GALLIUM AND INDIUM

ANNUAL SURVEY COVERING THE YEAR 1975

Rokuro OKAWARA
Department of Applied Chemistry, Osaka University, Yamadakami,
Suita, Osaka, (Japan)

The study of gallium and indium derivatives has remained at about the same level during 1975 as during 1974* with a modest amount of structural and spectroscopic work, studies on synthesis and reaction chemistry and applications. This survey will deal with these topics in this order.

Reviews on 'Organometallic Compounds of Group III (Al, Ga, In and Tl)' with 253 references [1] and with 264 references [2], on 'Organometallic Complexes containing Bonds between Transition Metals and Group IIIB Metals (Al, Ga, In and Tl)' with 103 references [3], and on 'X-ray Diffraction Studies of the Molecular Structure of a Number of B, Al, Ga, In and Tl Compounds' with 67 references [4] have been published. In a general review on 'Electrochemical Synthesis of Organometallic Compounds' [5], two patents dealing with the preparation of $(C_2H_5)_3In$ were cited.

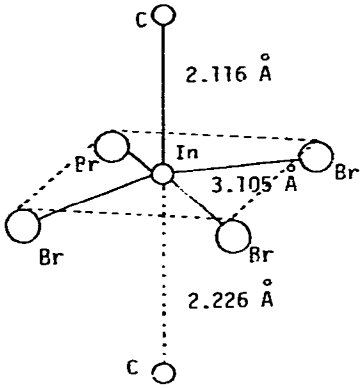
Structural and Spectroscopic Studies

Dimethylindium bromide, $(CH_3)_2InBr$, forms an ionic lattice similar to that of $(CH_3)_2TlCl$. However, an X-ray study showed that each indium atom is surrounded

---

* Gallium and Indium, Annual Survey covering the year 1974 see J. Organometal. Chem., 98 (1975) 445.

by two carbon atoms with two clearly different In-C distances and four bromine atoms as shown below [6].

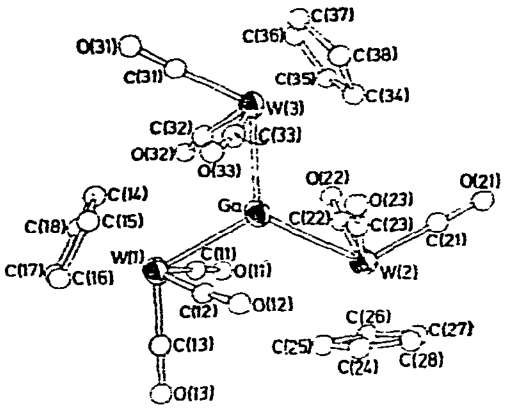


The existence of a linear InC_2 group in the solid state has been established for the first time. Thus, the contradictory structures of this compound as suggested by its vibrational spectrum and NQR spectrum have been resolved.

Trialkylgallium compounds react with tungsten hydrides, $(C_5H_5)W(CO)_2LH$, to give $(C_5H_5)W(CO)_2LGaR_2$ (R= CH_3, L= CO, PPh_3; R= C_2H_5, L= CO). The following decomposition process was found to occur in hot hydrocarbon solvent.

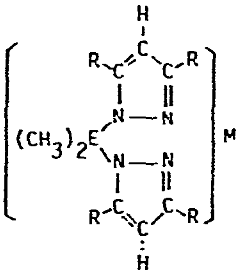
$$\begin{array}{l} (C_5H_5)W(CO)_3Ga(CH_3)_2 \\ \quad\downarrow \\ [(C_5H_5)W(CO)_3]_2Ga(CH_3) \\ \quad\downarrow \\ [(C_5H_5)W(CO)_3]_3Ga \end{array}$$

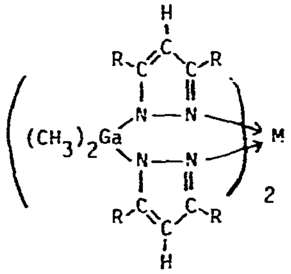
By IR evidence, these compounds, unlike $[(C_5H_5)W(CO)_3Al(CH_3)_2]_2$, have no -CO- bridges. An X-ray study of $[C_5H_5W(CO)_3]_3Ga$ showed that the coordination at gallium is planar as shown below [7].



$[C_5H_5W(CO)_3]_3Ga$. [From reference 7.]

The dimethylgallium and indium derivatives, shown below, and sodium dihydridobis(pyrazol-1-yl)gallate, $Na[H_2Ga(pz)_2]$ have been isolated and characterized by ^1H NMR, absorption spectra and magnetic moment [8].





R=	E=	M=
H	Ga	$(CH_3)_4N$, Na
	In	$(C_2H_5)_4N$
CH_3	Ga	$(C_2H_5)_4N$

R= H; M= Ni [I]
Cu [II]
Co
R= CH_3; M= Cu [III]
Co

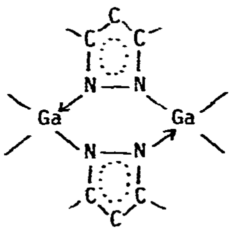
An X-ray structural study of I has already been reported briefly (J. Chem. Soc. Chem. Comm., (1974) 406: See, also J. Organometal. Chem., 98 (1975) 446)

Now, precise data on I have been reported by the same authors [9], who extended their X-ray studies to the analogous two copper compounds, II and III [10]. The molecule II, as in the case of the corresponding nickel complex I, is in a pseudo-chair conformation with the two six-membered Ga(-N-N-)$_2$Cu rings in boat conformation. The copper atom lies on a crystallographic center of symmetry in the middle of a planar arrangement of four nitrogen atoms. Steric requirements of the ligands in III necessitate adoption of pseudotetrahedral geometry about the central copper atom, with a dihedral angle of 71.9° between the two N-Cu-N coordination planes, and an almost planar arrangement for the Ga(-N-N-)$_2$Cu six-membered rings. These complexes are studied spectroscopically in solution [11]. Variable-temperature ^{1}H NMR data suggest that I is stereochemically non-rigid in solution. For copper complexes II and III, the results of electronic absorption, ESCA, and ESR spectroscopic measurements can be interpreted to provide tentative one-electron orbital sequences for copper in these complexes.

The same research group reported X-ray crystallographic results for the following three dimeric dimethylgallium compounds [12], and for two compounds (VId and VIe) [13], schematically shown below, and discussed their structures

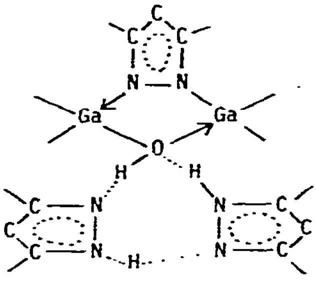
VIa	$[(CH_3)_2GaN_2C_3H_3]_2$	pyrazolyldimethylgallium
VIb	$[(CH_3)_2GaN_2C_4H_5]_2$	3-methylpyrazolyldimethylgallium
VIc	$[(CH_3)_2GaN_2C_7H_5]_2$	indazolyldimethylgallium

with reference to that of the previously reported $[D_2GaN_2C_3H_3]_2$, VI. It is clearly shown that changing deuterium for methyl groups on the gallium atoms and introducing substituents on the bridging ligands causes a pronounced flattening of the Ga(-N-N-)$_2$Ga boat conformation found in VI. The strain of the ring in VId is reduced by the attack of moisture to produce VIe, in which one of the bridging 3,5-dimethylpyrazolyl moieties is replaced with a bridging hydroxyl group to form a non-planar five-membered Ga_2N_2O ring.



VId

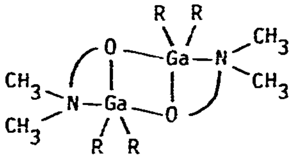
$[(CH_3)_2GaN_2C_5H_7]_2$



VIe

$(CH_3)_2Ga(OH)(N_2C_5H_7)Ga(CH_3)_2 2N_2C_5H_8$

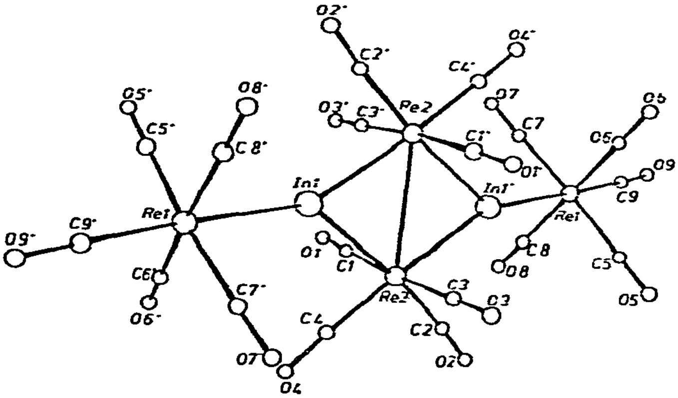
The presence of five coordinated gallium atoms in the N-methyldiethanolaminogallane dimer $[(CH_3)N(CH_2CH_2O)_2GaH]_2$ has been established by an X-ray study. The same research group extended their study to the following two compounds and showed the presence of a similar structure [14].



$[(CH_3)_2NCH_2CH_2OGaR_2]_2$ R= H, CH_3

The ^7Li chemical shifts of $LiM(CH_3)_4$ (M= B, Al, Ga, Tl) in $(C_2H_5)_2O$, THF and DMF have been reported, and the observed changes in the ^7Li chemical shift were discussed in terms of solvation of the lithium ion and ion pair formation in solution [15].

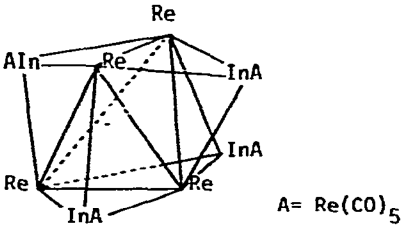
By treatment of In with $Re_2(CO)_{10}$ in a bomb tube, the thermally stable solids I and II were obtained.



I

Re$_2$(CO)$_8$[μ-InRe(CO)$_5$]$_2$

[From reference. 16]

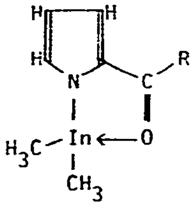


II

Re$_4$(CO)$_{12}$[μ$_3$-InRe(CO)$_5$]$_4$

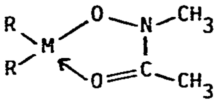
The molecule I contains a planar Re$_2$In$_2$ ring in which the Re-Re distance is 3.232(1) Å and the acute angle at the bridging In atom is 71.07(3)°. These data are consistent with the existence of Re-Re bond. The Re atoms of the two Re(CO)$_5$ ligands have a trans configuration with respect to the plane of the Re$_2$In$_2$ metal ring [16]. A single-crystal X-ray analyses of II showed that the central molecular fragment $Re_4(CO)_{12}$ contains a tetrahedral arrangement of four bonded Re atoms and the triangles of this fragment are capped with a μ_3-$Re(CO)_5$ group. A higher stability of II, such that II dissolves monomerically in acetone, whereas I dissociates yielding $Re(CO)_5^-$ anions, may be explained by this higher coordinated structure of the indium atoms [17].

The following two pyrrole derivatives of dimethylindium have been prepared and ^1H NMR and IR data were reported [18].



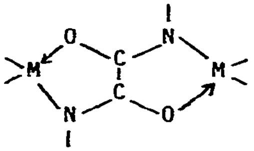
R= H, CH_3

The reaction of $HON(CH_3)C(O)CH_3$ with trialkyls of gallium and indium yields monomeric five-membered dialkyl metal hydroxamates, $R_2MON(CH_3)C(O)CH_3$ (M= Ga, R= CH_3, C_2H_5; M= In, R= CH_3).



The IR, Raman and ^1H NMR spectra of these compounds were discussed [19].

The reaction of N, N'-dimethyloxamide with trialkyl derivatives of aluminum, gallium and indium yielded bis(dialkylmetal) compounds of structural formula $(R_2M)_2[O_2C_2(NCH_3)_2]$ (M= Al, Ga, In; and R= CH_3, C_2H_5). The $M_2O_2C_2N_2$ skeleton of these monomeric products forms an almost planar system of two fused five-membered rings with S_2 symmetry as shown below [20].



For $[(CH_3)_2M]_2[O_2C_2(NCH_3)_2]$ (M= Ga, In), ^1H and ^{13}C NMR spectra show the presence of two conformational isomers which differ in the orientation of the N-methyl relative to the two metal bound CH_3 groups.

The dimethyldiazidometal anionic complexes I were obtained by the following reaction [21].

$$[(CH_3)_2MN_3]_3 \ + \ 3[N(CH_3)_4]N_3 \longrightarrow [(CH_3)_4N][(CH_3)_2M(N_3)_2]$$

[I] M= Al, Ga

These complexes reacted with the trimethyl compounds of aluminum and gallium to give 2:1 anionic complexes, II:

$$[(CH_3)_4N][(CH_3)_2M(N_3)_2] \ + \ 2(CH_3)_3M'$$

$$\longrightarrow \ [(CH_3)_4N][(CH_3)_2M(N_3)_2(M'(CH_3)_3)_2]$$

[II] M'= Al, Ga

Thermal decomposition of [II] in high vacuum resulted in loss of one mole of $M'(CH_3)_3$ to give the 1:1 complex, $[(CH_3)_4N][(CH_3)_2M(N_3)_2M'(CH_3)_3]$ (M, M'= Al, Al; Al, Ga). The vibrational spectra (IR and Raman) of these compounds were discussed.

Preparation of tetrameric dimethylmetal cyanides $[(CH_3)_2MCN]_4$ (M= Al, Ga, In) and their spectroscopic properties (IR, Raman and mass) have been reported [22].

The vibrational spectra (IR and Raman) of following three ionic complexes were discussed [23].

$[(CH_3)_4Sb]^+[SbCl_6]^-$
$[(CH_3)_4Sb]^+[CH_3InCl_3]^-$
$[(CH_3)_4As]^+[CH_3InCl_3]^-$

These complexes were obtained by methylating $SbCl_5$, $(CH_3)_3SbCl_2$ and $(CH_3)_3AsCl_2$, respectively, with $(CH_3)_2InCl$.

By IR and Raman spectroscopies, the tetrahedral configuration of $(GaH_4)^-$ anion in dyglyme irrespective of the cations (Na, K, Rb, Cs) has been suggested, however, in the solid state the Td configuration seems to be distorted. The force constant of the Ga-H bond has been found to be $3.05 \times 10^6\ cm^{-2}$ [24].

Synthesis and Reactions

Cyclopentadienyldialkyl derivatives of gallium and indium were prepared in 30-60% yield using alkalimetal cyclopentadienides.

$$R_2MCl \ + \ M'Cp \ \xrightarrow[50\text{-}70^\circ]{C_6H_{12}} \ R_2MCp \ + \ M'Cl$$

$R = CH_3,\ C_2H_5;\ M = Ga,\ In;\ M' = Na,\ K$

They could be purified by distillation or sublimation and are soluble in organic solvents such as C_6H_{12}, C_6H_6, CH_2Cl_2, $CHCl_3$ and CCl_4. However, the solubility of the indium derivatives decreases remarkably. In diethyl ether, the gallium derivatives dissolve well without reaction, and can be recovered. The degree of association of the dimethyl- or diethylgallium derivatives in benzene is 1.3 -1.4. ^1H NMR data for these compounds and IR and Raman for the diethyl compound have been summarized [25]. In non-polar solvents the practically insoluble $(CH_3)_2InCp$, can be prepared either by the reaction of $(CH_3)_3In$ or $[(CH_3)_2InN(CH_3)_2]_2$ with freshly distilled cyclopentadiene [26].

$$(CH_3)_3In \; + \; C_5H_6 \xrightarrow{\text{toluene}} (CH_3)_2InCp \; + \; CH_4$$

$$(CH_3)_3In \xrightarrow{HN(CH_3)_2} (CH_3)_3InHN(CH_3)_2 \xrightarrow{\Delta} [(CH_3)_2InN(CH_3)_2]_2$$

$$\xrightarrow{C_5H_6} (CH_3)_2InCp.HN(CH_3)_2 \xrightarrow{KOH} (CH_3)_2InCp$$

$(CH_3)_2InCp$ is stable in air and a polymeric structure similar to that of $(CH_3)_2AlCp$ [A. Haaland and J. Weidlein, J. Organometal. Chem., 40 (1972) 29] was proposed. ^1H NMR (in DMF), IR and mass spectra of this compound were shown.

Kovar et al. reported previously the preparation of tri-n-butylgallium in high yield and purity by the reaction of gallium trichloride and n-butyllithium in 1:3 molar ratio in benzene (R..A. Kovar, G. Loaris, H. Derr and J. Callaway, Inorg. Chem., 13 (1974) 1476). Now this work has been extended to the preparation of various other alkylgallium compounds [27].

$$nRLi \; + \; GaCl_3 \longrightarrow nLiCl \; + \; R_nGaCl_{3-n}$$

$$R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ i\text{-}C_4H_9,\ s\text{-}C_4H_9,\ t\text{-}C_4H_9,\ CH_2{=}CH;\ n = 1\text{-}3.$$

Alkylgallium dichlorides and dialkylgallium chlorides are produced when lithium alkyls and gallium trichloride were allowed to react in a 1:1 and 2:1 molar ratio,respectively. Reaction of an alkyllithium compound and gallium trichloride in a molar ratio in excess of 3:1 results in formation of the corresponding lithium tetraalkylgallate.

$$4n\text{-}C_3H_7Li \; + \; GaCl_3 \longrightarrow 3LiCl \; + \; LiGa(n\text{-}C_3H_7)_4$$

Trivinylgallium tetrahydrofuranate was produced by the reaction of vinyllithium and gallium trichloride in 3:1 molar ratio in tetrahydrofuran. Infrared, ^1H

NMR and mass spectra of R_nGaCl_{3-n} compounds (R= C_2H_5 to C_4H_9 isomers and n= 1-3) were reported and discussed. The ^1H NMR spectra reveal that the chemical shifts for protons on α-carbon atoms are sensitive to the other substitution on the gallium. An explanation for these chemical shift data along with molecular association data for R_nGaCl_{3-n} compounds was given. Mass spectroscopy can be used as a convenient, diagnostic tool for the identification of organogallium compounds of this type. Ion abundance data for all compounds were presented and the fragmentation processes believed to give these ions discussed.

Ether-free tri-t-butylgallium can be obtained in 50-60% yield by vacuum distillation of the reaction mixture of $t\text{-}C_4H_9MgCl$ and $GaBr_3$ in diethyl ether in 3:1 molar ratio [28]. As expected, this compound is not overly sensitive to water or atmospheric oxygen. On exposure to light, decomposition occurs and this colorless oil becomes dark. It is a monomer in solution at various concentrations. Di-t-butyl derivatives were prepared as follows:

$$2(t\text{-}C_4H_9)_3Ga \quad + \quad GaX_3 \longrightarrow 3(t\text{-}C_4H_9)_2GaX \qquad (X= Cl,\ Br)$$

$$(t\text{-}C_4H_9)_3Ga \quad + \quad HY \longrightarrow (t\text{-}C_4H_9)_2GaY \quad + \quad (CH_3)_3CH$$

$$(Y= OCH_3,\ OCOCH_3,\ OCOCD_3,\ O(t\text{-}C_4H_9))$$

Both the halides and the methoxide are strictly dimeric in benzene. However, the degree of association of the acetate and the t-butoxide is clearly dependent on their concentrations and is in the range of 1.4 to 1.6. This was attributed to the presence of the bulky t-butyl group, for dimethylgallium methoxide in benzene was reported [G. Mann, H. Olapinski, R. Ott and J. Weidlein, Z. Anorg. Allgem. Chem., 410 (1974) 195] to be trimer. ^1H NMR and vibrational spectra (IR and Raman) of the skeletal vibrations, $\nu(GaC_2)$, $\nu(Ga_2X_2)$ and $\nu(CO_2)$, were discussed briefly.

Two useful methods of synthesis of alkylgallium diiodides, $[RGaI_2]_2$, R= CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, and their IR, Raman and mass spectra have been reported [29]. (1) An excess of an alkyl iodide was condensed onto a stoichiometric mixture of gallium metal and iodine in vacuo and mechanically shaken at room temperature. The iodine rapidly dissolved and the yellow solution decolorized after about 30 min. The gallium metal slowly reacted over a period of 1-2 weeks and pure products could be obtained. In a separate experiment it was confirmed by chemical analysis and Raman spectrum that gallium (III) iodide had been formed when the solutions become colorless. It appears that the gallium(III) iodide formed in this initial process undergoes redistribution reactions with the sesquihalides [See, M. J. S. Gynane and I. J. Worrall, J. Organometal. Chem., 40 (1972) C59] formed by the separate metal reactions.

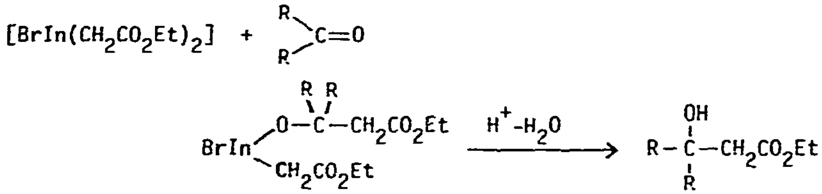
$$Ga_2I_6 \quad + \quad 2R_3Ga_2I_3 \longrightarrow 3R_2Ga_2I_4$$

(2) Samples of composition GaI which contained metallic gallium together with some low valent gallium iodides, were obtained by heating stoichiometric quantities of gallium and iodine in vacuo at 250° in a furnace for 24h. The reaction mixtures were made up by condensing an excess of the anhydrous alkyl iodide onto the above sample in vacuo. They were shaken mechanically at room temperature for 1 or 2 weeks until all the halide and excess metal had completely reacted.

Activated indium powder, prepared by reducing anhydrous $InCl_3$ with freshly cut potassium metal in dry xylene, has the average particle size of 4.0 μm. Reaction of this activated indium metal with α-bromo (or chloro) esters is rapid and give the proposed intermediate compound [30].

$$2In^* \quad + \quad 2BrCH_2CO_2Et \longrightarrow [BrIn(CH_2CO_2Et)_2] \quad + \quad InBr$$

This intermediate reacts with ketones or aldehydes to give β-hydroxy esters:



Yields of the product were discussed with relation to the reagents used and the reaction conditions.

Diarylindium compounds, R_2InI (R= C_6H_5, p-$CH_3C_6H_4$) also were prepared by the reaction of aryl iodides with the activated indium [31].

Oxidative arylation of the indium(I) halides or indium metal with various mercurials has been reported [32].

$$\mathrm{InX} + \mathrm{RHgX} \longrightarrow \mathrm{RInX_2} + \mathrm{Hg}$$

$$\mathrm{InX} + \mathrm{R_2Hg} \longrightarrow \mathrm{R_2InX} + \mathrm{Hg}$$

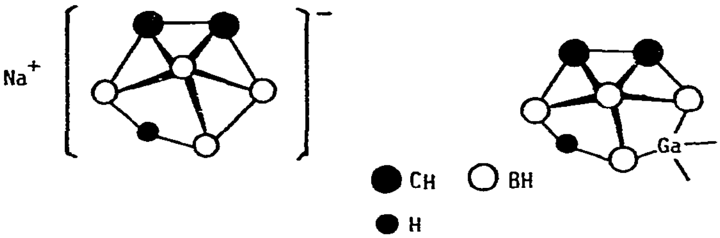
$$2\mathrm{InX} + \mathrm{R_2Hg} + \mathrm{HgX_2} \longrightarrow 2\mathrm{RInX_2} + 2\mathrm{Hg}$$

$$2\mathrm{In} + n\mathrm{R_2Hg} + (3-n)\mathrm{HgX_2} \longrightarrow 2\mathrm{R}_n\mathrm{InX}_{3-n} + 3\mathrm{Hg} \quad (n = 1,2)$$

Thus, $(C_6H_5)_nInX_{3-n}$ (n= 1,2; X= Cl, Br, I) and R_nInBr_{3-n} (n= 1, 2; R= 4-FC_6H_4 4-$CH_3C_6H_4$) were prepared. The structure of these compounds in the solid state has been investigated using IR, Raman, ^{115}In NQR and mass spectral as well as conductivity data. The compounds of stoichiometry $(C_6H_5)_2InX$ (X= Cl, Br, I) are best described as adopting a polymeric lattice with multiply-associated halogen atoms linking together nearly linear $(C_6H_5)_2In$ groups. The compounds $C_6H_5InX_2$ (X= Cl, Br) also adopt a polymeric lattice, but $C_6H_5InI_2$ is more consistent with an ionic formulation, $(C_6H_5)_2In^+InI_4^-$. The dioxane adducts $(C_6H_5)_nInCl_{3-n}$·dioxane (n= 0-3) do not contain multiply-associated chlorine atoms.

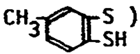
The reaction of sodium salts of the 2,3-$C_2B_4H_7^-$ anion with $(CH_3)_2GaCl$ effected insertion of the metal atom into a bridging position on the base of the pyramidal carborane cage, with the metal apparently linked to the cage by a B-Ga$(CH_3)_2$-B three-center, two-electron bond.

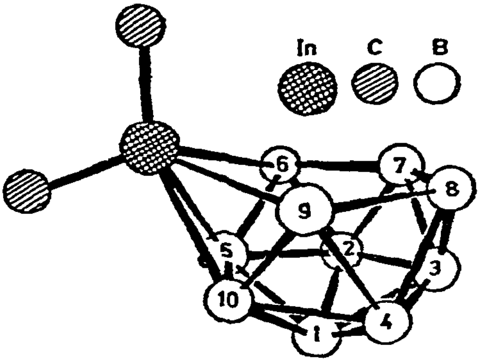
$$Na^+[2,3\text{-}C_2B_4H_7]^- \quad + \quad (CH_3)_2GaCl \longrightarrow \mu[(CH_3)_2Ga]C_2B_4H_7 \quad + \quad NaCl$$



The product is a slightly volatile, thermally stable clear liquid. It reacted readily with HCl to generate $C_2B_4H_8$ and $(CH_3)_2GaCl$ analogous to the case of μ-$(CH_3)_3MC_2B_4H_7$ (M= Si, Ge, Sn or Pb) [33].

Deprotonation of decaborane, $B_{10}H_{14}$, by trimethylindium in 1:2 molar ratio in benzene at room temperature yielded the complex $[(CH_3)_2In]^+[B_{10}H_{12}In(CH_3)_2]^-$. When the reaction was carried out in 1:1 molar ratio, the ionic complex shown above was again formed, but a second product, $B_{10}H_{12}InCH_3$, remained in solution and could be isolated as a pale yellow solid. It was suggested, on the basis of analytical data, electrical conductivity, IR and ^1H and ^{11}B NMR spectra, that in the ionic complex two distinct dimethylindium groups exist, one of which is coordinated by the dodecahydro-nido-decaborate (2-) anion, as shown below.

Habeeb and Tuck have previously reported briefly on an unusual dimeric intermediate $[CH_3In(OAc)(HTDT)]_2$ (HTDT= ) in which a potentially reactive methyl group and an acidic hydrogen atom are present in the same molecule. The same authors have extended their study to similar reactions between dimethylindium(III) compounds (especially $(CH_3)_2In(OAc)$) and various dibasic organic acids (especially toluene-3,4-dithiol, H_2TDT). The structures



Proposed heavy-atom structure of the $[B_{10}H_{12}In(CH_3)_2]^-$ ion; numbering as in decaborane(14). Each boron atom carries one external hydrogen atom and there are bridging hydrogen atoms between B(6)-B(7) and between B(8)-B(9). [From ref. 34.]

of the dimeric intermediate and similar species were discussed in terms of the relationship to the polymeric parent $(CH_3)_2In(OAc)$ and to its adducts with neutral donors [35].

Trimethylphosphonium-methylide, $(CH_3)_3P{=}CH_2$, reacts rapidly with Group III trialkyls, MR_3(M= Ga, In, Tl; R= CH_3, C_2H_5), in an inert solvent to give quantitatively adducts of the type $[(CH_3)_3\overset{+}{P}{-}CH_2{-}\overset{-}{M}R_3]$. These compounds are highly reactive, but thermally stable. They dissolve as monomers in benzene, and their ^1H and ^{13}C NMR data were discussed [36]. A Russian report [37] showed that the rate of metalation of $C_4H_9{-}C{\equiv}CH$ by $MGaH_4$(M= Li, Na, K) was less than that by $MAlH_4$.

Several simple compounds of indium(I), InX, with the anions of bidentate monoprotic organic ligands, such as quinoline-8-olate, have been prepared for the first time by the reaction of the parent acid with cyclopentadienylindium(I) in organic solvents [38].

$$\mathrm{In(Cp)} + \mathrm{HX} \longrightarrow \mathrm{InX} + C_5H_6$$

X= 4,4,4-trifluoro-1-(thien-2-yl)butane-1,3-dionate,
6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate,
quinoline-8-olate
2-mercaptopentan-3-one anion
2-mercaptocyclohexanone anion

Indium(I) quinoline-8-olate gave indium(III) species on reaction with mild oxidizing agents or weak acids.

Application and Patents

$(CH_3)_3Ga$ was isolated by thermal decomposition of the etherate prepared by treating purified $(CH_3)_3Ga.O(C_2H_5)_2$ with a high boiling ether [39].

The reaction of gallium or indium halides with highly pure triethylaluminum served in the preparation of $(C_2H_5)_3Ga$ and $(C_2H_5)_3In$ of high purity for vapor phase crystal growth of electric semiconductors, such as GaAs, InGaP [40]. Extra pure trimethylgallium, in which the overall content of organometallic impurities such as $(CH_3)_2Zn$, $(CH_3)_2Cd$ and $(CH_3)_3Al$ did not exceed 5×10^{-5} wt% can be prepared from gallium(III) chloride and trimethylaluminum followed by rectification of the product through a column reactor by adding heptane [41]. Also, the preparation of especially pure trialkylgallium compound was described [42].

REFERENCES

1. J. P. Maher, Organometal. Chem., 3 (1975) 36.
2. E. A. Forman and K. Wade, MTP Int. Rev. Sci.: Inorg. Chem., Ser Two 4 (1975) 119.
3. A. T. T. Hsieh, Inorg. Chim. Acta, 14 (1975) 87.
4. M. B. Hursthouse, Mol. Struct. Diffr. Methods, 2 (1975) 429.

5. G. A. Tedorazde, J. Organometal. Chem., 88 (1975) 1.

6. H. D. Hausen, K. Mertz, J. Weidlein and W. Schwarz, J. Organometal. Chem., 93 (1975) 291.

7. A. J. Conway, P. B. Hitchcock and J. D. Smith, J. Chem. Soc. Dalton Trans. (1975) 1945.

8. K. R. Breakell, D. J. Patmore and A. Storr, J. Chem. Soc. Dalton Trans., (1975) 749.

9. D. F. Rendle, A. Storr and J. Trotter, J. Chem. Soc. Dalton Trans., (1975) 176.

10. D. J. Patmore, D. F. Rendle, A. Storr and J. Trotter, J. Chem. Soc. Dalton Trans., (1975) 718.

11. F. G. Herring, D. J. Patmore and A. Storr, J. Chem. Soc. Dalton Trans., (1975) 711.

12. D. F. Rendle, A. Storr and J. Trotter, Can. J. Chem., 53 (1975) 2930.

13. D. F. Rendle, A. Storr and J. Trotter, Can. J. Chem., 53 (1975) 2944.

14. S. J. Retting, A. Storr and J. Trotter, Can. J. Chem., 53 (1975) 58.

15. R. J. Hogan, P. A. Scherr, A. T. Weibel and J. P. Oliver, J. Organometal. Chem., 85 (1975) 265.

16. H. Preut and H. -J. Haupt, Chem. Ber., 108 (1975) 1447.

17. H. -J. Haupt, F. Neumann and H. Preut, J. Organometal. Chem., 99 (1975) 439.

18. H. L. Chung and D. G. Tuck, Can. J. Chem., 53 (1975) 3492.

19. H. -U. Schwering and J. Weidlein, J. Organometal. Chem., 99 (1975) 223.

20. H. -U. Schwering, J. Weidlein and P. Fischer, J. Organometal. Chem., 84 (1975) 17.

21. K. Dehnicke and N. Töder, J. Organometal. Chem., 86 (1975) 335.

22. J. Müller, F. Schmock, A. Klopsch and K. Dehnicke, Chem. Ber., 108 (1975) 664.

23. H. J. Widler, H. D. Hausen and J. Weidlein, Z. Naturforsch., 30B (1975) 645.

24. A. P. Kurbakova, L. A. Leites, V. V. Gavrilenko, Yu. N. Karaksin and L. I. Zakharkin, Spect. Chim. Acta, 31A (1975) 281.

25. J. Stadelhofer, J. Weidlein and A. Haaland, J. Organometal. Chem., 84 (1975) C1.

26. P. Krommes and J. Lorberth, J. Organometal. Chem., 88 (1975) 329.

27. R. A. Kovar, H. Derr, D. Brandau and J. O. Callaway, Inorg. Chem., 14 (1975) 2809.

28. H. -U. Schwering, E. Jungk and J. Weidlein, J. Organometal. Chem., 91 (1975) C4.

29. M. Wilkinson and I. J. Worrall, J. Organometal. Chem., 93 (1975) 39.

30. L. Chao and R. Rieke, J. Organometal. Chem., 40 (1975) 2253.

31. L. Chao and R. D. Rieke, Synth. React. Inorg. Met.-Org. Chem., 5 (1975) 165.

32. S. B. Miller, B. L. Jelus and T. B. Brill, J. Organometal. Chem., 96 (1975) 1.

33. C. P. Magee, L. G. Sneddon, D. C. Beer and R. N. Grimes, J. Organometal. Chem., 86 (1975) 159.

34. N. N. Greenwood, B. S. Thomas and D. W. Waite, J. Chem. Soc. Dalton Trans., (1975) 299.

35. J. J. Habeeb and D. G. Tuck, J. Organometal. Chem., 101 (1975) 1.

36. H. Schmidbaur, H. -J. Füller and F. H. Köhler, J. Organometal. Chem., 99 (1975) 353.

37. L. I. Zakharkin, V. V. Gavrilenko, L. L. Ivanova, B. A. Palei, V. S. Kolesov and M. P. Semenova, Dokl. Vses. Konf. Khim. Atsetilena, 1 (1972) 90: C.A. 83 (1975) 10238m.

38. J. J. Habeeb and D. G. Tuck, J. Chem. Soc. Dalton Trans., (1975) 1815.

39. B. G. Gribov, B. I. Kozyrkin, E. N. Zorina, L. G. Tonoyan, I. G. Tonoyan and V. I. Bregadze, U.S.S.R. 466, 238 (Cl. C07f): C.A. 83 (1975) 59016 b.

40. E. Ichiki, K. Iida and M. Ogura, Japan Kokai, 7553,331 (Cl. C07F): C.A. 83 (1975) 131748m.

41. V. A. Fedorov, A. A. Efremov and E. A. Efremov, Zh. Prikl. Khim. (Leningrad) 48 (1975) 1810: C.A. 83 (1975) 193424m.

42. V. A. Krutikov, V. A. Vedorov and E. B. Sokolov, Sb. nauch. tr. po probl. mikroelektron. Mosk. in-t elektron. tekhn. (1974) 46: C.A. 84 (1975) 17458n.