GALLIUM AND INDIUM

ANNUAL SURVEY COVERING THE YEAR 1971

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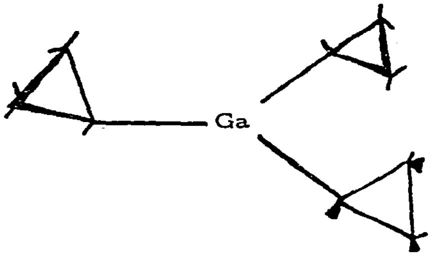
No structural studies on organoindium or gallium compounds were reported in 1971, however several investigations related to their spectral properties were reported. Ruch'eva et al. [1] recorded the infrared spectra on suspensions of $(C_6D_5)_3Ga$ and $(C_6D_5)_3In$ in vaseline oil, CS_2 and CCl_4 between 200 and 2600 cm^{-1}. They calculated in-plane and out of plane normal vibrations for the C_6D_5M model and compared these results with the experimentally observed frequencies. Margiolis and Dehnicke [2] studied both the ir and Raman spectra of tricyclopropylgallium. On the basis of these studies they proposed the structure in I, in which the propeller-like twisting of the cyclopropane rings gives the molecule C_1 symmetry.



I

Glockling and Stafford [3] reported mass spectral studies on Group III derivatives including Me_3Ga, Vi_3Ga, and Me_3In. Study of metastable peaks supported the following transtions for the methyl compounds:

$$\begin{tikzcd} Me_3M^{+\cdot} \arrow[r] & Me_2M^{+} \arrow[r, "-Me^{\cdot}"] \arrow[rr, bend right, "-C_2H_6"'] & MeM^{+\cdot} \arrow[r, "-Me^{\cdot}"] & M^{+} \end{tikzcd} \tag{1}$$

They also observed the ions $(Me_3Ga)_3^{+}$ and $Me_3Ga_2^{+}$ in samples of Me_3Ga prepared from Me_2Hg and Ga metal, but not in samples prepared from $GaCl_3$ and Me_3Al. No satisfactory explanation for these results was available. Decomposition of Vi_3Ga included a variety of different fragments as indicated in 2, 3 and 4.

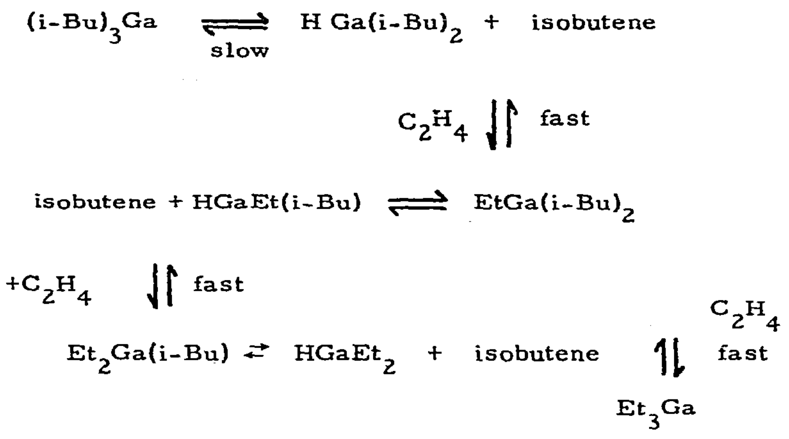
$$(CH_2{:}CH)_2Ga^{+} \rightarrow CH_2{:}CHGaH^{+} + C_2H_2 \tag{2}$$

$$CH_2{:}CHGaH^{+} \rightarrow Ga^{+} + C_2H_4 \tag{3}$$

$$(CH_2{:}CH)_2Ga^{+} \rightarrow Ga^{+} + C_4H_6 \tag{4}$$

These studies also showed that the abundances of the molecular ions were in the order $Al > B > Ga > In > Tl$ for the methyl species while that of Vi_3Ga was barely detectable. They also obtained a value of the mean bond dissociation energy, $\overline{D}(Me\text{-}Ga) = 55.6 \pm 2$ kcal/mole from appearance potential data.

Egger [4] has studied the gas phase thermal decomposition of $(i\text{-}Bu)_3Ga$ in the presence of ethylene and proposed the following reaction scheme:



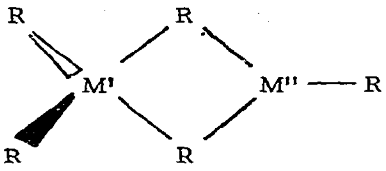
(5)

overall:

$$(i\text{-}Bu)_3Ga + 3C_2H_4 \rightarrow Et_3Ga + 3\ \text{isobutene} \qquad (6)$$

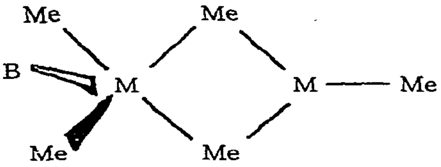
The rate constants and activation energies for the various steps are discussed and compared with those reported for other Group III derivatives For this reaction a least-squares analysis of the rate constants $k_1 sec^{-1}$ is given by $\log k_1 = (11.57 \pm 0.29)-(30.40 \pm 0.58)/\Theta$ where $\Theta = 2.303 \times 10^{-3}$ RT with R in kcal $mole^{-1}$.

Two papers have dealt with the exchange of methyl derivatives of gallium and indium with other organometallic compounds. The first deals with the exchange of Me_3Ga with Me_6Al_2 and a modified reaction mechanism for this exchange was proposed [5]. This is discussed in detail in the annual survey on aluminum compounds. The second report by Soulati, et. al. [6] provides data on the exchange of Me_3Ga with Me_2Cd and on the exchange of Me_3In with Me_2Zn. The systems have been shown to obey second order rate laws in both coordinating and non-coordinating sovlents. Major differences in the activation energies and rates of reaction were observed, however, as a function of the solvent. These differences were accounted for in terms of the proposed transition states. In non-coordinating solvents it has been proposed that the formation of II is rate determining



II

where M' and M'' are group III and II metals respectively. If a coordinating solvent is present, then the group III derivative is present in the form of a complex R_3M-base and to account for the observed second order kinetics one of the following paths has been proposed. The first involves the rate determining formation of III in which a five coordinate metal is present



III

while the second possible route is described by 7 and 8.

$$R_3M\cdot B \rightleftarrows R_3M + B \qquad (7)$$

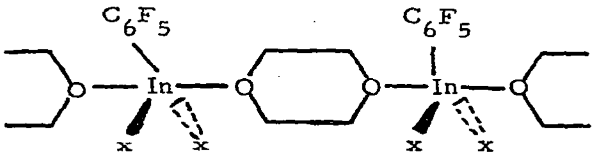
$$R_3M + R_2M' \rightleftarrows [AC] \rightarrow \text{exchange products} \qquad (8)$$

In 7 a steady state equilibrium concentration of R_3M is established with the rate determining step determined by the formation of the transition state, [AC] in 8. The catalytic effects of basic solvents on the exchange of group II metal alkyls is also described.

The preparation and properties of several pentafluorophenylindium derivatives have been reported by Deacon and Parrott [7, 8]. They have shown that the reaction given in 9 proceeds smoothly in a sealed tube to give the tris(pentafluorophenyl)indium which can be

$$3C_6F_5I + 4In \xrightarrow{160^o} (C_6F_5)_3In + 3InI \qquad (9)$$

sublimed from the reaction mixture. No evidence for the formation of InI_3 was found. The $(C_6F_5)_3In$ was also produced by exchange of $(C_6F_5)_2Hg$ with indium metal. The product is soluble in hydrocarbons and was shown to be monomeric in benzene. Infrared and nmr spectral parameters were reported. The adduct $(C_6F_5)_3In\cdot OEt_2$, was prepared by direct reaction of the two compounds while the para-dioxane adduct was obtained either from the reaction of $(C_6F_5)MgCl$ or $(C_5F_5)_2Mg$ with $InCl_3$ in ether-dioxane solvent. $C_6F_5InCl_2\cdot$diox was also obtained from the latter reaction when excess $InCl_3$ was used. The low solubility and other properties of the dioxane complexes lead to the suggested polymeric structure containing five coordinate indium given in IV.



$x = C_6F_5$ or Cl

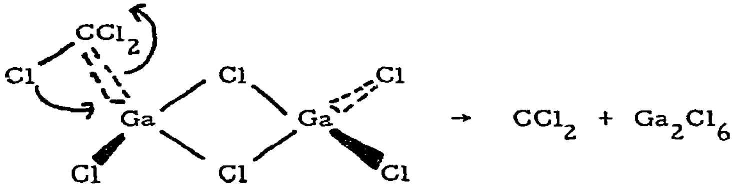
IV

It was also shown that reaction of $In(OAc)_3$ with pentofluorobenzoic acid yielded the indium benzoate and did not eliminate CO_2 to give the pentafluorophenyl derivative.

Gallium (I) and indium (I) halides have been shown to add to C-X bonds. Thus InBr or $InInBr_4$ adds to methylbromide to yield the methylated derivative as indicated in 10. If $InInBr_4$ is used, $InBr_3$ is

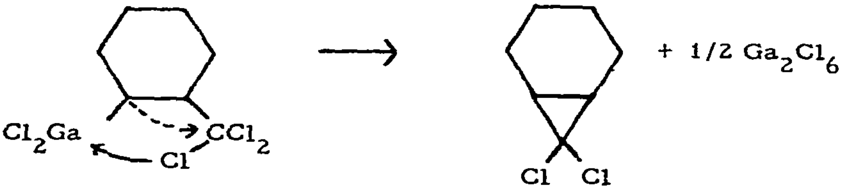
$$2InBr + 2MeBr \rightarrow (MeInBr_2)_2 \qquad (10)$$

present and leads to additional mixed products [9, 10]. It has been shown that in the reaction between $GaGaCl_4$ and CCl_4, CCl_2 adds to cyclohexene yielding 7, 7-dichloronorcarane [11]. This is compatable with the formation of a carbinoid intermediate, as indicated in 11 during



(11)

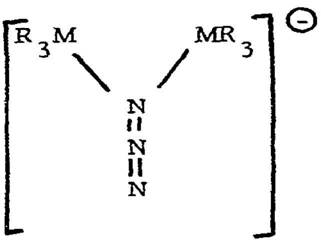
decomposition or with additionof the Ga-C bond across the double bond followed by elimination as indicated in 12. The authors prefer the latter route.



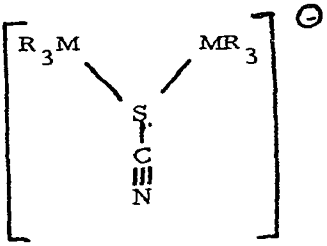
(12)

The exchange of CpIn with Tl^o, has been reported [12]. This reaction proceeds readily to give the exchange product. It was also shown that exchange between the indium compound and other cyclopentadienide containing derivatives occurs readily.

Organogallium compounds characteristically act as Lewis acids. This mode of reaction was utilized in preparing a series of different types of adducts as indicated in V, VI and VII. The structures of the $[NMe_4]^+$ salts were assigned on the bases of infrared studies [13]. Other complexes of similar structure were prepared with Cl^-, Br^-, and NCO^-.



V



VI

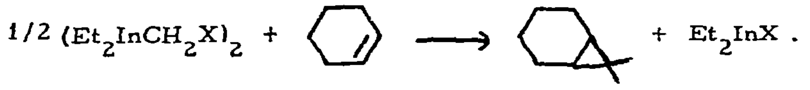
$$[R_3M{-}C{\equiv}N{-}MR_3]^-$$

VII

R = Me, Et

Triethylindium has been shown to react with CH_2I_2, CH_2Br_2, CCl_4 and $CHCl_3$, but not with CH_2Cl_2. The evidence supports the following sequence of reactions:

$$Et_3In + CH_2X_2 \rightarrow \underset{\text{VIII}}{Et_2InCH_2X} + EtX \qquad (13)$$



(14)

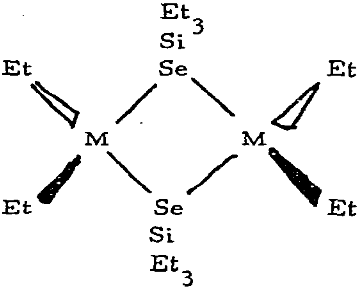
VIII appeared to be moderately stable in solution as demonstrated by the reaction, but was not isolated. The Et_2InX species were characterized by their ir spectra.

$$Et_2InCH_2I + CH_3OH \rightarrow Et_2InOCH_3 + CH_3I \qquad (15)$$

With X = I, Br, and Cl the molecules were dimeric with a non-linear C-In-C structure, while Et_2InF was polymeric with a linear C-In-C unit suggested.

A number of cleavage and insertion reactions have also been reported for gallium and indium derivatives. These include the reaction of Et_3Ga and Et_3In with Et_3SiSeH [15]. This reaction yields dimeric products as indicated in 16 as determined by cryoscopic

$2Et_3M + 2Et_3SiSeH \rightarrow$



(16)

M = Ga, In

molecular weight measurements. These derivatives are relatively stable, but undergo disproportionation or decomposition at elevated temperatures as shown in 17.

$$(Et_3SiSeMEt_2)_2 \rightarrow Et_3M + \{[Et_3SiSe)_2\ MEt\}$$

$$(Et_3Si)_2Se + 1/n\ (Et\ MSe)_n \qquad (17)$$

Attempts to prepare the bis(silylseleno) derivatives always led to disproportionation products. The reaction of three equivalents of Et_3SiSeH with Et_3In lead to $(Et_3SiSeInSe)_n$.

Similar reactions of $Ph_3Ga \cdot C_4H_8O_2$ and $Ph_3In \cdot C_4H_8O_2$ with equal molar amounts of $C_{12}H_{25}SH$ at -60° in Et_2O gave $Ph_2MSC_{12}H_{25}$ [16]. Treatment with 2 moles of thiol per mole of Ph_3M gave

$PhM(SC_{12}H_{25})_2$, unlike the previously discussed selinols; a 3:1 ratio gave $M(SC_{12}H_{25})_3$. It was also shown that the acetates, Ph_2GaOAc and $In(OAc)_3$ reacted with $C_{12}H_{25}SH$ and, on removal of HOAc, yield the corresponding gallium and indium derivatives [16].

A series of volatile cyclic imino compounds of gallium and indium have been prepared by reaction of amine with the metal alkyl via reactions <u>18</u> and <u>19</u>.

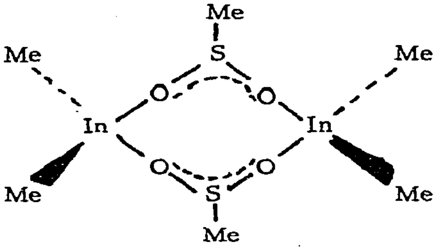
$$\overline{CH_2\cdot(CH_2)_x\cdot NH} + R_3M \rightarrow \overline{CH_2(CH_2)_xNH}\cdot MR_3 \qquad (18)$$

$$\overline{CH_2(CH_2)_xNH}\cdot MR_3 \xrightarrow[\Delta]{} [\overline{CH_2(CH_2)_xN}\cdot MR_2]_n + RH \qquad (19)$$

The products have been characterized by molecular weight measurements, mass spectra, and nmr spectra. With the exception of $\overline{CH_2CH_2N}\cdot InMe_2$ which appears to be trimeric the other gallium and indium compounds were dimeric. All compounds are thought to have four or six membered metal-nitrogen ring systems [17].

Several reports of addition of organogallium or indium derivatives to SO_2, SCO, and related species have appeared. Hsieh [16] has investigated the reaction of SO_2 with a number of R_3In derivatives (R = Me, Et, Ph, or $PMeC_6H_4$). Me_3In reacts smoothly with SO_2 between -45° and room temperature yielding $Me_3In(SO_2)_3$ which is thought to be an O, O'- sulphinate based on ir, and Raman spectral studies. Mass spectral studies (source temperature 180°) lead to a variety of unexpected fragments thought to arise from rearrangement.

Under controlled conditions at -50°, one mole of SO_2 reacted with Me_3In to yield the dimeric product, $Me_4In(O_2SMe)_2$. The structure, shown in IX is based on ir, Raman, mass, and nmr spectral data, and is similar to that reported for aluminum compounds and earlier for the indium adducts.



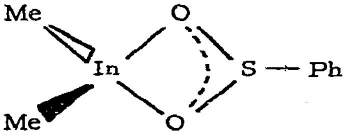
IX

Reaction of Et_3In with SO_2 only yields $Et_3In(SO_2)_3$ and is thought to have a similar structure to the methyl derivatives. Addition of Ph_3In to SO_2 gives an unstable product Ph_3InSO_2 which loses SO_2 slowly in vacuo, but does not lead to arenesulphinates. These were obtained by reaction 20.

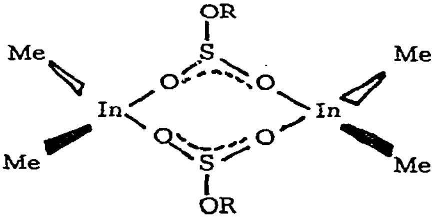
$$InCl_3 + ArSO_2Na \rightarrow (ArSO_2)_3In + 3NaCl \qquad (20)$$

with Ar = Ph or $PMeC_6H_4$.

Reaction of SO_2 with Me_2InOR (R = Me, Et, Ph) leads to insertion into the In-O bond yielding products thought to have structures X and XI.



X



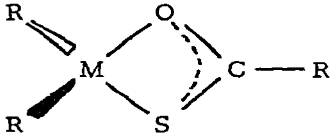
XI

R = Me or Et

$Me_2InOC_5F_6$ appears to react difficultly with insertion into the In-C bond yielding $C_6F_5InMe_2 \cdot 2SO_2$.

Diethylindium thiobenzoate was prepared by the direct reaction of thiobenzoic acid with Et_3In. It was shown to be monomeric in benzene. On hydrolysis it yielded both benzoic acid and thiobenzoic acid while pyrolysis gave EtInS and 1, 1-dibenzoylethane [19]. Alkylindium sulfides were also prepared by reaction of R_3In with other organometallic sulfides such as $(Me_2SnS)_3$ or $(Me_2SiS)_3$ [20].

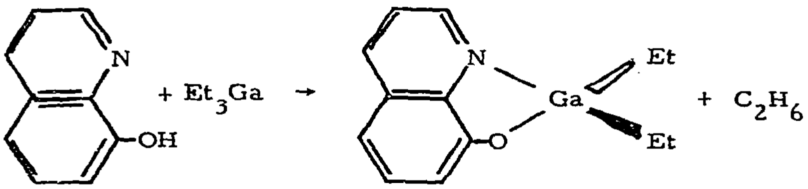
Other thiocarboxylates were formed by the reaction of gaseous COS with R_3Ga and R_3In [21]. These derivatives have also been shown to be monomeric and appear to have the structure shown in XII:



XII

based on extensive ir and Raman spectral studies.

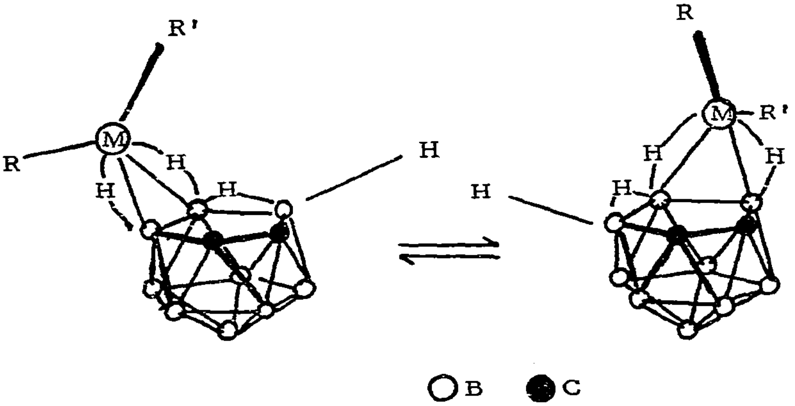
Reactions of gallium alkyls with compounds containing active hydrogens have been reported. Sen and White [22] have prepared diethylgallium-8-quinolinolate by reaction 21.



(21)

Nmr, ir, mass spectral, and molecular weight data all have supported the reaction as shown.

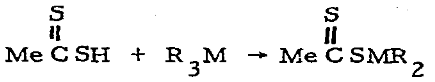
Young et al. [23] reacted Et_3Ga with (3)-1, 2-$B_9C_2H_{13}$ in benzene solution and obtained 1, 2-$B_9C_2H_{12}GaEt_2$ under mild conditions. The same reaction heated to 70° for 76 hours yielded 1, 2-$B_9C_2H_{11}GaEt$. Passing this product through glass wool at 400° caused rearrangement with formation of 1, 7-$B_9C_2H_{12}GaEt$ along with decomposition products. The products were characterized by a variety of techniques including their mass spectra and nmr spectra. The latter showed a temperature dependence for the diethyl derivative which was thought to arise from the process indicated in 22 with exchange between the endo and exo positions.



(22)

A variety of complexes and other derivatives of gallium and indium have been reported over the past year. Haran and Laurent [24] studied the formation of $Me_3P{\cdot}Ga$ -$Bu_{3-n}Cl_n$ adducts and reported both formation constants and ^{31}P-^{1}H coupling constants. The formation constants were 15, 15, 20 and 130 while the $J_{^{31}P\text{-}Me}$ varied from -6.0 to 12.9 Hz going from the adduct with R_3Ga to $GaCl_3$.

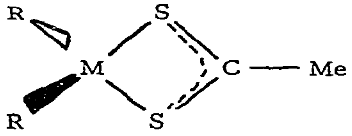
Weidlein [25] reported that dialkylthioacetates reacted with aluminum, gallium and indium derivatives via <u>23</u> yielding 60-70% of the



$$\mathrm{Me}\overset{\overset{S}{\|}}{C}\mathrm{SH} + R_3M \rightarrow \mathrm{Me}\overset{\overset{S}{\|}}{C}\mathrm{SMR}_2 \qquad (23)$$

M = Al, Ga, In and R = Me or Et

corresponding thioacetate. When the reaction was carried out in benzene at 5-10°. The gallium and indium derivatives were shown to be monomeric and the ir and Raman spectra were consistent with a planar four membered ring as shown in XIII.



XIII

R = Me, Et, Me = Ga, In

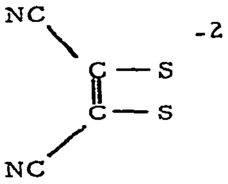
This product reacted with HCl as shown in 24 and 25.

$$R_2GaSSCMe + HCl \rightarrow RH + R\ ClGaSSCMe \qquad (24)$$

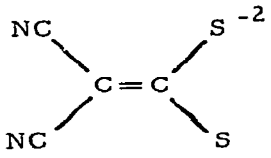
$$R_2Ga\ SSCMe + 2HCl \rightarrow 2RH + Cl_2GaSSCMe \qquad (25)$$

The $Me_2GaSSCMe$ formed a 1:1 adduct with pyridine which could be sublimed in a vacuo at room temperature.

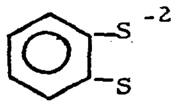
Several other indium derivatives have been reported [26, 27] which contain In-S bonded groups. The first groups are best considered as simple coordination compounds formed by the reaction of



XIV

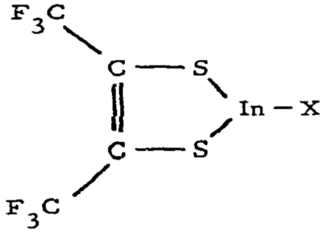


XV



XVI

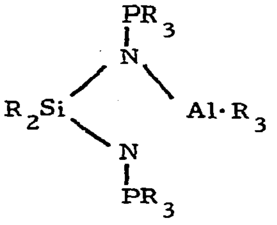
with In^{+3} and are noted here because of their use in aiding characterization of organometallic species containing In-S bonds. The second group result from a redox reaction between In (I) and 1, 2-bis(trifluoromethyl)dithieten, the monomer product is thought to have the structure which is thought to polymerize through interaction of the sulfur to yield



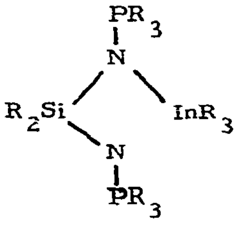
XVII

four (or six) coordinate indium. The In(III) species interacts with DMSO or other strongly coordinating ligands to give complexes which were characterized by several means showing that the oxidative addition to the S-S bond had occurred.

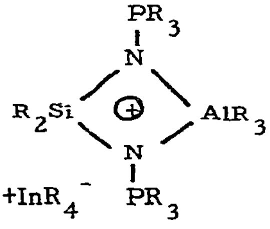
A number of studies have dealt with synthesis or structure of gallium and indium amides and related compounds. The reaction of Me_3In with XVII or Me_3Al with XIX yields the cation XX and $InMe_4^-$ [28].



XVIII



XIX



XX

The product was characterized by its nmr and ir spectra.

The silylamides were prepared by reaction 25. The compounds

$$MCl_3 + 3LiN(SMe_3)_2 \rightarrow 3LiCl + M[N(SIMe_3)_2]_3 \qquad (25)$$

M = Al, Ga, In

were all shown to be monomeric with the central metal in a trigonal environment. A variety of physical measurements were carried out including a complete study of the Raman and ir spectra. The results from the normal coordinate analysis provide good agreement between observed and calculated frequencies and may be interpreted to indicate a close relationship of the $MN(SiMe_3)_2$ fragments with the trisilylamine $X_3Si\text{-}N(SiMe_3)_2$ [29].

A series of simple gallazanes were also reported [30]. However, these all appear to be more complex in nature than the silylamide derivatives. In general they are formed by reactions <u>26</u> and <u>27</u>

$$Me_3N{\cdot}GaH_3 + RNH_2 \rightleftarrows RNH_2GaH_3 + Me_3N \qquad (26)$$

$$RNH_2GaH_3 \rightarrow RNH{\cdot}GaH_2 + H_2 \qquad (27)$$

where

R = Et, n-Pr, i-Pr, n-Bu, i-Bu, t-Bu

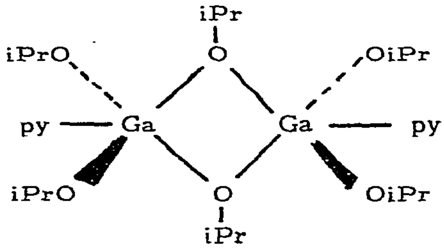
and are associated to some degree with dimers and trimers predominating. The compounds were characterized by ir, mass spectroscopy and extensive nmr results were reported. The latter were interpreted in terms of complex conformational equilibria.

Gallium "dihalides" have been reported to react with ethanol by two routes depending on temperature [31].

$$Ga_2X_4 + 3\,EtOH \xrightarrow{-0^{\circ}} Ga(OEt)_2X + GaX_3{\cdot}EtOH + H_2 \qquad (28)$$

$$Ga_2X_4 + 2EtOH \xrightarrow{25^{\circ}} Ga(OEt)X_2 + H_2 \qquad (29)$$

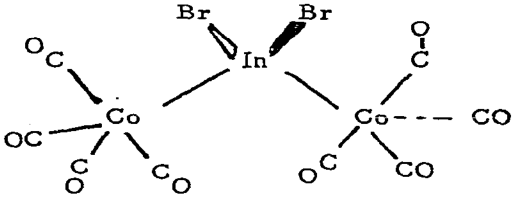
The products were characterized by their nmr and mass spectra and by cryoscopic molecular weight measurements. The latter showed that dimeric and trimeric species were present and an unstable form of $Ga(OEt)Br_2$ was reported to have a degree of aggregation near four. Various structures were proposed. These workers [32] also studied $[Ga(O\text{-}i\text{-}Pr)_3]_n$ and found that n varied as a function of time and temperature at least over the range of 2 to 4. Furthermore, they observed that it formed a 1:1 complex with pyridine which had an incongruent melting point. They suggested that in addition to the monomer adduct that some adduct such as that indicated in XXI might be present.



XXI

A study of the thermal decomposition of $Et_2InOCMe_3$ has been reported [33]. The results of this study show that decomposition at 230° for 25 hours yields $Et\,In(OCMe_3)_2$, In, C_2H_6, C_2H_4, butenes and Me_3COH. The indium compounds disproportionated into Et_3In and other derivatives.

Finally several others have reported on a series of compounds containing indium to transition metal bonds that should be included in the "organometallic" chemistry of this element. First Cradwick [34] reported the crystal structure of $Et_4N^+\,[Br_2Co_2(CO)_8In]^-$ which is essentially as shown in XXII



XXII

Hsieh and Mays [35] reported that a variety of compounds containing metal-metal bonds could be prepared under reasonably mild conditions, thus, In (I) halides were found to insert into $Mn_2(CO)_{10}$, $[\pi\text{-}CpFe(CO)_2]_2$ and $[\pi\text{-}CpM(CO)_3]_2$ (M = Mo or W) to yield the corresponding In(III) species. Studies by Robinson and Schussler [36] have shown that additional species may be formed in which indium is coordinated with four $Co(CO)_4^-$ groups giving $In[Co(CO)_4]_4^-$. This compound may undergo dissociation via <u>30</u> and <u>31</u>.

$$In[Co(CO_4]_4^- \rightleftharpoons In[Co(CO)_4]_3 + Co(CO)_4^- \qquad (30)$$

$$In[Co(CO)_4]_3 \rightleftharpoons In^{+3} \quad 3[Co(CO)_4]^- \qquad (31)$$

The three coordinate indium species may also form an adduct as indicated by the formation of $Ph_3PO\cdot In[Co(CO)_4]_3$.

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