

GALLIUM AND INDIUM

ANNUAL SURVEY COVERING THE YEAR 1977

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Introduction and Reviews

Studies on organogallium and -indium chemistry during 1977 have remained at nearly the same activity as those during 1976.* This survey describes these in the order of 1) reviews, 2) structure and bonding, and 3) synthesis and reaction chemistry, including two patents.

Reviews on 'Group III Elements (Al, Ga, In, and Tl)', one with 225 references [1] and the other with 91 references [2], and on 'X-Ray Diffraction of Inorganic, Coordination, and Organometallic Compounds of Group III Elements (B, Al, Ga, In, and Tl)' with 79 references [3] were published. An account on 'Preparation of Highly Reactive Metal Powders (including In) and Their Use in Organic and Organometallic Synthesis' with 51 references [4] and a dissertation on 'Indium Derivatives of Transition Metal Carbonyl Anions' [5] also were reported.

Structure, Bonding, and Thermodynamics (Including Synthesis)

The complete mass spectrum of $(\text{CH}_3)_3\text{Ga}$ was reported [6]. The total intensity of gallium-containing ions represents about 97.84 % of the overall ion current. The molecule shows low stability against electron impact. Analysis of the mass spectrum permitted the establishment of a fragmentation scheme for $(\text{CH}_3)_3\text{Ga}$ ions, which decomposed by successive elimination of methyl groups.

The vapor pressure of $(\text{CH}_3)_3\text{Ga}\cdot\text{O}(\text{C}_2\text{H}_5)_2$ at various temperatures was determined, from which the enthalpy and entropy of dissociation of the adduct were calculated as 12.1 ± 0.2 kcal/mole and 31.5 ± 0.5 e.u., respectively [7]. The heats of mixing of $(\text{CH}_3)_3\text{Ga}$ and other metal alkyls such as $(\text{CH}_3)_2\text{M}$ (M= Zn, Cd) with the $(\text{CH}_3)_2\text{E}$ type donors (E= S, Se, Te) were measured at 298 K [8]. In the resulting complex formation the relative donor ability of $(\text{CH}_3)_2\text{E}$ decreases in the order of $\text{S} \geq \text{Te} > \text{Se}$.

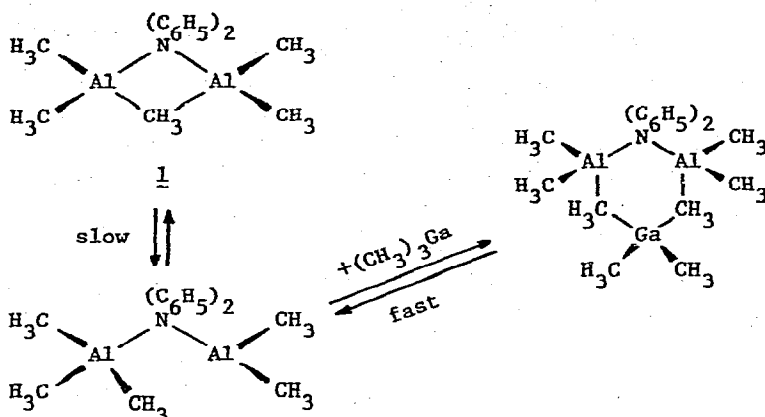
In solution chemistry, intermolecular exchange of the methyl group between $(\text{CH}_3)_3\text{Ga}$ and μ -methyl- μ -diphenylaminotetramethyldialuminum (1) was examined by variable temperature ^1H NMR spectroscopy in toluene [9]. The reaction was found

* T. Tanaka, Gallium and Indium, Annual Survey Covering the Year 1976,

J. Organometal. Chem., 147 (1978) 183.

to be zero-order in $(\text{CH}_3)_3\text{Ga}$ and first-order in the aluminum dimer, with activation parameters: $E_a = 20.7 \pm 0.8$ kcal/mole, $\Delta H^\ddagger = 20.1 \pm 0.8$ kcal/mole, and $\Delta S^\ddagger = +16.6 \pm 4.2$ e.u. at 290 K. A mechanism for this process has been proposed in which the rate-determining step is the opening of the methyl bridge accompanied by substantial distortion in the aluminum dimer, as shown in Scheme 1.

Scheme 1.



Recent ^{13}C NMR and ^{69}Ga , ^{71}Ga , and ^{115}In NQR studies on a series of substituted triarylgallium and -indium compounds have shown that ring-to-metal electron delocalization (pp_π or pd_π) does not occur in the ground state, that is, the Ga-C and In-C bonds should be thought of as single σ -bonds. A complete picture of such bonding, however, may be obtained from the study on the higher energy states. Smith and Brill measured the near ultraviolet spectra of $(\text{C}_6\text{H}_5)_3\text{B}$, $(\text{XC}_6\text{H}_4)_3\text{Ga}$ (X = a series of substituents), and $(\text{C}_6\text{H}_5)_3\text{In}$ in methylcyclohexane to examine the tendency for charge-transfer (CT) to occur in these compounds [10]. The results have indicated that moving down in the group, the energy of the CT band (E_{CT}) increases and the intensity of the band (ϵ_{max}) decreases; $(\text{C}_6\text{H}_5)_3\text{B}$, 4.32; $(\text{C}_6\text{H}_5)_3\text{Ga}$, 5.10; $(\text{C}_6\text{H}_5)_3\text{In}$, 5.26 eV. Ring substitution by alkyl or halogen in the para position of $(\text{C}_6\text{H}_5)_3\text{Ga}$ caused an increase of E_{CT} as the ionization potential of the monosubstituted benzene increases. Meta and ortho substitution led to practically no change in E_{CT} and ϵ_{max} compared with $(\text{C}_6\text{H}_5)_3\text{Ga}$. These results have been interpreted by the assumption that the spatial requirement of the ortho and meta substituents causes structural changes in the compounds that effectively insulate the gallium atom from an active role in the π -excited states.

N-Chloro-2-propanimine, $(\text{CH}_3)_2\text{C}=\text{NCl}$, reacts with $(\text{CH}_3)_3\text{M}$ (M = B, Al, Ga) in cyclohexane or toluene to yield colorless dimeric imino compounds $[(\text{CH}_3)_2\text{C}=\text{N}-\text{M}-(\text{CH}_3)_2]_2$, 24-88 % yields. The dimeric structure was confirmed by cryoscopic measurement in benzene and (for the gallium compound) the mass spectrum.

Infrared and Raman spectra have indicated the presence of a four-membered M_2N_2 ring with the point group D_{2h} [11]. The X-ray structure analysis showed that the gallium dimer crystallizes in the triclinic form, space group $P\bar{1}$ with $Z=1$, and the monomeric units are combined to a Ga_2N_2 four-membered ring including the center of symmetry, as depicted in Fig. 1. The structure was refined by the least squares analysis to $R=0.028$. The mean distances are: Ga-N 1.989 and Ga-C 1.966 Å [12].

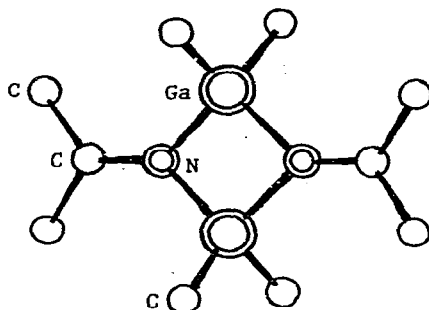


Fig. 1. Molecular structure of $[(CH_3)_2C=N-Ga(CH_3)_2]_2$.

The $(CH_3)_3In \cdot NH(CH_3)_2$ adduct evolves CH_4 on heating at 155-160°C to yield $[(CH_3)_2In \cdot N(CH_3)_2]_2$, mp 174-175°C, whose dimeric structure was characterized by 1H NMR and vibrational spectra. X-ray analysis of this compound showed that the crystals are monoclinic, space group $P2_1/c$ with two dimers per unit cell, and the structure, which was refined to $R=0.068$, consists of a slightly distorted square plane of alternating In and N atoms with each atom bonded to two methyl groups, as shown in Fig. 2 [13].

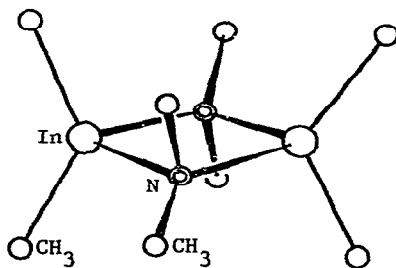


Fig. 2. Molecular structure of $[(CH_3)_2In \cdot N(CH_3)_2]_2$.

The reaction of $(\text{CH}_3)_3\text{Ga}\cdot\text{O}(\text{C}_2\text{H}_5)_2$ with a double ylide, methanidobis(dimethylphosphonium-methylide) $(\text{CH}_3)_3\text{P}=\text{C}=\text{P}(\text{CH}_3)_3$, in benzene gave a cyclic dimethylgallium complex (see Fig. 3), colorless needles of mp 41°C , 65 % yield [14, 15]. The X-ray structure analysis ($R=0.047$) showed that the crystals are monoclinic, space group $P2_1/n$ with $Z=4$, and the molecule forms a six-membered ring with a quasi-tetrahedral configuration of substituents at the Ga and P atoms which are bridged by two CH_2 and one planar CH bridge, as shown in Fig. 3 [14].

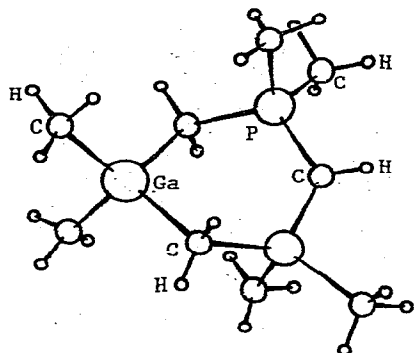


Fig. 3. Molecular structure of $(\text{CH}_3)_2\text{Ga}[\text{CH}_2\text{-P}(\text{CH}_3)_2]_2\text{CH}$.

Trimethylgallium reacts with N-methyldifluorophosphoramidate, $\text{HNCH}_3\text{P}(=\text{O})\text{F}_2$, in pentane to give a dimethylgallium derivative, $[(\text{CH}_3)_2\text{GaNCH}_3\text{P}(=\text{O})\text{F}_2]_2$, colorless liquid of bp $38\text{-}39^\circ\text{C}$ at 10^{-2} mmHg, 65 % yield. The dimeric structure was confirmed by cryoscopic measurement in benzene. ^1H , ^{31}P , and ^{19}F NMR spectra of this compound are best interpreted by assuming the geometry shown in Fig. 4.

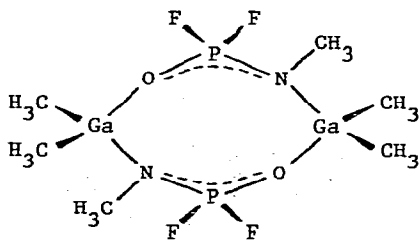
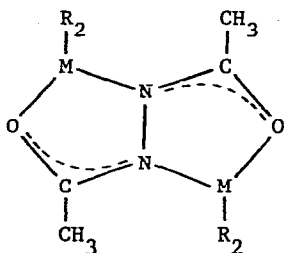


Fig. 4. Configuration of $[(\text{CH}_3)_2\text{GaNCH}_3\text{P}(=\text{O})\text{F}_2]_2$.

There has, however, been found no rule of mutual exclusion in the vibrational spectra, suggesting a low symmetry of this molecule (C_2 or lower than that) [16].

The reactions of R_3M ($M = Ga, In$; $R = \text{alkyl}$) with N,N -diacetylhydrazine (L) in pentane or benzene yield compounds of the $(R_2M)_2L$ type (2a-2c). The mass spec-



2a: $M = Ga, R = CH_3$; mp 180-182°C

2b: $M = Ga, R = C_2H_5$; mp 92-94°C

2c: $M = In, R = CH_3$; mp >250°C (dec.)

trum of 2a suggested the presence of a double five-membered ring. On the basis of this geometry, the infrared and Raman spectra in the 2000-200 cm^{-1} range have been interpreted [17].

The structural and solution chemistry of organometallic compounds which contain a transition metal-Group III metal bond are of interest because of the redistribution reaction which may occur. In this respect, metal-metal derivatives $(CH_3)_{3-x}Ga[M(CO)_3C_5H_5-\pi]_x$ ($M = Mo, x = 1-3$; $M = W, x = 1$) were synthesized by reaction of $(CH_3)_3Ga$ with $M(CO)_3C_5H_5-\pi$ in methylcyclohexane [18]. They are pale yellow to dark orange crystals, very soluble in aromatic and ethereal solvents, and sensitive to air oxidation and to moisture. 1H NMR and infrared evidence indicated that methyl exchange in toluene is (i) very rapid between $(CH_3)_3Ga$ and $(CH_3)_2Ga \cdot Mo(CO)_3C_5H_5-\pi$, (ii) considerably slower between $(CH_3)_3Ga$ and $CH_3Ga[Mo(CO)_3C_5H_5-\pi]_2$, and (iii) slow or non-existent in the $(CH_3)_2Ga \cdot Mo(CO)_3C_5H_5-\pi$ and $CH_3Ga[Mo(CO)_3C_5H_5-\pi]_2$ system. The exchange of $Mo(CO)_3C_5H_5-\pi$ was slow on the NMR time scale. The crystal structure of $(CH_3)_2Ga \cdot W(CO)_3C_5H_5-\pi$ was determined from single-crystal X-ray data. This compound crystallizes in the monoclinic form, space group $P2_1/n$ with $Z = 4$. Full-matrix least squares refinement gave $R_1 = 0.075$ and $R_2 = 0.089$ for 1936 data having $I > 3\sigma(I)$. The solid state structure of this compound consists of discrete monomers. The molecule consists of a W atom bonded to three CO ligands, to a $(CH_3)_2Ga$ moiety, and to a π -bonded cyclopentadienyl group, as depicted in Fig. 5. The structural parameters are very similar to those observed in $Ga[W(CO)_3C_5H_5-\pi]_3$ (A. J. Conway et al., J. Chem. Soc., Dalton, (1975) 1945).

Following to the X-ray study on $[(CH_3)_4M]^+[CH_3InCl_3]^-$ ($M = As, Sb$) reported previously (H. J. Guder et al., Z. Naturforsch., 31b (1976) 1185), single crystal X-ray analyses were performed for two ionic crystals, tetramethylarsonium-dichlorodimethylgallate $[(CH_3)_4As]^+[(CH_3)_2GaCl_2]^-$ and -trichloromethylgallate $[(CH_3)_4As]^+[CH_3GaCl_3]^-$. The former crystallizes in the monoclinic form, space group $P2_1/c$ with $Z = 4$, and the latter in the monoclinic form, space group Pc with $Z = 2$. Mean bond lengths: Ga-Cl 2.223 and Ga-C 1.934 Å. Both the As and Ga atoms in these

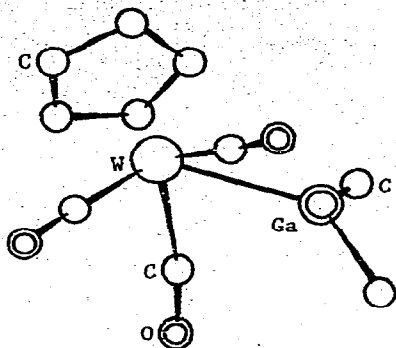


Fig. 5. Molecular structure of $(\text{CH}_3)_2\text{Ga}\cdot\text{W}(\text{CO})_3\text{C}_5\text{H}_5\text{-}\pi$.

compounds are tetrahedrally surrounded; the anionic tetrahedra are markedly distorted [19].

The chalcogen ions X^{-2} ($\text{X} = \text{O}, \text{S}, \text{Se}$) in their potassium salts react with excess $(\text{CH}_3)_3\text{M}$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) at $50\text{-}90^\circ\text{C}$ to afford complexes of the $[\text{X}(\text{M}(\text{CH}_3)_3)_4]^{2-}$ type almost quantitatively. They are colorless, microcrystalline, hygroscopic powders. Infrared and Raman spectra indicated that the chalcogen ions are surrounded tetrahedrally by the metal atoms which are bridged by the methyl group, as shown in Fig. 6. The Raman spectrum of $(\text{CH}_3)_3\text{In}$ was also reported [20].

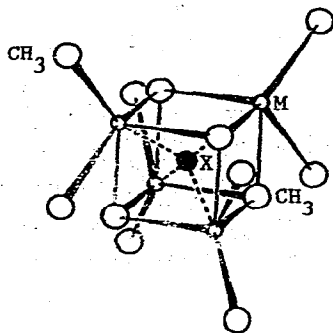


Fig. 6. Geometry of $[\text{X}(\text{M}(\text{CH}_3)_3)_4]^{2-}$: $\text{M} = \text{Al}, \text{Ga}, \text{In}$; $\text{X} = \text{O}, \text{S}, \text{Se}$.

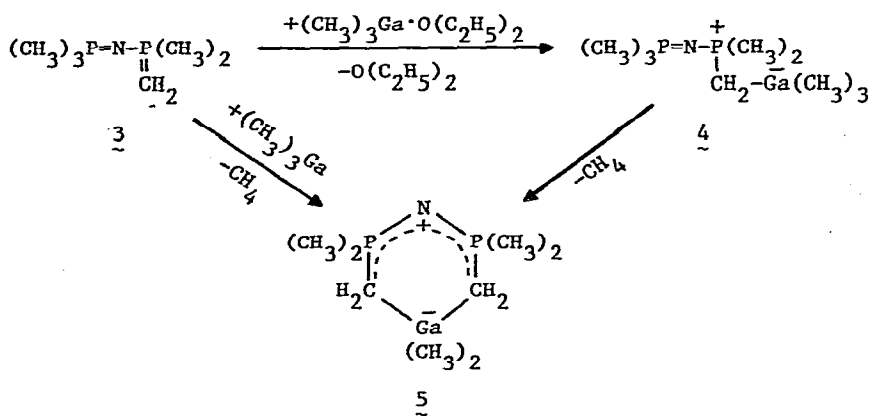
Synthesis and Reaction Chemistry

Trialkylgallium was purified by treating its vapor with a Ga melt (previously heated with hydrogen at $400\text{-}500^\circ\text{C}$) at $80\text{-}100^\circ\text{C}$, followed by distillation [21]. The methylation of various hydrides, SiH_4 , CH_3SiH_3 , Si_2H_6 , GeH_4 , and B_2H_6 , with

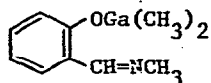
$(\text{CH}_3)_3\text{Ga}$ were examined neat in Pyrex reaction vessels with and without Pyrex beads, which act to increase the surface area and to decrease the volume, at 230–324°C. The products from the SiH_4 and Si_2H_6 reactions were CH_3SiH_3 , $(\text{CH}_3)_2\text{SiH}_2$, and $(\text{CH}_3)_3\text{SiH}$. Methylgermanium hydrides and $(\text{CH}_3)_4\text{Ge}$ were obtained from GeH_4 . The only methylated product from B_2H_6 was $(\text{CH}_3)_3\text{B}$. The results obtained for reactions in the vessel with and without beads suggested that the silane reactions are surface-catalyzed (presumably by surface hydroxyl groups of the beads), while those of GeH_4 and B_2H_6 may occur via a gas-phase free radical process [22].

Trimethylgallium etherate reacted with a double ylide, dimethyl(methylene)-[(trimethylphosphoranyliden)amino]phosporan (3) in diethyl ether at 0°C to give the 1:1 complex (4), 91 % yield, which on heating in benzene or toluene afforded the chelate complex (5), 97 % yield. Compound 5 also was obtained directly from a mixture of 3 with $(\text{CH}_3)_3\text{Ga}$ or its etherate on heating (Scheme 2). The characteristic $\nu(\text{PNP})$ and $\nu(\text{GaC}_4)$ frequencies, and ^1H and ^{31}P NMR data were presented [23].

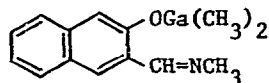
Scheme 2.



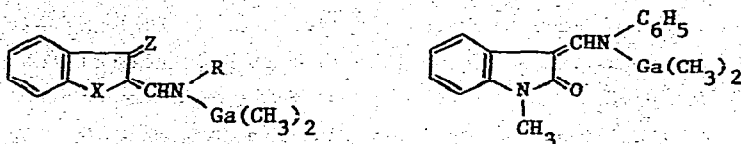
Dimethylgallium derivatives of aromatic and heterocyclic azomethines, 6–9, were prepared by heating an equimolar mixture of $(\text{CH}_3)_3\text{Ga}\cdot\text{O}(\text{C}_2\text{H}_5)_2$ with the corresponding azomethine in benzene at 50–80°C, 30–60 % yields [24].



6



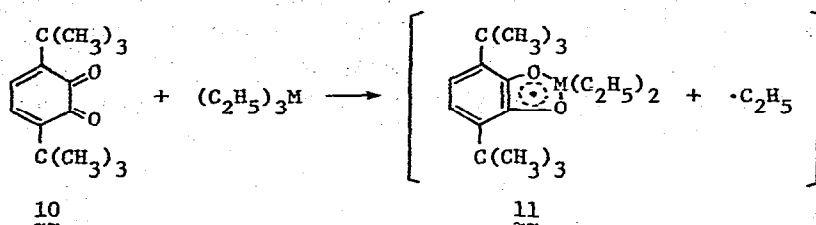
7



8: R = C₆H₅, C₆H₄CH₂; X =
CO, O, S; Z = O, S

9

Reaction of (C₂H₅)₃M (M = Al, Ga, In, Tl) with sterically hindered 3,6-di-tert-butyl-o-quinone (10) was reported to proceed by a one electron transfer mechanism via a paramagnetic chelate intermediate (11) to give 2-ethoxy-3,6-di-tert-butylphenol, 70-90 % yields [25].

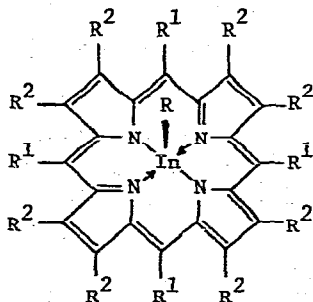


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11

Some mixed complexes of gallium of the NaGaH_nR_{4-n} and NaGaR_nR'_{4-n} types (R, R' = CH₃, C₂H₅) were prepared by the alkyl-hydride and alkyl-alkyl exchange reactions in the systems of NaGaR₄-NaGaH₄, NaGaR₄-NaGaR'₄, NaGa(C₂H₅)₄-(CH₃)₃Ga, and NaGaH₄-(C₂H₅)₂Mg. Reaction of (C₂H₅)₃Ga with MH (M = Na, K) in diethyl ether gave MGa(C₂H₅)₃H. With LiH, however, LiH·2(C₂H₅)₃Ga was formed [26]. Analogous indium complexes, MIn(CH₃)₃H (M = Li, Na, K), were prepared by treating MH with (CH₃)₃In. The Li and Na salts are unstable and decomposed to MIn(CH₃)₄, MH, and In [27].

Isolation of metalloporphyrins involving metal-carbon or metal-sulfur bonds is a currently important problem in the study on the insertion reactions of small gaseous molecules or to find biomimetic systems. In this respect, the first indium porphyrins containing indium-carbon bonds, 12, were synthesized by treating



12: R = CH₃, C₂H₅, n-C₄H₉,
t-C₄H₉, C₆H₅;
R¹ = C₆H₅ when R² = H;
R¹ = H when R² = C₂H₅

mesotetraphenyl- or octaethylporphyrin (TPP or OEP) with alkyl- or aryllithiums in dry benzene, 35-75 % yields. The structure of the compounds was established by their ^1H NMR spectra; the alkyl or aryl protons are strongly shielded.

Indium-sulfur bond containing porphyrins, $\text{TPPInSC}_6\text{H}_5$ and $\text{OEPInSC}_6\text{H}_5$, were also obtained by treating TPPH_2 or OEPH_2 with InCl_3 in thiophene, 50 or 60 % yield. These compounds are stable in contrast with the iron analogs [28].

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