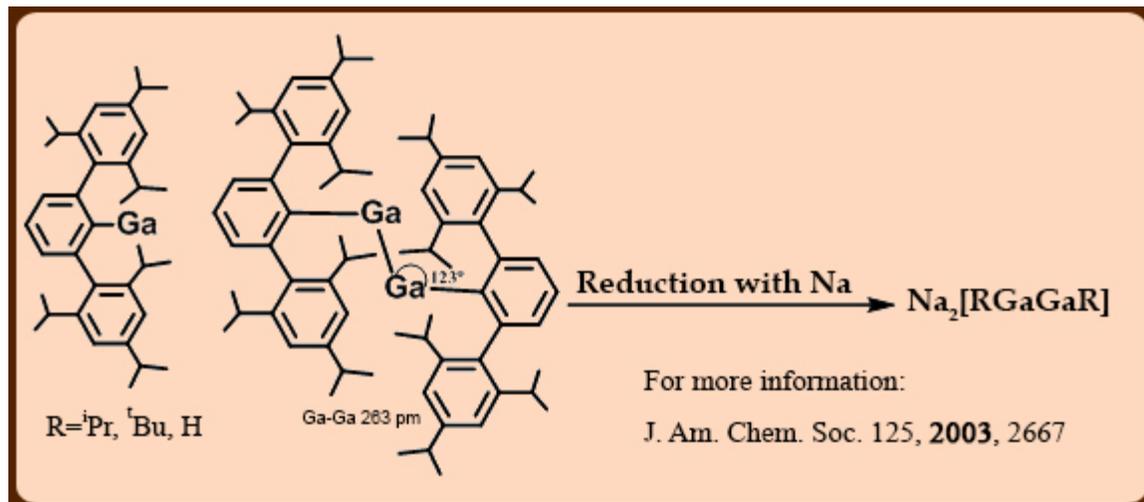
CpIn and CoTl exist as monomers in the gas phase but are associated in solids {Inert-pair effect is displayed for In and Tl}. CpTl is useful as a synthetic reagent in organometallic chemistry because it is not as highly reducing as NaCp .





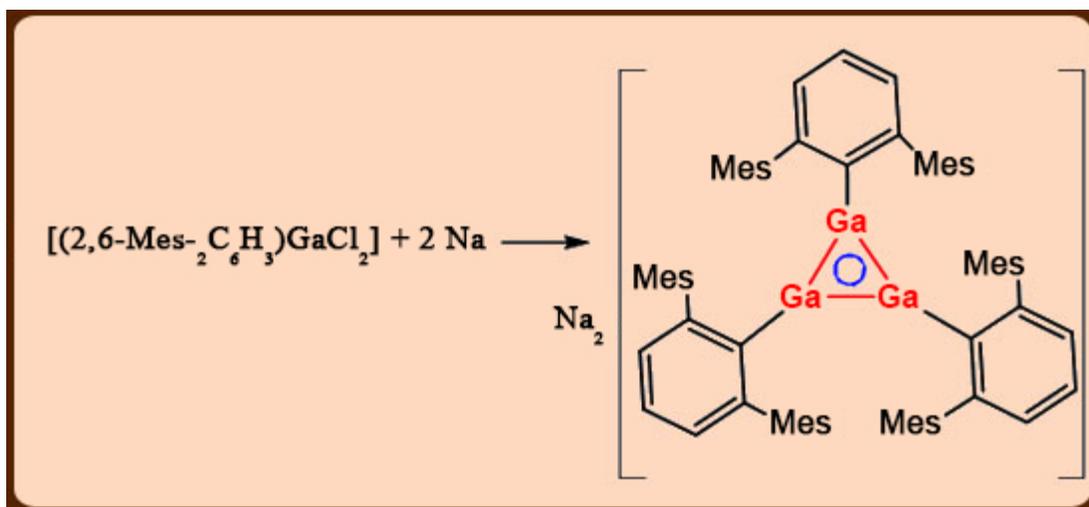
Species of the type R_4E_2 (single E-E bond) and $[R_4E_2]^-$ (with E-E bond order of 1.5) can be prepared for Ga and In with bulky R groups ($R = (Me_3Si)_2CH$, $2,4,6\text{-}^iPr_3C_6H_2$), and reduction of $[(2,4,6\text{-}^iPr_3C_6H_2)_4Ga_2]$ to $[(2,4,6\text{-}^iPr_3C_6H_2)_4Ga_2]^-$ is accompanied by a shortening of the Ga—Ga bond from 252-234 pm.

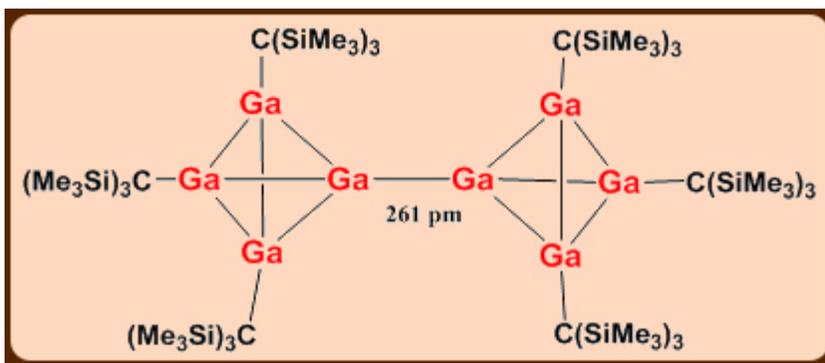
Using even bulkier substituents, it is possible to prepare gallium(I) compounds, RGa starting from GaI . No structural data are yet available for these monomers (We are working on it).



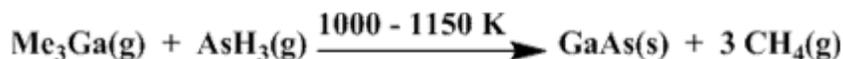
Crystallized as dimer but reverts to monomer when dissolved in cyclohexane.

Predict the structure of monomeric, Cp_3Ga ; polymeric Cp_3In and $CpIn$. Organometallics 1985, 4, 751., Inorg. Chem. 1972, 11, 2832., Organometallics 1988, 7, 105.





Interest in organometallic compounds of Ga, In and Tl is mainly because of their potential use as precursors to semiconducting materials such as GaAs and InP. Volatile compounds can be used in the growth of thin films by MOCVD (metal organic chemical vapor deposition) or MOVPE (metal organic vapor phase epitaxy) techniques. Precursors include appropriate Lewis base adducts of metal alkyls, e.g. $\text{Me}_3\text{Ga}\cdot\text{NMe}_3$ and $\text{Me}_3\text{In}\cdot\text{PET}_3$. Thermal decomposition of gaseous precursors result in semiconductors (III-V semiconductors) which can be deposited in thin films.



III-V semiconductors: Derive their name from the old groups 13 and 15, and include AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs and InSb. Of these GaAs is of the greatest commercial interest. Although Si is probably the most important commercial semiconductor, a major advantage of GaAs over Si is that the charge carrier mobility is much greater. This makes GaAs suitable for high-speed electronic devices.

Another important difference is that GaAs exhibits a fully allowed electronic transition between valence and conduction bands (i.e. it is direct band gap semiconductor) whereas Si is an indirect band gap semiconductor. The consequence of difference is that GaAs (also other III-V types) are more suited than Si for use in optoelectronic devices, since light is emitted more efficiently. The III-Vs have important applications in light-emitting diodes (LEDs).

Problems:

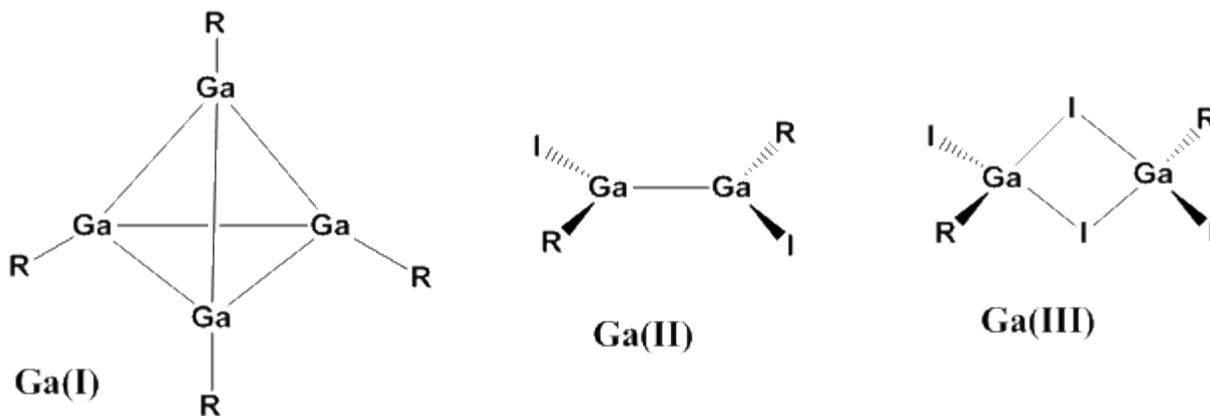
1. Predict the structure of monomeric, Cp_3Ga ; polymeric Cp_3In and CpIn .

Solution:

See the articles Organometallics 1985, 4, 751.
Inorg. Chem. 1972, 11, 2832.
Organometallics 1988, 7, 105.

2. The reaction of $[(\text{R}_3\text{C})_4\text{Ga}_4]$ (R = a bulky substituent) (i) with I_2 in boiling hexane results in the formation of $[(\text{R}_3\text{C})\text{Ga}]_2$ (ii) and $[(\text{R}_3\text{C})\text{GaI}_2]_2$ (iii). Draw the structure and state the oxidation state for (i) - (iii).

Solution:



3. The I_2 oxidation of $[(^t\text{Bu})_4\text{In}_4]$ leads to the formation of the In^{II} compound $[(^t\text{Bu})_4\text{In}_4\text{I}_4]$ in which each indium atom retains a tetrahedral environment. Draw the correct structure.

Solution:

