GALLIUM AND INDIUM

ANNUAL SURVEY COVERING THE YEAR 1972

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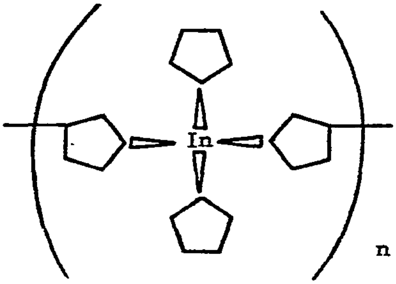
The study of gallium and indium derivatives has remained at about the same level during 1972 as during 1971 with a modest amount of structural and spectroscopic work, studies on the synthesis and reactions of organic derivatives, and studies on species containing metal-metal bonds. This survey will deal with these topics in this order.

Structural and Spectroscopic Studies

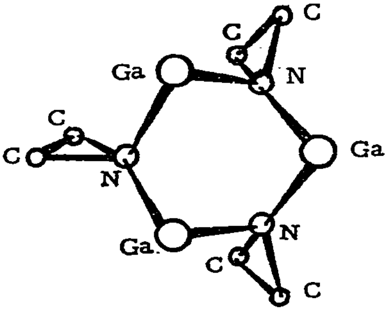
Among the simplest derivatives of indium, the alkali metal (Li, Na, K Rb, Cs) tetramethylindates, have been prepared either by addition of LiMe to Me_3In or by reaction of M with Me_3In.[1] The crystal structure of $LiInMe_4$ and $NaInMe_4$ have been determined from single-crystal X-ray intensities and have been shown to be isostructural. They crystallize in cubic primitive lattices with one molecule per unit cell. The ionic units, $InMe_4^-$ is a regular tetrahedron with In-C distances of 2.22Å. The crystallographic data and ir data are in agreement with the assumption that the cations and anions are isolated.

The crystal structure of a more complex system, tris(cyclopentadienyl)-indium has been determined by Einstein et al.[2] at -100°. They found two types of cyclopentadienyl groups in this molecule in the solid state, one type is essentially bonded to the indium while the second serves as a bridging group and appears to be bonded through the 1 and 3 atoms of the ring to two indium atoms. This gives rise to a chain structure as indicated in I with the indium in an essentially tetrahedral enviornment. In solution the molecule is monomeric with rapidly exchanging cyclopentadienyl groups as shown by the equivalence of all of the protons by nmr studies.



I

Another interesting structure is that of aziridinylgallane trimer $[(CH_2)_2NGaH_2]_3$ which has been determined by X-ray techniques and has the molecular structure indicated in II in which the aziridine rings are nearly perpen-



II

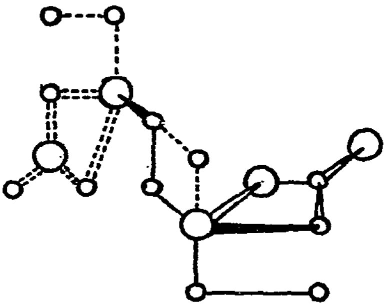
dicular to the $(GaN)_3$ ring.[3] The latter ring system is in a chair conformation.

Trialkylindium derivatives have been shown to undergo the reaction indicated in 1 yielding products which have been characterized by ir, Raman

$$R_3In + HOOCR' \xrightarrow[\text{benzene}]{5^o - 10^o} R_2InOOCR' + RH \qquad (1)$$

R = Me, Et; R' = Me, Et

and X-ray studies.[4] These studies have shown that the individual molecules are dimeric and are centrosymmetric as indicated in III with bridging alkyl



III

groups in the solid state. In solution the compounds were monomeric.

In continued studies on the reactions of group III alkyls with carboranes and their structures, it has been shown that trimethylgallium and indium react with $C_2B_4H_8$ to yield the 1-$MeMC_2B_4H_6$ derivative in moderate yields.[5]

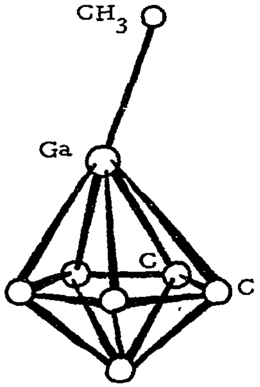
$$C_2B_4H_8 + Me_3M \rightarrow MeMC_2B_4H_6 + Me_3B + \text{solids} \qquad (2)$$

Both the indium and gallium derivatives react as indicated in 3 with bromine.

$$MeGaC_2B_4H_6 + Br_2 \xrightarrow[CS_2,\ 25^{\circ}]{AlBr_3} (Me_2GaBr)_2 + MeBr + HBr \qquad (3)$$

Reaction of the gallium derivative with HCl yield $C_2B_4H_8$, however, with the indium derivative decomposition of the cage occurs.

A single crystal X-ray study was carried out on the 1-$MeGaC_2B_4H_6$. The structure is shown in IV. The gallium atom is not symmetrically bound to the carborane cage but is displaced toward the boron atoms. The methyl group is also tipped to one side. The bonding in this derivative has been discussed in some detail.



IV

Beran et al.[6] have determined the structures of a series (Al, Ga, In, and Tl) of 2, 2', 2''-terpyridyl complexes of group III chlorides and have shown that the metal is located in a distorted octahedral environment in all of these systems. The assignment of the structures from ir data for this type of system are discussed in view of the known structures of these derivatives.

An interesting sidelight to the structural studies on gallium species is seen in the structure of cis-dichlorobis-(2,2'-bipyridyl)gallium(III) tetrachlorogallate(III).[7] It was shown that the cation of this species contained the chlorine atoms cis to one another rather than trans as previously suggested on the basis of ir studies. This paper also provides additional data on Ga-N and Ga-Cl bond distances for comparison with those obtained in other oxganometallic derivatives.

Additional studies dealing with the halide structures has been presented in a study of the force constants for the indium derivatives InX_4^- (X = Cl, Br or I)' $InCl_5^{-2}$, $InCl_6^{-3}$, and for InX_3^{-2} (X = Cl, Br and I) using a simplified quadratic valence force field model.[8] These results have been compared with results on tin species previously reported.

The ir spectra of $C_6H_5MX_2$ (M = B, Al, Ga; X = Cl, Br) were measured in the 200 - 3500 cm^{-1} region.[9] The assignment of the individual bands was carried out based on the calculated and experimental data of the in-plane and out-of-plane vibrations. The analysis of the frequencies and of the changes of the shapes of the vibrations containing the substituents M or X showed an increase of the force constant for the C - M and MX bonds for B in comparison with Al or Ga. The structures of the compounds were discussed.

Studies by Shriver and Alich[10] have provided some information on the electronic and molecular structure of carbonyl complexes. They examined the electronic spectra of Et_3Al, $(i\text{-}Bu)_3Al$ and Me_3Ga with $Mo(phen)(PPh_3)_2$-$(COAlEt_3)_2$ and observed a large blue shift in the charge transfer band in the molybdenum complex which they associated with a decrease in energy of the $Mo(CO)_2$ π_b, molecular orbital. This resulted in additional Mo→CO back bonding and a greater separation in the energy states as indicated. They further noted that shifts in the charge transfer spectra may be used to establish the following order of electron-pair acceptor strength: $Et_3Al > (i\text{-}Bu)_3Al > Me_3Ga$. They noted that the O in the CO group only interacts with the relatively hard acids of Al and Ga but appears not to interact with the soft acid BH_3. It was therefore concluded that the carbonyl oxygen served only as a hard base which accounts for the fact that carbonyl bridges of the type M-C=O-M are not observed.

Several studies based on nmr measurements have delt with exchange and rotational phenomena in derivatives of these metals. Dunn and McDowell[11] have studied the ^1H nmr of H_3GaNMe_3 from 63-300°K and derived expressions related to the relaxation behavior of the methyl groups on the NMe_3. These studies included evaluation of activation energies for motions of the methyl groups and rotation about the Ga-N bond which was found to be 3.6 ± 0.3 kJ/mole.

Visser and Oliver[12] have reported the exact analysis of a number of vinylmetallic derivatives, including those of the Group III metals, and have discussed the exchange particularly between trivinylindium and its trimethyl amine adduct and for trivinylgallium and its trimethylamine adduct. These exchange reactions appear analogous to those reported earlier for the exchange of the methyl derivatives with the indium species exchanging with a lower activation energy than that of gallium. The spectrum of $Vi_3Al\cdot NMe_3$ was also reported. The lines in this spectrum were broadened due to metal proton coupling and possibly due to quadrupolar relaxation making the parameters determined less accurate.

In another study Brown and Murrell[13] have reported further data on the exchange between Me_3Ga and Me_6Al_2 as well as the exchange between Me_3Ga and $Me_3Al\cdot B$ (B = 2, 6-lutidine, pyridine, or OEt_2). They discussed these exchange reactions in terms of an initial dissociation step followed by a psuedo chain reaction involving exchange of alkyl groups.

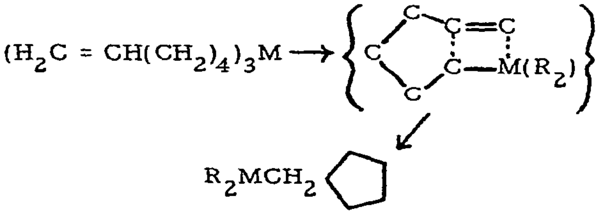
Synthesis and Reactions of Organic Derivatives

Several studies have appeared dealing with the properties and reactions of the alkyl derivatives of gallium and indium.

One of these studies was a determination of the thermodynamic parameters for the synthesis and pyrolysis of triethylgallium during the reaction of EtCl with gallium metal.[14] In another study the heat of combustion was determined calorimetrically for Et_3Ga to be 1182± 0.9 kcal/mole. The standard heat of formation was calculated as -23.6± 1.3 kcal/mole for liquid Et_3Ga.[15] The heat of evaporation is 9.2± 0.1 kcal/mole.

It has been shown that $(n\text{-}Bu)_3Ga$ catalyzes cis/trans isomerization of stereoregular n-octenes when irradiated with uv light.[16] The effect is diminished if the $(n\text{-}Bu)_3Ga$ is complexed with NEt_3. Et_3In does not serve as a catalyst either in the free or complexed form.

St. Denis et al.[17] have investigated the synthesis and reactions of hex-5-enyl derivatives of gallium and indium. The compounds were prepared by exchange between the metal and the mercury derivative, R_2Hg. The compounds were both shown to undergo cyclization as shown in 4 on heating for



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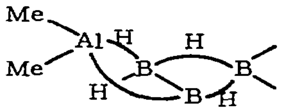
extended periods. This reaction represents the first reported cyclization reactions for gallium and indium compounds and also shows that interaction occurs between the metal center and the double bond.

Borlin and Gaines[18] have prepared the interesting derivative $Me_2GaB_3H_8$ via reaction 5. Variable temperature nmr studies have shown that the compound undergoes a variety of exchange reactions. The low temperature studies are compatible with the structure indicated in V.

$$Me_2GaCl + NaB_3H_8 \longrightarrow Me_3GaB_3H_8 + NaCl \qquad (5)$$



V

Several papers have appeared dealing with the reactions of R_3M derivatives with acids, phosphates and related compounds which yield species with a variety of ring structures containing both metal, oxygen, and possibly an additional element.

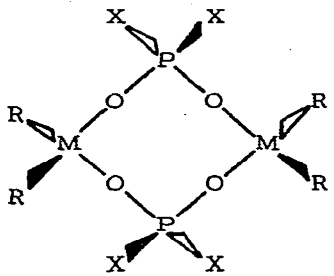
Weidlein and co-workers have studied the reaction indicated in 6 and have reported the results in a series of papers.[19, 20, 21] The general structure proposed is indicated in VI and is based on ir, Raman, ^1H, ^{19}F, and ^{31}P nmr

$$R_3M + HOOPX_2 \longrightarrow R_2MOOPX_2 + RH \qquad (6)$$

R = Me, Et

X = F, Cl, Me

M = Ga, In



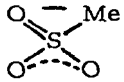
VI

studies. Studies on the dimethylarsinates of aluminum, gallium and indium also have been reported but the structural determinations were inconclusive.[21]

In subsequent studies Olapinski and Weidlein[22] discussed the preparation of R_2InSO_3R (R = Me, Et) via reactions 7 and 8. The compounds were characterized by the physical properties and spectroscopic measurements. On this

$$R_3In + SO_3 \longrightarrow R_2InO_3SR \tag{7}$$

$$R_3In + MeSO_2OH \longrightarrow R_2InO_3SMe \tag{8}$$

basis it was proposed that the species Me_2In^+ and  were present.

It has also been reported that gallium and indium alkyls react with oxalic acid as indicated in 9.[23] The resulting metal derivatives have been studied

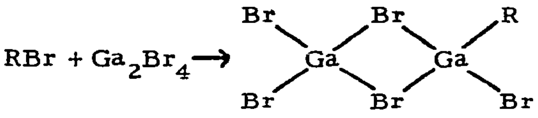
$$2R_3M + H_2O_2C_4 \rightarrow (R_2M)_2O_4C_2 + 2RH \tag{9}$$

R = Me, Et

M = Ga, In

by ir, Raman, and mass spectroscopy and on the basis of these studies a nonplanar structure of D_2 symmetry has been proposed.

Lind and Worrall[24] have investigated the oxidative addition of Ga_2Br_4 to a variety of alkyl halides. They observed two types of reaction, the first is shown in equation 10 and lead to the pure product indicated. This was



(10)

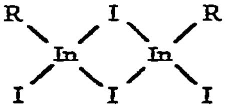
established by nmr, ir, and mass spectral studies. The second reaction was observed for n-propyl, n-butyl, benzyl, sec-propyl and t-butylbromides and similar processes also appeared to occur for 1,2-dibromoethane, 1,3-dibromopropane and 1,5-dibromopentane. This reaction appeared to be initial oxidative addition followed by decomposition.

In a subsequent paper they described the reaction between Ga_2X_4 (X = Cl, Br, I) and RX (R = Me, Et).[25] All of the gallium derivatives undergo oxidative addition with methyl bromide and iodide but only Ga_2I_4 and Ga_2Br_4 react with methyl chloride. The reactions with the ethyl halide appear to be similar but the products were difficult to isolate. The methyl derivatives $MeGa_2X_5$, $MeGa_2Cl_4I$ and $MeGa_2Br_4I$ were isolated and characterized by Raman, ir, ^1H nmr and mass spectroscopy.

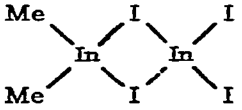
Poland and Tuck[26] have reported on the preparation of $RInI_2$ derivatives by oxidative addition as indicated in 11. The initial products formed for this

$$RI + InI \longrightarrow RInI_2 \qquad (R = Me,\ Et,\ n\text{-}Bu) \qquad (11)$$

reaction appears to have the iodine bridged structure indicated in VII for



VII

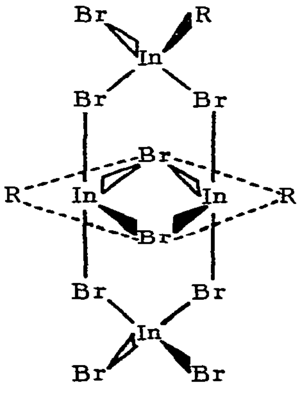


VIII

R = Et and n-Bu, but appears to undergo rearrangement yielding the unsymmetrical product VIII when R = Me. The proposed structures were based primarily on ir evidence but were also supported by mass spectral studies. The vibrational spectra of the unsymmetrical derivatives $MeIInI_2InI_2$ and $MeIInI_2InMe_2$ were also reported and discussed.

Similar results have been reported by Gynane and Worrall[27] who have examined the oxidative addition of InI to MeI. The compound $MeInI_2$ obtained appears to have the structure $Me_2In^+InI_4^-$ with a linear Me_2In^+ ion based on spectral observations on the $Me_2In_2I_4$ species.

Gynane et al.[28] have also studied the oxidative addition of InBr or InI to alkyl halides where the alkyl group is Me, Et, Pr, or Bu. The products obtained by them were examined by spectroscopic means. They interpreted these data as showing all compounds as halide bridged dimers with the exception of Me_2In^+, InI_4^- which has the indicated ionic structure corresponding to that reported in the preceding paper while $MeInBr_2$ and $EtInBr_2$ appeared to contain halide bridges but are polymeric in nature. All except $EtInBr_2$ are dimeric in the gas phase and this appears to be tetrameric. The structure shown in IX is one of the possibilities for this species.



IX

Direct reactions between metal and alkyl halides have also been described. Gynane and Worrall[29] have shown that gallium metal reacts with alkyl halides as indicated in 12 yielding the indicated products after several weeks at room

$$3RX + 2Ga \longrightarrow RGaX_2 + R_2GaX \qquad R = Me,\ Et;\ X = Br,\ I \tag{12}$$

temperature. It was also shown that indium metal reacts with alkyl halides by the same route yielding the mixed alkyl halides.[30] All products were characterized by their ir spectra.

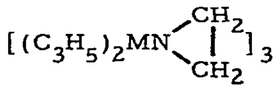
Tricyclopentadienylindium has been prepared in good yield by the reaction of $InCl_3$ and CpLi as indicated in 13.[31] It was suggested that excess CpLi

$$InCl_3 + 3CpM \longrightarrow Cp_3In + 3MCl \tag{13}$$

resulted in the reaction of Cp_3In via 14 yielding CpIn. In addition the methyl-

$$Cp_3In^{III} + 2Cp^- \longrightarrow CpIn^I + 2Cp_2 \tag{14}$$

cyclopentadienyl species and the indenyl derivative have also been studied. The tricyclopentadienyl derivatives show fluxional behavior where as the indenyl derivative does not. The adducts Cp_3InPPh_3, $Cp_3In\cdot Bipy$, $Cp_3In\cdot Phen$ and $(Indenyl)_3In\cdot OEt_2$ were prepared and it was stated that the indenyl derivative served as a stronger Lewis acid. The "ate" derivative $LiIn(Indenyl)_4$ was also prepared. All compounds were characterized by ir, nmr, and mass spectra.

Muller et al.[32] have prepared the trimeric species  $[(C_3H_5)_2MN{<}\overset{CH_2}{\underset{CH_2}{|}}]_3$ (M = Al, Ga) by reaction of the amine with $(C_3H_5)_3M$. The degree of aggregation was established by cryoscopic measurement in benzene. The

^{1}H nmr spectra were reported and were typical of cyclopropylmetal compounds. All cyclopropyl groups were equivalent on the nmr time scale at room temperature and theamideprotons gave rise to a single line under these conditions. The ir and Raman spectra of $(C_3H_5)_6Al_2$ both in the crystaline and fused (Raman) state were obtained as well as the ir and Raman spectra of $[(C_3H_5)_2MNC_2H_4]_3$, the latter were examined in detail and shown to be consistant with a nonplanar six-membered metal nitrogen ring system.

Storr et al.[33] have studied the synthesis and spectral properties of (N-polymethylene)cyclogallata-azonianes, $[CH_2(CH_2)_x \cdot N \cdot GaH_2]_n$, and some of the properties of the boron and aluminum derivatives for comparison. The compounds were prepared via reaction 15 with the related compound

$$CH_2 \cdot (CH_2)_x \cdot NH_{(g)} + Me_3N \cdot GaH_{3(s)} \longrightarrow$$

$$1/n[CH_2 \cdot (CH_2)_x \cdot N \cdot GaH_2]_n + H_2 + Me_3N \qquad (15)$$

$$x = 1,\ 2,\ 3,\ \text{or } 4$$

prepared from B_2H_6 and cyclic amine while the aluminum species were obtained by reaction of the cyclic amine with $(Me_3N)_2AlH_3$. The degrees of association were determined and it was shown that the ring size was critical in the degree of aggrégation. Trimers were obtained for x = 1 for all compounds while for x = 2 the boron and aluminum derivatives were dimeric. The unusual behavior of aluminum to yield trimers in all cases except with x = 4 (n = 2.35) could not be accounted for on steric grounds.

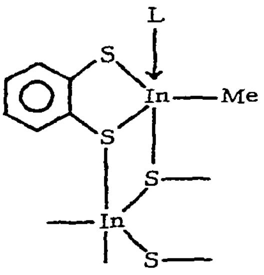
The nmr spectra of all derivatives were reported and it was noted that in the trimeric $[\sqsubset NGaH_2]_3$ rapid inversion of the chain form must occur in order to account for the equivalence of the methylene protons. It was also suggested that a rapid dimer - trimer equilibrium appeared to take place since only a single line was observed in the nmr spectrum for the CH_2 groups, while the average degree of aggregation is 2.6. Additional discussions of the reactions of those species were presented.

Berniaz and Tuck[34] have reported work on the formation of toluene-3,4-dithiolate complexes of indium. The initial product was obtained from the reaction shown in **16** with possible intermediate formation of a complex with

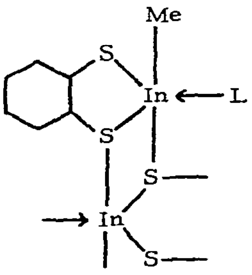
$$Me_3In + MeC_6H_3(SH)_2 \longrightarrow (MeC_6H_3S_2)InMe + 2CH_4 \qquad (16)$$

the dithiol. This species was shown to form complexes with NMe_3, DMSO, pyridine, 2,2'-bipyridine and 1,10-phenanthroline.

The bidentate ligands appear to form monomeric four coordinate indium complexes while the monodenates, with the exception of NMe_3, appeared to yield dimers with the possible stereoisomers indicated in X and XI. These



X



XI

isomers were postulated primarily on the basis of nmr studies which show two kinds of Me groups and are also consistant with ir studies.

Deacon and Parrott[35] have prepared a number of complexes, $(C_6F_5)_3In \cdot L$ (L = Ph_3P, Ph_3PO, Ph_3AsO, N,N,N',N'-tetramethylenediamine) as well as $(C_6F_5)_3In(OSMe_2)_2$ and $[(C_6F_5)_3In]_2\cdot$bipy by displacement of dioxane from $(C_6F_5)_3In\cdot$diox. Several other complexes have been obtained by displacement of OEt_2 from $(C_6F_5)_3In\cdot OEt_2$. These compounds have been characterized by ir and molecular weight measurements. Structures containing four and five coordinate indium have been proposed.

Equimolar mixtures of R_nGaCl_{3-n} and Et_3Z (R = Me, Et; n = 2, 3; Z = As, N, Sb) gave 1:1 coordination compounds.[36] Alternatively they were prepared from $Me_3Ga\cdot Et_2O$. The reactions were exothermic and the products which were largely distillable liquids were stable in air and attacked weakly by H_2O or acids; the compounds involving amines were less stable than the others and were decomposed by light.

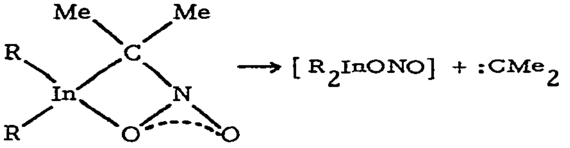
Maeda et al.[37] have investigated the reaction of trimethylstibine sulfide with R_2InX and $RInX_2$ (R = Me, Et; X = Cl, Br, I) derivatives. They reported that these species formed stable 1/1 adducts with In-S bonds suggested on the basis of ir measurements. They also noted that on refluxing of these complexes reaction occurred with both sulfur and alkyl migration yielding RInS and RMe_3SbX. This reaction was facilitated in polar solvents such as methanol.

It has been shown that trialkylindium derivatives react with α-mononitroalkanes by the reaction indicated in **17**.[38] Et_3In gave good yields of the product.

$$R_3In + InC(NO_2)R'_2 \longrightarrow R_2In[C(NO_2)R'_2] + RH \qquad (17)$$

$$R' = H,\ Me;\ R = Me,\ Et$$

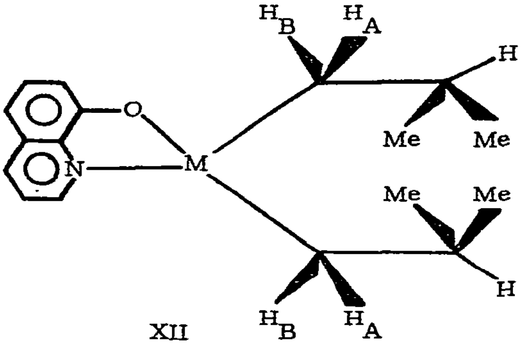
A pure sample of diethyl(nitromethyl)indium decomposed explosively at 100°. The dimethyl and diethyl(nitromethyl)indium decomposed to yield the corresponding fulminate R_2InONC. The general mode of decomposition was thought to proceed via the following reaction with interaction between



(18)

the In and O leading to the formation of the carbene intermediate. Evidence for this was obtained from the decomposition products, which contained among other things tetramethylethylene and from an examination of the ^{115}In nqr which indicated In-O coordination.

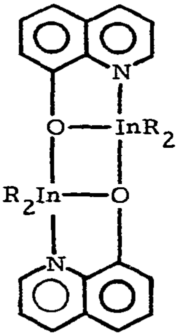
Sen et al.[39] have prepared the quinolinolato-complexes of the form R_2MQ (R = Me, Et, i-Bu; M = Al, Ga, In) and have studied their nmr spectra in some detail. These complexes have the general structure indicated in XII which gives rise to diastereotopic methylene protons in the systems. The



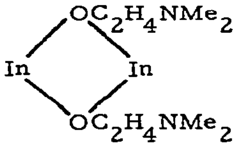
XII

changes in the nmr parameters were discussed as a function of the central metal particularly as this influences the diastereotopic character of the methylene protons.

The compounds Me_2InDtc (Dtc = $SSCNMe_2$)$RInDtc_2$, Et_2InOx (Ox = Oxinate) and $R_2InOC_2H_4NMe_2$ (R = Me, Et) were synthesized.[40] It has been proposed that Me_2InDtc and $RInDtc_2$ contain tetra and penta coordinated indium respectively. It has also been suggested that R_2InOx derivatives have the dimeric structure indicated in XIII containing five coordinate indium while $R_2InOC_2H_4$-NMe_2 derivatives have the structure indicated in XIV probably containing weak In-N bonds.



XIII



XIV

A variety of mixed isopropoxides of the form $In[M(\underline{i}\text{-}PrO)_4]_3$ have been prepared by reaction 19.[41] These materials and the corresponding mixed

$$InCl_3 + KM(O\text{-}i\text{-}Pr)_4 \longrightarrow In[M(O\text{-}i\text{-}Pr)_4]_3 + KCl \qquad (19)$$

$$M = Al,\ Ga$$

isopropoxides, $Al[Ga(\underline{i}\text{-}PrO)_4]_3$ and $Ga[Al(\underline{i}\text{-}PrO)_4]_3$ have also been obtained by heating the pure metal isopropoxides in the appropriate ratios. The compounds were characterized by ir, nmr, and molecular weights and their structures were discussed in terms of these studies.

Metal-Metal Bonded Derivatives

A series of species containing the M-Sn bond where M = Al, Ga, In, and Tl have been prepared by the reaction indicated in 20.[42] The products

$$Li[SnMe_3] + Me_3 \xrightarrow{DME} Li[Me_3MSnMe_3] \qquad (20)$$

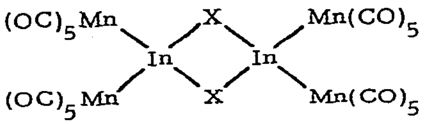
obtained are thermally unstable decomposing to $LiMMe_4$, $LiSn(SnMe_3)_3$ and $SnMe_4$ within one to two days at 0°. The stability follows the order $Al < Ga < In < Tl$. In the reaction leading to the thallium derivative, there are at least three products containing Sn-Tl bonds thought to be $Me_nTl(SnMe_3)_{4n}$ type species.

The compounds were characterized by their ^1H nmr spectra and it was shown that $^3J_{SnCH}$ increased regularly through the series as a function of the size of the central atom $Al > Ga > In > Tl$. No similar trend was noted, however, for $^4J_{SnMCH}$.

Additional studies on metal-metal bonded derivatives have been reported by Hsieh and Mays.[43] They synthesized a variety of compounds containing In-transition metal bonds where the transition metal is Mo, W, Re, Fe, or Co. They also discussed a variety of different techniques for the preparation of these compounds and the general applicability of these synthetic procedures to the synthesis of derivatives of this type.

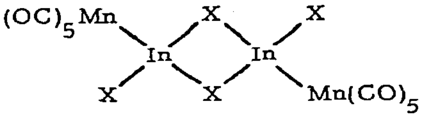
In a subsequent paper,[44] they reported the preparation of indium derivatives including $In[Mn(CO)_5]_3$, $XIn[Mn(CO)_5]_2$ and $X_2In[Mn(CO)_5]$ which involve In-Mn bonds. They have characterized these species by their ir and mass spectra as well as by their chemical reactions. Several of the derivatives appear to be dimeric with halide bridges while others are monomeric. Monomeric species have also been noted in ethers such as THF and 1,4-

dioxane. Possible structures are indicated below. It has also been suggested



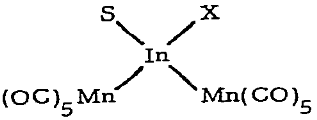
X = Br

XV

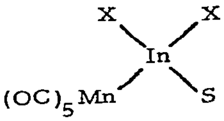


X = Br, Cl

XVI



XVII



XVIII

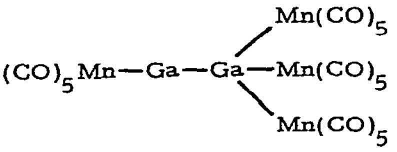
that in acetonitrile ionic equilibria such as indicated in 21 and 22 are present.

$$\mathrm{In[Mn(CO)_5]_3} \rightleftharpoons \mathrm{In[Mn(CO)_5]_2}^{+} + \mathrm{Mn(CO)_5}^{-} \qquad (21)$$

$$\mathrm{XIn[Mn(CO)_5]_2} \rightleftharpoons \mathrm{In[Mn(CO)_5]_2}^{+} + \mathrm{X}^{-} \qquad (22)$$

An extensive discussion of these reactions has been presented.

Haupt and Newmann have prepared the compounds $Ga_2[Mn(CO)_5]_4$ and $In[Mn(CO)_5]_3$ by direct reaction of gallium or indium metal with $Mn_2(CO)_{10}$. The compounds were characterized by spectroscopic techniques. It was shown that $In[Mn(CO)_5]_3$ has a planar $InMn_3$ skeleton with D_{3h} symmetry. The novel structure, indicated in XIX was proposed for the gallium derivative.



XIX

REFERENCES

1. K. Hoffmann and E. Weiss, J. Organometal. Chem., 37 (1972) 1.
2. F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, Inorg. Chem., 11 (1972) 2832.
3. W. Harrison, A. Storr, and J. Trotter, J. C. S. Dalton (1972) 1554.
4. H. D. Hausen, J. Organometal. Chem., 39 (1972) C37.
5. R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan and P. T. Greene, J. Amer. Chem. Soc., 94 (1972) 1865.
6. G. Beran, K. Dymock, H. A. Patel, A. J. Carty, and P. M. Boorman, Inorg. Chem., 11 (1972) 896.
7. R. Restino and G. J. Palenik, J. C. S. Dalton (1972) 341.
8. J. G. Conteras and D. G. Tuck, Inorg. Chem., 11 (1972) 2967.
9. A. N. Rodionov, N. I. Ruch'eva, G. V. Zenina, I. M. Viktorova, V. A. Grubova, N. I. Sheverdina, D. N. Shigorin, and K. A. Kocheshkov, Zh. Prikl. Spectrosk., 16 (1972) 740; C. A. 77 (1972) 40864f.
10. D. F. Shriver and A. Alich, Inorg. Chem., 11 (1972) 2984.
11. M. B. Dunn and C. A. McDowell, Mol. Phys., 24 (1972) 969.
12. H. D. Visser and J. P. Oliver, J. Organometal. Chem., 40 (1972) 7.
13. T. L. Brown and L. L. Murrell, J. Amer. Chem. Soc., 94 (1972) 378.
14. Yu. Kh. Shaulov, A. N. Shinkarev, G. S. Pesotskii, Zh. Fiz. Khim., 46 (1972) 2168; C. A. 77 (1972) 16569t.
15. Yu. Kh. Shaulov, V. G. Genchel, R. M. Aizatullova, and G. S. Pesotskii, Zh. Fiz. Khim., 46 (1972) 2379; C. A. 77 (1972) 169532a.
16. S. Warwel and H. P. Hemmerich, Liebigs. Ann. Chem., 763 (1972) 83.
17. J. St. Denis, T. Dolzine, and J. P. Oliver, J. Amer. Chem. Soc., 94 (1972) 8260.
18. J. J. Borlin and D. F. Gaines, ibid., 94 (1972) 1367.
19. J. Weidlein and B. Schaible, Z. Anorg. Allg. Chem., 386 (1971) 386.

20. B. Schaible and J. Weidlein, J. Organometal. Chem., 35 (1972) C7.

21. H. Olapinski, B. Schaible, and J. Weidlein, ibid., 43 (1972) 107.

22. H. Olapinski and J. Weidlein, ibid., 35 (1972) C53.

23. H.-U. Shwering, H.-D. Hausen, and J. Weidlein, Z. Anorg. Allg. Chem., 391 (1972) 97.

24. W. Lind and I. J. Worrall, J. Organometal. Chem., 36 (1972) 35.

25. W. Lind and I. J. Worrall, ibid., 40 (1972) 35.

26. J. S. Poland and D. G. Tuck, ibid., 42 (1972) 315.

27. M. J. S. Gynane and I. J. Worrall, Inorg. Nucl. Chem. Letters, 8 (1972) 547.

28. M. J. S. Gynane, L. G. Waterworth, and I. J. Worrall, J. Organometal. Chem., 43 (1972) 257.

29. M. J. S. Gynane and I. J. Worrall, ibid., 40 (1972) C59.

30. M. J. S. Gynane, L. G. Waterworth, and I. J. Worrall, ibid., 40 (1972) C9.

31. J. S. Poland and D. G. Tuck, ibid., 42 (1972) 307.

32. J. Müller, K. Margiolis, and K. Dehnicke, ibid., 46 (1972) 219.

33. A. Storr, B. S. Thomas, and A. D. Penland, J.C.S. Dalton (1972) 326.

34. A. F. Berniaz and D. G. Tuck, J. Organometal. Chem., 46 (1972) 243.

35. G. B. Deacon and J. C. Parrott, Aust. J. Chem., 25 (1972) 1169.

36. B. Gribov, B. I. Kozyrkin, and E. N. Zorina, Dokl. Akad. Nauk. SSSR 204 (1972) 350; C.A. 77 (1972) 114477f.

37. T. Maeda, G. Yoshida, and R. Okawara, J. Organometal. Chem., 44 (1972) 237.

38. L. M. Golubinskaya, V. I. Bregadze, E. V. Bryuchova, V. I. Svergun, G. K. Semin, and O. Yu. Okhobystin, ibid., 40 (1972) 275.

39. B. Sen, G. L. White, and J. D. Wander, J.C.S. Dalton (1972) 447.

40. T. Maeda and R. Okawara, J. Organometal. Chem., 39 (1972) 87.

41. A. Mehrotra and R. C. Mehrotra, Inorg. Chem., 11 (1972) 2170.

42. A. T. Weibel and J. P. Oliver, J. Amer. Chem. Soc., 94 (1972) 8590.

43. A. T. T. Hsieh and M. J. Mays, J. Organometal. Chem., 37 (1972) 9.

44. A. T. T. Hsieh and M. J. Mays, J. C. S. Dalton (1972) 516.

45. H. J. Haupt and F. Newmann, Z. Anorg. Allg. Chem., 394 (1972) 67.