GALLIUM AND INDIUM
ANNUAL SURVEY COVERING THE YEAR 1974

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 1974 as during 1973 [See, R. Okawara, J. Organometal. Chem., 83 (1974) 55, 'Annual Survey Covering the year 1973'] 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 207 references (1) and on Al, Ga, In and Tl with 57 references (2) have been published. In a general review 'Organometallic Compounds and Living Organisms' (3), it was shown that very little work has been done on the biological effects of Ga and In.

Structural and Spectroscopic Studies

By vapor phase electron diffraction method, the planar structure of $(CH_3)_3Ga$ was established for the first time (4) and that of $(CH_3)_3In$ was reconfirmed (5). The result of an X-ray crystal structure study (6) of $(CH_3)_2InCl$ showed that the indium

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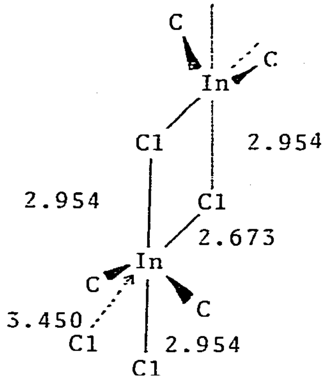
[+] **Gallium and indium, Annual Survey covering the year 1973 see J. Organometal. Chem., 83(1974)55-63.**

atom is in the center of a distorted octahedron and is surrounded by two carbon and four chlorine atoms, with distinctly different In-Cl distances as shown below.

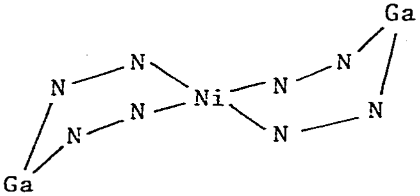


In-C 2.179Å

C-In-C 167.3°

The routes for preparing R_2InX and $RInX_2$ (R= CH_3, C_2H_5; X= Cl, Br, I) were summarized, and the ir and Raman spectra were also discussed.

Bis[dimethylbis(1-pyrazolyl)gallato]nickel(II) $[(CH_3)_2Ga(N_2C_3H_3)_2]_2Ni$ was prepared from sodium dimethylbis-(1-pyrazolyl)gallate and nickel chloride in aqueous solution (7). The single crystal X-ray diffraction study of this compound showe that the two six-membered $Ga(N-N)_2Ni$ rings are in the boat conformation with a planar arrangement of four nitrogen atoms about the nickel atom which lies on a crystallographic center of symmetry, giving the whole molecule a pseudo chair conformation, as shown schematically below.

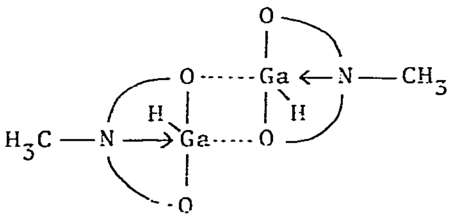


The N-methyldiethanolaminogallane dimer was prepared as follows (8).

$$CH_3N(CH_2CH_2OH)_2 \ + \ (CH_3)_3NGaH_3 \longrightarrow$$

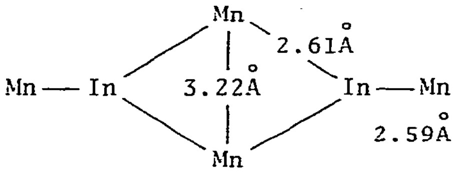
$$CH_3N(CH_2CH_2O)_2GaH \ + \ 2H_2 \ + \ (CH_3)_3N$$

An X-ray crystallographic study showed that the dimerization occurred via the formation of a four membered Ga_2O_2 ring as schematically shown below.

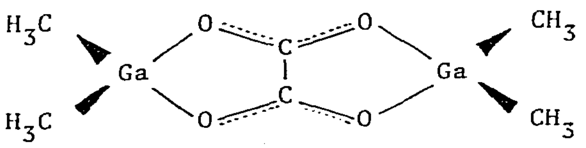


Thus the gallium atoms in the dimer provide the first known crystallographic example of pentacoordination.

Clusters of the type $M_2Mn_4(CO)_{18}$ (M= Ga, In) have been synthesized by allowing the respective metals to react in a bomb tube with $Mn_2(CO)_{10}$, $Hg[Mn(CO)_5]_2$, or Hg and $Mn_2(CO)_{10}$. $In_2Mn_4(CO)_{18}$ also was formed by thermolysis of $In[Mn(CO)_5]_3$ in the presence of xylene. The new clusters coordinate donor molecules at M to form complexes $M_2Mn_4(CO)_{18}.2D$ (M= In, D= pyridine, acetone; M= Ga, D= pyridine). In pyridine, dissociation of $Mn(CO)_5^-$ anions takes place without decomposition of the metal ring (9). All $M_2Mn_4(CO)_{18}$ compounds were shown by an X-ray analysis (10) to be isomorphous. As shown below, they contain a planar bridged ring of 2M and 2Mn atoms, in which $2Mn(CO)_4$ groups form the Mn-Mn bond, each being connected with $2[\mu\text{-MMn(CO)}_5]$ units; the $Mn(CO)_5$ ligands at M have trans-positions with respect to the planar metal ring.



Bis(dialkylgallium)oxalates, $[R_2Ga]_2C_2O_4$ (R= CH_3, C_2H_5) were prepared in good yield from R_3Ga and anhydrous oxalic acid in dry ether (11). These compounds sublime in vacuum and dissolve in non-polar organic solvents. In benzene and in the vapor state th are monomeric. They dissolve in cold water without decomposition and dissociate into hydrated R_2Ga^+ and $C_2O_4{}^{2-}$ ions. The vibratio spectra of these compounds suggested that the $Ga_2C_2O_4$ skeleton may not be planar [See, H. U. Schwering, H. D, Hausen, and J. Weidlein, Z. anorg. allg. Chem., 391 (1972) 97]. However, the mass spectrum of the methyl compound can be interpreted by assuming following structure. The structure, which is very rare



in a series of oxalates, has been established by an X-ray study. The results showed that the $Ga_2C_2O_4$ skeleton forms an almost planar system composed of two fused five-membered rings, and the presence of a considerable ionic character in the Ga-O bonding has been suggested by the data of interatomic distances and bond angles.

The same research group (12) discussed the vibrational spectra of bis(dialkylmetal)squarates, $[R_2M]_2C_4O_4$, which were obtained by the reaction of squaric acid, $H_2C_4O_4$ with R_3M (M= Al, Ga, In; R= CH_3, C_2H_5) in a 1/2 molar ratio. These squarates are amorphous solids and thermally stable up to ca 300°. However, they cannot be sublimed, even in high vacuum. Derivatives of gallium and indium are stable for a long time under dry atmosphere at room temperature. They are soluble in cold water (In) or in a mixture of water and methanol (Ga), and dissociate into R_2M^+ and $C_4O_4^{2-}$ ions without decomposition. Only the solution of dimethyl derivatives is stable at room temperature for a long time. From these aqueous solutions, the hydrates, $[(CH_3)_2Ga.H_2O]_2C_4O_4$ and $[(CH_3)_2In.2H_2O]_2C_4O_4$ can be crystallized.

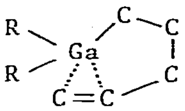
By the same research group the ^1H, ^{19}F and ^{31}P nmr (13) and vibrational (14, 15) spectra of the following dialkylmetalphosphoric and phosphinic acid derivatives were discussed.

$(CH_3)_2MO_2PH_2$, $(C_2H_5)_2GaO_2PH_2$, $(CH_3)_2MO_2PF_2$,
$(CH_3)_2MO_2PCl_2$, $(CH_3)_2MOSP(CH_3)_2$, $(CH_3)_2GaS_2P(CH_3)_2$.
(M= Ga, In)

Also, the vibrational spectra (ir and Raman) of the compounds R_2MOR' (R= CH_3, CD_3, C_2H_5; R'= CH_3, CD_3; M= Ga, In) have been studied; the trimeric methyl derivatives are considered to have puckered six-membered M_3O_3-ring systems (16).

The ^1H nmr data for $M(CH_3)_3$ and $LiM(CH_3)_4$ were compared with those of $Li[(CH_3)_3SnM(CH_3)_3]$ (M= Al, Ga, In and Tl) (17). The presence of tin-metal bonding in these derivatives was establishe by the observed tin-across-metal coupling constants. The variati in the magnitudes of $^{2}J(SnCH)$, $^{3}J(SnMCH)$ was reported as a functi of M. Proposals concerning the factors governing the changes in these coupling constants and the chemical shifts have been presented.

From the ^{1}H nmr and cryoscopic molecular weight data for several terminal trialkenyl and trialkyl aluminum derivatives, it was concluded that a direct intramolecular interaction between the metal center and the π-electron system of the olefinic site is assumed. This conclusion was extended to tri-1-pent-4-enylgallium and its trimethylamine adduct (18).



R= $(CH_2)_3CH=CH_2$

In the case of the gallium derivative shown above, a weaker interaction than that of the aluminum analog was shown to be operative.

The same authors extended this result to intramolecular cyclization reactions of tri-1-hex-5-enyl Group III (Ga, In) derivatives (19). These metals are allowed to react with di-1-hex-5-enylmercury without solvent at 95° and 110°, respectively. ^{1}H nmr spectra taken at intervals less than required for complete reaction (3 weeks) gave rise to complex patterns resulting from mixtures which contained unreacted alkenylmercury, alkenylmetal derivatives, and cyclized products, as shown below.

$$3/2\mathrm{Hg}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_2 \quad + \quad \mathrm{M} \quad \longrightarrow$$

$$\mathrm{M}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_3 \quad + \quad 3/2\mathrm{Hg}$$

$$\mathrm{M}[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_3 \longrightarrow \mathrm{M}[\mathrm{CH_2}(\text{cyclo-}\mathrm{C_5H_9})]_3$$

$$\mathrm{M} = \mathrm{Ga},\ \mathrm{In}$$

The cyclized products, tris(cyclopentylmethyl)gallium or indium are stable at 100° and form 1/1 complexes with trimethylamine.

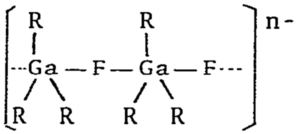
The preparation and vibrational spectra (ir and Raman) of the following complexes were reported (20).

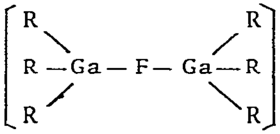
$\mathrm{K[R_3GaF]}$, $\quad (\mathrm{CH_3})_4\mathrm{N}[(\mathrm{R_3Ga})_2\mathrm{X}]$.

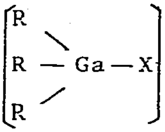
(R= $\mathrm{CH_3}$, $\mathrm{C_2H_5}$; X= F, Cl)

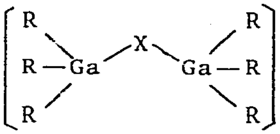
$(\mathrm{CH_3})_4\mathrm{N}[(\mathrm{CH_3})_3\mathrm{GaBr}]$, $\quad (\mathrm{CH_3})_4\mathrm{N}[((\mathrm{C_2H_5})_3\mathrm{Ga})_2\mathrm{Br}]$.

From ν(Ga-C) and ν(Ga-X), the following structures have been assumed for these compounds.





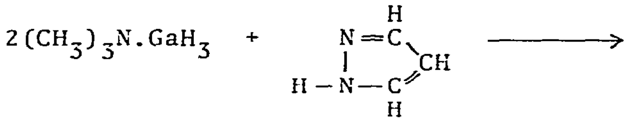




(X= Cl, Br)

The same research group prepared $(\mathrm{CH_3})_3\mathrm{GeN_3Ga(CH_3)_3}$ at low temperatures from $(\mathrm{CH_3})_3\mathrm{GeN_3}$ and $(\mathrm{CH_3})_3\mathrm{Ga}$ (21). At elevated temperatures the complex decomposes to give $[(CH_3)_2GaN_3]_3$. $[(CH_3)_2InN_3]_3$ was also prepared by an analogous route. The vibrational spectra (ir and Raman) of the trimeric azides were discussed.

The reaction of Group III alkyls and hydrido-compounds with ligands containing active hydrogen is known to produce adducts which readily eliminate hydrogen or alkane to yield co-ordinativ unsaturated intermediates. In the majority of cases these intermediates oligomerize to produce co-ordinatively saturated cyclic derivatives. An additional study along this line has been carri out by reacting appropriate Ga (or Al) compounds with a stoichiometric amount of pyrazole in benzene at room temperature (22).



$$[C_3H_3N_2.GaH_2]_2 \quad + \quad 2H_2 \quad + \quad 2(CH_3)_3N$$

$$2R_3Ga \quad + \quad 2C_3H_4N_2 \longrightarrow [C_3H_3N_2.GaR_2]_2 \quad + \quad 2RH$$

$$R = CH_3,\ C_2H_5$$

The dimeric compounds have been characterized by elemental analysis, molecular weight determinations, and by ^1H nmr and mass spectroscopic measurements. In all cases a boat conformation for the six-membered ring of four nitrogen and two metal atoms was suggested, analogous to the case of $[C_3H_3N_2.GaD_2]_2$ whose structur has been established by an X-ray analysis [D. F. Rundle, A. Storr and J. Trotter, J. Chem. Soc. Dalton Trans., (1973) 2252]. The dimethyl and diethyl-gallium compounds are quite stable in the open air and remain unchanged after prolonged exposure to atmosph

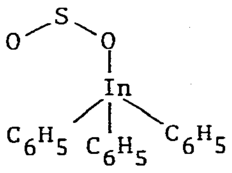
In recent years, a considerable amount of data has accumulated on insertion reactions involving SO_2, and to a lesser extent SO_3. [See, W. Kitching and C. W. Fong, Organometal. Chem. Rev., A (1970) 281.] Insertion reactions of SO_3 involving trialkyls of Al, Ga, In and Tl, and the vibrational spectra of dialkylmetal alkylenesulfonates thus formed have been discussed (23).

$$R_3M \; + \; SO_3 \longrightarrow R_2MO_3SR$$

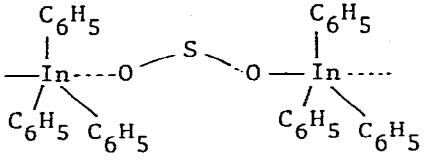
$$(R= CH_3,\ C_2H_5;\ M= Ga,\ In)$$

Also, these dialkylmetal sulfonates can be prepared easily by the reaction of the trialkyls with the respective alkansulfonic acid. Almost quantitative yields of pure compounds are obtained by both ways. They are colorless solids and can be sublimed in vacuum. The degree of association of the gallium derivatives in benzene was between two and three. The indium derivatives are stable in air and in water. Molecular weight determination indicated that in aqueous solution, dissociation into R_2In^+ and $CH_3SO_3^-$ ions takes place.

The product from the reaction of triphenylindium with sulfur dioxide, previously considered to be O-benzene-sulfinatodiphenylindium(III), was formulated as the 1/1 adduct, $(C_6H_5)_3In(O_2S)$. The structure (I) was suggested for the adduct, although the possibility of it being a five coordinate polymer (II) cannot be entirely excluded (24).

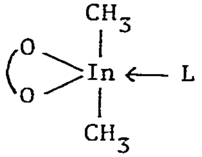


(I)



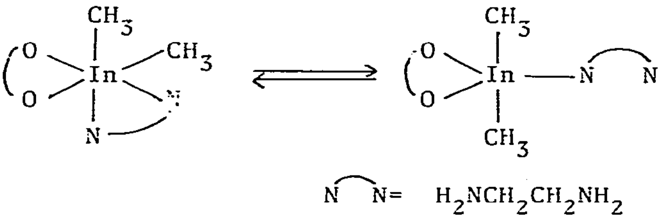
(II)

The reaction of $(CH_3)_2In(OCOCH_3)$ with donors has been report (25). The monodentate donors gave the five coordinated monomer in solution as shown below.



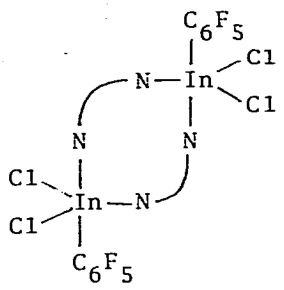
L= DMSO, Pyridine.

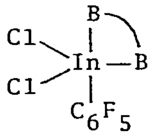
With bidentate donors, the product was either the monomeric six-coordinated $(CH_3)_2In(OCOCH_3)L$ (L= $H_2NCH_2CH_2NH_2$, $(C_6H_5)_2PCH_2CH_2$-$P(C_6H_5)_2$) or the complex $[(CH_3)_2In(OCOCH_3)]_2L$ (L= 2,2'-bipyridine, 1,10-phenanthroline). Vibrational and ^1H nmr spectra suggested that the ethylenediamine adduct is in rapid equilibrium as shown below.



N N= $H_2NCH_2CH_2NH_2$

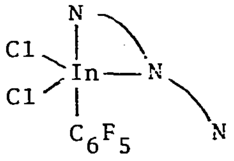
The adducts $C_6F_5InCl_2.L$ have been prepared by reaction of $C_6F_5InCl_2$.dioxane with the appropriate ligands, and are considered on the basis of their molecular weight, conductance and ir spectra to contain five-coordinate indium, as shown below (26).





N⌒N : $(CH_3)_2N(CH_2)_4N(CH_3)_2$

B⌒B : $((C_6H_5)_2PCH_2)_2$,
1,10-phenanthroline
2,2'-bipyridine



N⌒N⌒N : 2,2':6',2''-terpyridine

Reaction of $C_6F_5InCl_2$.dioxane with the monodentate ligands shown below causes quantitative rearrangement into the corresponding indium trichloride and trispentafluorophenylindium complexes.

$$3C_6F_5InCl_2.\text{dioxane} + (n + 2m)L \xrightarrow{\text{ether}} (C_6F_5)_3In.L_n + 2InCl_3.L_m + 3\text{dioxane}$$

L= pyridine, n= 1, m= 3
L= $(CH_3)_2SO$, n= 2, m= 3
L= $(C_6H_5)_3P$, n= 1, m= 2

The derivatives $(C_6F_5)_nIn(OX)_{3-n}$ (n= 1 or 2 : OX= quinoline-8-olate) have been prepared by cleavage of $(C_6F_5)_3In$.dioxane with quinolin-8-ol, and $C_6F_5In(OX)_2$ has also been obtained from

$C_6F_5InCl_2$.dioxane and thallous quinolin-8-olate.

^{115}In and halogen nqr have been observed in several dimethylindium compounds, two monoalkylindium dihalides, and indium tribromide (27). The nqr data indicate that Me_2InI and Me_2InBr have the Me_2TlBr type of structure with linear dimethylindium groups equatorially surrounded by a square-planar arrangement of halogens The structure of Me_2InCl is indicated to be distorted from this and Me_2InF appears to have a nonlinear dimethylindium group like Me_2InOAc, whose nqr parameters are consistent with its known structure. $MeInI_2$ is confirmed by its nqr spectrum to be $[Me_2In][InI_4]$, consistent with the nqr results shown by Welsh and Brill (28), whereas those of $MeInBr_2$ and $EtInI_2$ are consistent with halogen-bridged dimers, $[RInX_2]_2$.

Synthesis and Reactions

Two reports (29, 30) on the alkylation of $GaCl_3$ by $(CH_3)_3Al$ have been published; the yield of $(CH_3)_3Ga$ was 55~8% at 1/3 or 1/4 mole ratios of the both reagents (30). Russian researchers also reported the purification by distillation of $(CH_3)_3Ga$, and $(CH_3)_3Ga.O(C_2H_5)_2$ prepared by the reaction of Ga-Mg alloy with CH_3I or by the Grignard method (31), and the preparation of $NaGa(C_2H_5)_4$ by heating $NaGaH_4$, $(C_2H_5)_3Ga$ and ethylene in an autoclave (32).

Several methods for the preparation of organometallic compoun of gallium have been discussed in detail by Kovar et al. (33), and a convenient method has been developed for the preparation of base-free $(n\text{-}C_4H_9)_nGaCl_{3-n}$ compounds in benzene as follows.

$$GaCl_3 + n\ Li(C_4H_9\text{-}n) \longrightarrow n\ LiCl + (n\text{-}C_4H_9)_nGaCl_{3-n}$$

$$n = 1, 2, 3$$

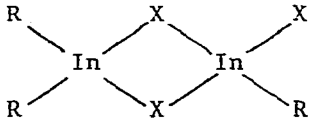
The work-up procedure involves filtration to remove by-product lithium chloride, removal of benzene in vacuo, and vacuum distillation of the n-butylgallium product. In a typical reaction, analytically pure tri-n-butylgallium was isolated in 97% yield. Alternatively, the chlorides $(n\text{-}C_4H_9)_nGaCl_{3-n}$ (n= 1, 2) were prepared essentially quantitatively according to the following disproportionation reactions carried out in the absence of solvent.

$$2Ga(n\text{-}C_4H_9)_3(l) + GaCl_3(s) \longrightarrow 3(n\text{-}C_4H_9)_2GaCl(l)$$

$$Ga(n\text{-}C_4H_9)_3\ (l) + 2GaCl_3(s) \longrightarrow 3(n\text{-}C_4H_9)GaCl_2(l)$$

Tri-n-butylgallium is monomeric, while the n-butylgallium chlorides are dimeric in benzene, in agreement with previous reports on the methyl and ethyl analogs [See, K. Yasuda and R. Okawara, Organometal. Chem. Rev., 2 (1967) 255].

The reactions between indium metal and alkyl halides, RX, gave products having the sesquihalide composition, $R_3In_2X_3$, [See, M. J. S. Gynane, L. G. Waterworth and I. J. Worrall, J. Organometal. Chem., 40 (1972) C9]. From their ir (ν(In-C)), Raman (ν(In-C) and ν(In-X)), mass and ^1H nmr spectra, it was suggested that most of them are pure sesquihalides as shown below (34).



X= Br, I; R= C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$

X= I; R= CH_3

However, in the case of $(CH_3)_3In_2Br_3$, a mixture of mainly CH_3InBr and $(CH_3)_2InBr$ has been suggested. A convenient method is descri to prepare dialkylindium halides from these sesquihalides $R_3In_2X_3$ (X= Br, R= CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X= I, R= CH_3, C_2H_5) by heat together equimolar quantities of the sesquihalide and dry powdere potassium halide in vacuo at 80-100°. At these temperatures, the dialkyl compounds sublimed away from the less volatile monoalkyl compounds.

Highly reactive indium powder, prepared by alkali metal reduction of anhydrous indium chloride in xylene, gave R_3In (R= CH_3, C_6H_5, p-$CH_3C_6H_4$) on treatment with R_2Hg (35), and it reacted easily at 80° with alkyl iodides to give nearly quantitative yields of a single product, the dialkylindium iodide (36).

$$InCl_3 + 3M \longrightarrow In^* + 3MCl \qquad (M= K \text{ or } Na)$$
$$2In^* + 2RI \longrightarrow R_2InI + InI \qquad (R= CH_3 \text{ or } C_2H_5)$$

Under these conditions, the indium monoiodide does not react further with additional alkyl iodide as has been reported [J. S. Poland and D. G. Tuck, J. Organometal. Chem., 42 (1972) 315]. $(CH_3)_2InI$ was prepared by electrolyzing CH_3I in aqueous solution of K_2HPO_4 or in a CH_3CN solution of $NaClO_4$ by using In cathode and Pt-wire anode. Similarly $(NCCH_2CH_2)_2InI$ was prepared (37).

Oxidative addition reactions of indium monohalides (bromide and iodide) with alkyl halides are useful in the preparation of alkylindium dihalides [See, M. J. S. Gynane, L. G. Waterworth and I. J. Worrall, J. Organometal. Chem., 43 (1972) 257]. An investigation of the several intermediates formed in these comple oxidative addition reactions between InBr and alkyl bromides, RBr (R= CH_3, C_2H_5, n-C_3H_7, n-C_4H_9), was reported (38) by the same authors, and possible reaction schema were formulated.

The transfer of methyl groups from $(CH_3)_3Ga$ to tin, silicon and germanium films has been observed at 190, 230 and 285°C, forming $(CH_3)_4Sn$, $(CH_3)_6Si_2$, $(CH_3)_3SiH$ and $(CH_3)_4Ge$, respectively (39). Since methane was not obtained in the neat pyrolysis of $(CH_3)_3Ga$ below 285°, it is suggested that the reaction of $(CH_3)_3Ga$ with metallic tin or silicon did not involve free CH_3 radicals. The reaction with germanium occurs just at 285° and it was difficult to determine the mode of this reaction. The relative rates of the surface reaction are in the order Sn>Si>Ge, As. In the case of the reaction with arsenic at 340°, arsenic-containing compounds were not obtained. Thermal decomposition of $(C_2H_5)_3Ga$ and $(C_2H_5)_2$-$GaOC(CH_3)_3$ has been reported (40) to give hydrogen, ethane, ethylene, butane and butylene.

The reaction of $K_2[Hg(CN)_4]$, which may act as an N-donor, and an acceptor molecule, $Ga(CH_3)_3$, proceeded at 95°C quantitatively as shown below, without formation of the adduct (41).

$$K_2[Hg(CN)_4] + 2Ga(CH_3)_3 \longrightarrow 2K[Ga(CH_3)_2(CN)_2] + Hg(CH_3)_2$$

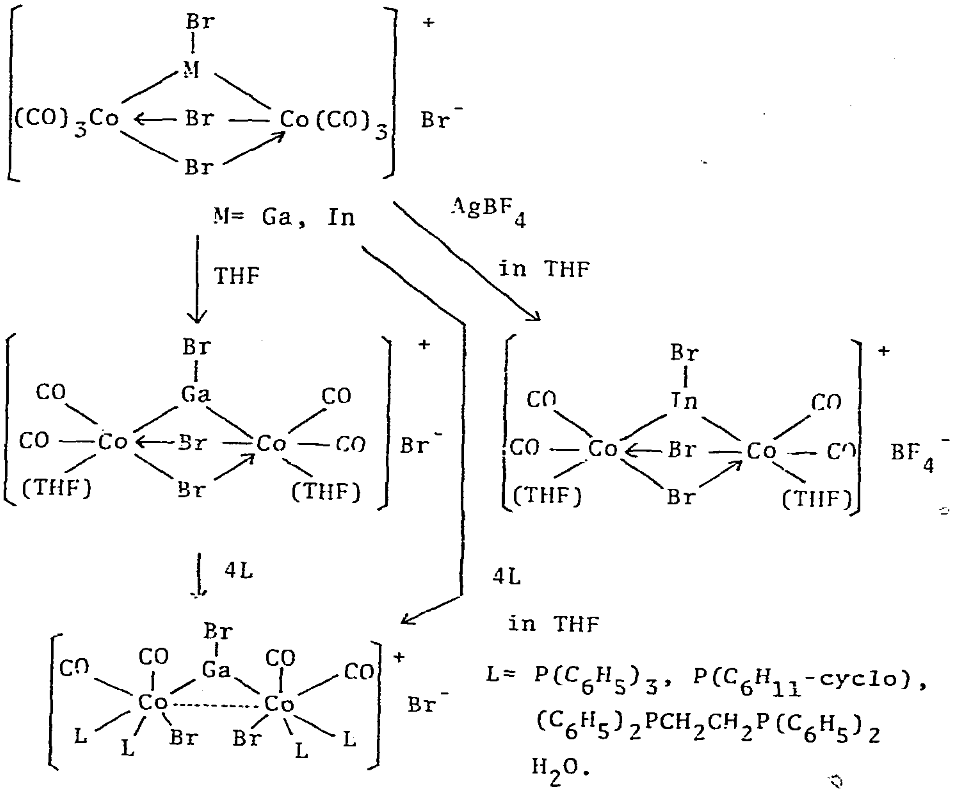
The gallium complex can be isolated by pumping off excess $Ga(CH_3)_3$ and $Hg(CH_3)_2$. It is a colorless, hygroscopic, and THF-soluble powder, and decomposes at 217°C. The ir spectrum of this complex suggests that the symmetry of the anion $[Ga(CH_3)_2(CN)_2]^-$ is C_{2v}. A similar reaction of $K_2[Hg(CN)_4]$ with $Al(CH_3)_3$ resulted in the formation of elemental mercury.

The complexes $(CH_3)_2InX$ (X= HCO_2, CH_3CO_2, $C_2H_5CO_2$, $(CH_3)_2CHC$ and $(CH_3)_3CCO_2$) were prepared by the reaction of $(CH_3)_3In.O(C_2H_5)$ with the corresponding acid in argon-saturated ether at room temperature and characterized by chemical analysis, ir, and Raman spectra (42).

Cyclopentadienylindium(I)(CpIn) in chloroform reacted with iodine to yield the solid $CpInI_2$; 2,2'-bipyridine and 1,10-phenanthroline adducts of this compound have been prepared (43). $CpInI_2$ reacted with tricyclopentadienylindium(III), and with tetra-n-propylammonium iodide, to give the unstable Cp_2InI and the anionic species $[CpInI_3]^-$, respectively. The cyclopentadieny ligand is in the monohapto form in all these compounds. CpIn reacts with methyl iodide, trifluoroiodomethane, and with iodine in the presence of ethanol to yield InI (43).

The reactions of dicobalt octacarbonyl with halides of the main Group III elements were studied (44). The boron halides BX_3 (X= Cl, Br, I) and $Co_2(CO)_8$ form the unstable adducts $Co_2(CO)_8.BX$ $AlCl_3$ and $AlBr_3$ give the stable adduct $Co_2(CO)_8.AlX_3$. $TlCl_3$ chlorinates $Co_2(CO)_8$ to $CoCl_2$. MBr_3 (M= Ga, In) behave different with $Co_2(CO)_8$, forming compounds of composition $MCo_2Br_4(CO)_6$. Le bases lead to the derivatives as shown below. Magnetochemical investigations, conductivity measurements and chemical behavior suggest these complexes to be ionic in character.

In both tetrahydrofuran and dichloromethane, $NaCo(CO)_4$, a compound which forms only weak ion pairs without covalent interac reacted with $In[Co(CO)_4]_3$ to give the complex $In[Co(CO)_4]_4^-$ (45). However, in the same solvents, $TlCo(CO)_4$ did not react with $In[Co(CO)_4]_3$ even upon standing, showing that the thallous compou exists as a tight ion pair with some degree of Tl-Co covalent bonding.

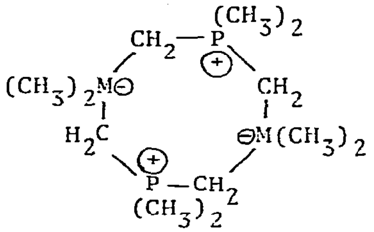


The reaction between acetato(dimethyl)indium(III) and toluene-3,4-dithiol (H_2TDT) involved elimination of either one or two moles of methane, depending on experimental conditions (46).

$$\begin{tikzcd}
(CH_3)_2In(OAc) + H_2TDT \arrow[rr, "C_2H_5OH", "-CH_4"'] \arrow[dr, "DMSO"', "-2CH_4"] & & {[CH_3In(OAc)(HTDT)]_2} \arrow[dl, "DMSO", "-2CH_4"'] \\
& In(OAc)(TDT) &
\end{tikzcd}$$

As shown above, the unusual dimeric intermediate, in which a potentially reactive methyl group and an acidic hydrogen atom are present in the same molecule, has been identified. It was also suggested that the stepwise elimination reaction appears to be common to other dimethylindium(III) species.

The reactions of $(CH_3)_2MX$ (M= Ga, X= Cl; M= In, X= Cl, Br) with $(CH_3)_3PCH_2$ in the mole ratio 1/2 yield new dimethylmetal-dimethylphosphonium-bis(methylides) $[(CH_3)_2MCH_2P(CH_3)_2(CH_2)]_n$ (47 The dimers (n= 2) can be isolated and the structure shown below has been suggested by their spectroscopic data.



M= Ga, In

Application and Patents

It has been reported (48) that epitaxial layers of $(CH_3)_3InSb(C_2H_5)_3$ were formed at 450° by the reaction of $(CH_3)_3InO(C_2H_5)_2$ with $(C_2H_5)_3Sb$. Russian patents claimed that R_3Ga (R= alkyl) were prepared by treating a Ga-Mg mixture or an alloy with the corresponding RI at 160° (49), and that the yield and purity of R_3M (R= alkyl, M= Ga, In) from the reaction of MCl_3 and R_3Al were improved by adding to the reaction mixture a hydrocarbon with a b.p. between those of the resp. R_3M and R_3Al; n-hexane and n-heptane were recommended for R_3Ga, and n-decane for R_3In (50).

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