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THE SYNTHESIS AND MASS SPECTRA OF TRIARYL-GALLIUM AND -INDIUM COMPOUNDS

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Summary

The synthesis of a number of symmetrically 2-, 3-, and 4-substituted triarylgallium and triarylindium compounds are reported using transmetallation of the corresponding mercurial with Ga or In metal. The electron impact mass spectra of these compounds are very similar and very simple and show the basic structural features of the molecules. With careful control of the conditions it is possible to obtain spectra in which metal-containing ions are the dominant species with little contamination from hydrolysis and pyrolysis products. The spectra provide evidence for dimers of these compounds as significant gaseous species.

Introduction

In the study of structure and bonding in organometallic compounds of gallium and indium [1—6], we have interpreted the ^{13}C NMR and the $^{69,71}Ga$ and ^{115}In nuclear quadrupole resonance spectra of triaryl-gallium and -indium in terms of the ground state electron distribution in the solid and solution [1]. The excited state was probed in solution by ultraviolet spectroscopy [2]. The molecules are monomeric in solution [1,2]. We have also synthesized and characterized by spectroscopy the aryl-gallium and -indium halides [3,4] and metal—metal bonds involving gallium and indium [5,6]. In this paper we report the synthesis and mass spectra of the triaryl-gallium and -indium compounds. This mass spectral analysis was prompted not only by the intrinsic novelty of main group molecules that lack an octet of electrons in their valence shell, but by the fact that the mass spectra give gas phase information to complement the solution and solid state data. It was also frequently necessary to fall back on mass spectral data as a means of verifying the existence and determining the purity of organometallic gallium and indium compounds [3,4].

Two synthetic routes to the air and moisture sensitive triaryl-gallium and

-indium compounds are sufficiently general to prepare a large series of compounds. These are the Grignard method [7] and the transmetallation method using mercurials [8]. The starting materials for the Grignard route, anhydrous metal halides and the Grignard reagents, are tedious to handle and yield a product complexed with dioxane. Significant decomposition of the desired compound resulted when the dioxane was removed. Instead, the mercurial route was adopted because the starting materials, gallium and indium metal and the diarylmercurials, are easy to handle and the products obtained were reasonably pure. The only drawback to the mercurial method is the need to prepare the mercurials.

Experimental

Synthesis. The synthesis of organomercurials, R_2Hg, can be found elsewhere [9]. These mercurials were used in two types of reactions to produce triarylgallium and -indium compounds.

Method A: Ga or In metal powder (ROC/RIC) (0.0174 mol) was placed in a 250 ml Schlenk flask with 0.0257 mol of diarylmercury under nitrogen. The flask was placed in an oil bath at 150°C for 48 h under a slight positive pressure of nitrogen. At the end of this time mercury metal had formed. The reaction mixture was extracted with about 30 ml of solvent, indicated in Table 1,

TABLE 1

SYNTHETIC DATA FOR TRIARYL-GALLIUM AND -INDIUM COMPOUNDS

Compound	Method	Yield (%)	Purification	M.p. (°C)
$(C_6H_5)_3Ga$	A, B	88	$CHCl_3$/hexane	169—171
$(2\text{-}CH_3C_6H_4)_3Ga$	B	89	vacuum distillation	b.p. 185—187 at 1.0 mmHg
$(3\text{-}CH_3C_6H_4)_3Ga$	B	49	hexane	116—117
$(4\text{-}CH_3C_6H_4)_3Ga$	B	92	toluene	176—178
$(4\text{-}C_2H_5C_6H_4)_3Ga$	B	58	n-pentane	93—94
$[4\text{-}(CH_3)_3CC_6H_4]_3Ga$	B	84	benzene/hexane	269—271
$(4\text{-}CH_3OC_6H_4)_3Ga$	B	73	benzene/hexane	162—164
$(3\text{-}FC_6H_4)_3Ga$	B	80	benzene/hexane	160—161
$(4\text{-}FC_6H_4)_3Ga$	B	98	toluene	200—201
$(2\text{-}ClC_6H_4)_3Ga$	B	65	benzene	129—131
$(3\text{-}ClC_6H_4)_3Ga$	B	59	cyclohexane	139—140
$(4\text{-}ClC_6H_4)_3Ga$	B	40	*o*-xylene	217
$(3\text{-}BrC_6H_4)_3Ga$	B	22	cyclohexane	148—150
$(4\text{-}BrC_6H_4)_3Ga$	B	38	*o*-xylene	198—200 (dec.)
$(C_6H_5)_3In$	A, B	78	chloroform/hexane	209—210 [b]
$(2\text{-}CH_3C_6H_4)_3In$	B	70	cyclohexane	151—153 [c]
$(3\text{-}CH_3C_6H_4)_3In$	B	65	benzene/hexane	131—133 [d]
$(4\text{-}CH_3C_6H_4)_3In$	B	90	toluene	243—244 [e]
$(4\text{-}C_2H_5C_6H_4)_3In$	A, B	52	n-pentane	119—121
$[4\text{-}(CH_3)_3CC_6H_4]_3In$	B	87	cyclohexane	230—233
$(4\text{-}CH_3OC_6H_4)_3In$	B	68	benzene/hexane	140—142
$(3\text{-}FC_6H_4)_3In$	B	71	benzene/cyclohexane	174—176
$(4\text{-}FC_6H_4)_3In$	B	85	toluene	252—254
$(4\text{-}ClC_6H_4)_3In$	B	31	toluene	267—269

[a] Based on R_2Hg as limiting reagent. [b] 208°C [7]. [c] 139°C [7]. [d] 104°C [7]. [e] 225°C [7].

filtered while hot, and the filtrate allowed to cool. Crystals of the desired colorless triarylmetal compound formed in yields indicated in Table 1.

Method B: Ga or In metal (0.027 mol), 0.040 mol of diarylmercury and 25 ml of dried degassed toluene were placed in a 250 ml of Schlenk flask under nitrogen. The mixture was refluxed for 60 h. At the end of this time, the light brown reaction mixture was reduced in volume to 15 ml and filtered. The filtrate was diluted with 10 ml of hexane and allowed to cool [1]. The triarylmetal compound crystallized, was filtered and washed with hexane, and recrystallized from the solvent listed in Table 1.

Mass spectrometry. All mass spectra were obtained with a DuPont 21-110B mass spectrometer which has been modified for Chemical Ionization (*CI*) operation [9,10]. The Electron Impact (*EI*) mass spectra were normally obtained with 70 eV electrons at a resolution of 1—2000 in a standard source. A few metastable decompositions were observed by varying the accelerating voltage. Precise mass measurements were made at resolutions of 5—10,000 on some of the more abundant ions to confirm their stoichiometry. The Cl mass spectra were obtained with a modified source at 0.7—1 Torr of reagent gas with 400—600 V electrons. The *EI* and *CI* mass spectra were insensitive to electron energy, reagent gas pressure, and accelerating voltage, but were sensitive to sample temperature and treatment.

The samples were introduced into the source of the mass spectrometer with a direct insertion probe. The probe was either a glass probe (Mass Spectrometer Accessories, College Station, Texas) which has a separate temperature control and monitoring system or a metal probe which was heated by contact with the source of the mass spectrometer. The samples were introduced into the well of the probes in 2 mm glass capillaries.

Many organometallic compounds are readily susceptible to thermal decomposition or hydrolysis and consequently, their mass spectra are highly sensitive to the precise conditions of sample preparation and introduction [11]. The triarylmetal compounds of Ga and In are particularly sensitive to hydrolysis prior to sample introduction. Consequently, much effort was spent trying to obtain "good" spectra of $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ as typical compounds. Although the general nature of the problems of obtaining mass spectra of sensitive compounds are known, it is worthwhile to discuss some of the problems with $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ in detail.

Untreated glass capillaries were filled with either $(C_6H_5)_3Ga$ or $(C_6H_5)_3In$ and sealed with a plug of stopcock grease in a dry box. The capillaries were then sealed in air with a torch and broken immediately before introduction into the mass spectrometer. Spectra were obtained at roughly 20°C intervals from room temperature to 200°C. This procedure gave *EI* spectra which contained large but variable amounts of m/z 78 (benzene) and m/z 154 (biphenyl) and hydrocarbon ions that could easily be attributed to these two compounds. It was possible that these ions came from decomposition of triarylmetal ions, but it was more likely that they came from impurities of benzene and biphenyl present in the samples as they were introduced into the mass spectrometer. The CH_4 *CI* spectra of these compounds obtained under similar conditions contained large and variable amounts of m/z 79 and 107, $(M + H)^+$ and $(M + C_2H_5)^+$ from benzene, and m/z 155 and 183, $(M + H)^+$ and $(M + C_2H_5)^+$ from biphenyl. As an illustration of the temperature variation of the spectra, the ratio, $(C_6H_5)_2In^+/C_6H_7^+$, varied from 0.06 at 180°C to 2.2 at 200°C in the CH_4 *CI* spectrum of a sample of $(C_6H_5)_3In$. Similarly, the ratio, $(C_6H_5)_2In^+/(C_6H_5)_2H^+$, varied from 0.6 to 5.2 in this experiment. Time dependence studies of *EI* spectra showed decreases in the abundances of benzene and biphenyl ions for samples at constant temperature, although the $C_6H_6^+$ and $C_{12}H_{10}^+$ ions did not vanish completely from the spectra. Similar observations were made for CH_4 *CI* spectra of these two compounds. The time and temperature variations noted, the irreproducibility of the relative abundances of hydrocarbon ions, and the appearance of protonated molecular ions in the CH_4 *CI* mass spectra indicated to us that the majority of the hydrocarbon ions resulted not from decompositions of the gaseous triarylmetal ions, but from ionization of hydrocarbons produced by hydrolysis and pyrolysis of the neutral triarylmetal compounds in the glass capillaries of the direct introduction system of the mass spectrometer.

The relative abundances of $C_6H_6^+$ and $C_{12}H_{10}^+$ in the *EI* spectra of $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ at any temperature decreased to essentially constant values after about 30 minutes within the source of the mass spectrometer. An increase in the temperature of the probe or the source (and therefore an increase in the temperature of the sample and capillary) always increased the absolute ion currents of these ions, even though their relative abundances decreased. We consider, therefore, that the major source of water to hydrolyze the triarylmetal compounds is the adsorbed water on the glass surfaces of the capillaries and the glass probe and not the water adsorbed by the sample in transfer to the instrument.

Our best spectra were obtained by using glass capillaries that had been silanized with chlorotrimethylsilane and heated overnight in a vacuum oven. The samples were introduced into capillaries in a dry box and then the capillaries were sealed with plugs of stopcock grease. The plugged capillaries were sealed with a small break tip as soon as possible after removal from the dry box. The capillaries were placed in metal probe tips and inserted into the source of the mass spectrometer and the tip broken within the vacuum system. The temperature of the samples was varied by changing the temperature of the source of the mass spectrometer. The temperature variation with this technique was substantially slower than that obtained by using the glass probe; however, the glass probe appeared to desorb significantly more water than the metal probe tip and form more hydrolysis products. We consider that the best spectra of these triarylmetal compounds are those in which the abundances of the hydrocarbon ions are the lowest.

Typical data for *EI* spectra of $(C_6H_5)_3Ga$ are shown in Fig. 1. These data were taken on a single sample which was introduced using the above procedure. The spectra were taken over a period of about an hour and this sample was completely evaporated by the end of the experiment at 120°C. Spectra have been obtained of $(C_6H_5)_3Ga$ at temperatures as high as 170°C. It is obvious that the choice of temperature for containing spectra is critical if one includes the hydrocarbon ions. However, the ratios of abundances of the five Ga-containing ions and $C_6H_5^+$ (corrected for some formation from benzene) are substantially constant and independent of experimental conditions from about 80 to 170°C. The basic pattern of the compound is not disturbed by the presence of the

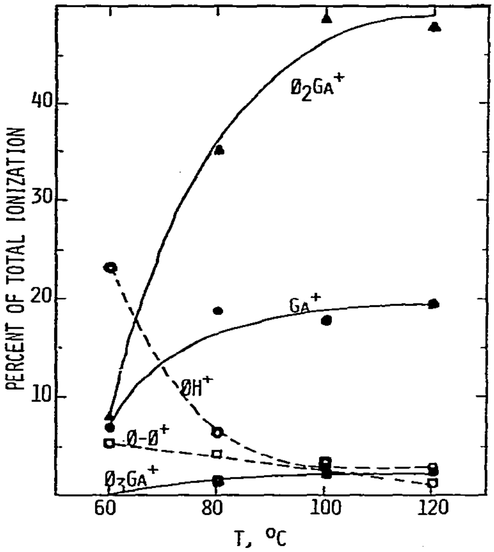

Fig. 1. Mass spectra of $(C_6H_5)_3Ga$ at different temperatures. Open points and dotted lines show hydrocarbon impurity ions. Solid points and solid lines show ions from triphenylgallium.

hydrocarbon ions. We have been able to obtain some spectra in which the sum of all the hydrocarbon ions (except $C_6H_5^+$) was less than 10% of the total sample ionization. Time dependence studies on $(C_6H_5)_3Ga$ at 125°C showed that the ratios of these five Ga-containing ions were constant, ±10%, for the full evaporation of the sample (approximately 1 h).

Similar experiments were performed with $(C_6H_5)_3In$, which is even more sensitive to hydrolysis than $(C_6H_5)_3Ga$. With very careful sample treatment it was possible to obtain spectra which contained less than 5% of $C_6H_6^+$ or $C_{12}H_{10}^+$. The same general observations were made for the *EI* and *CI* spectra of $(C_6H_5)_3In$ as for $(C_6H_5)_3Ga$ and we conclude that the hydrocarbon ions in the spectra of $(C_6H_5)_3In$ (except for $C_6H_5^+$) are formed from hydrocarbon impurities and not from decomposition of organometallic ions. Significantly higher temperatures were required to obtain spectra of $(C_6H_5)_3In$ than were required to obtain spectra of $(C_6H_5)_3Ga$.

Spectra of substituted triarylgallium and triarylindium compounds were obtained under conditions designed to reduce hydrolysis. Extensive hydrolysis was observed for some of the compounds, however, and these spectra are not reported in this paper. The triarylindium compounds required higher temperatures for volatilization than the triarylgallium compounds. The triarylindium compounds were generally more sensitive to hydrolysis than the triarylgallium compounds. However, both classes of compounds were sufficiently thermally stable to produce good, characteristic spectra.

Our observations on the thermal and hydrolytic instability of the triarylmetal compounds are similar to previous observations in the mass spectra of these compounds for which it was noted, for example, that hydrocarbon ions comprised 99% of the total ion current in the *EI* mass spectrum of $(C_6H_5)_3In$ [12]. The triarylgallium compounds appear to be substantially more susceptible to hydrolysis than the trialkylgallium compounds, since the latter compounds could be handled briefly in air with a microliter syringe and a standard oven introduction system [13]. Tributylgallium is notably more volatile than triphenylgallium since the former could be introduced from an oven at 110° C through a pinhole leak but triphenylgallium required vaporization directly into the source of the mass spectrometer at 100° C.

Separation of these compounds from Hg and the mercurials was readily achieved. In none of the spectra of the triarylgallium or triarylindium compounds were significant abundances of ions from mercury or diarylmercury found. The mass spectra were therefore used to indicate the purity.

Results and discussion

Table 2 shows the average *EI* spectra of $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$. Hydrocarbon ions other than $C_6H_5^+$ are less than 10—20% of the total ionization for all of the spectra from which these data are extracted. Since we feel that the hydrocarbon ions (except for $C_6H_5^+$) do not result from ionization of the triarylmetal compounds, the hydrocarbon ions have been omitted from this tabulation. The abundances of $C_6H_5^+$ ions have been corrected for a contribution from benzene. Since these corrections are sometimes significant with respect to the total amount of $C_6H_5^+$ ions, the variability of abundance of $C_6H_5^+$ is larger than that of the other fragment ions. There were no significant trends in the relative abundances of any of the ions of these two compounds except for $(C_6H_5)_3Ga^+$ and $(C_6H_5)_3In^+$. The abundance of $(C_6H_5)_3Ga^+$ decreased with increasing temperature in these experiments: about 7% at 80° C and about 3% at 170° C. Similarly, the abundance of $(C_6H_5)_3In^+$ decreased with increasing temperature: about 2.5% at 150° C and about 1% at 200° C. The data of Table 2 are in good agreement with the previously reported spectra of these two compounds for the distribution of the metal containing ions [12]. The major difference in the spectra is the much lower abundance of hydrocarbon ions, particu-

TABLE 2

PARTIAL ELECTRON IMPACT MASS SPECTRA OF TRIPHENYL-GALLIUM AND -INDIUM

Ion	Ionization (%) [a]			
	$(C_6H_5)_3Ga$		$(C_6H_5)_3In$	
$(C_6H_5)_3M$	2.8 ± 0.8, 2.9	(4.1)	1.9 ± 0.6, 2.1	(3.4)
$(C_6H_5)_2MC_6H_4$	2.5 ± 0.2, 2.6		2.5 ± 0.5, 2.8	
$(C_6H_5)_2M$	58.8 ± 6.0, 61.3	(58.7)	35.5 ± 3.4, 39.2	(39.4)
C_6H_5M	1.8 ± 0.2, 1.8	(1.3)	2.7 ± 0.1, 3.0	(2.9)
M	30.0 ± 3.8, 31.2	(29.3)	47.8 ± 2.5, 52.8	(50.2)
C_6H_5	4.2 ± 1.4		9.4 ± 2.6	

[a] Average of 10—13 measurements under similar, but different conditions. Both metal isotopes summed for each ionic species. ^{13}C species not included in calculations. Lower mass hydrocarbon ions may be present in spectra, but majority of hydrocarbon ions come from benzene and biphenyl. All hydrocarbon ions = 10—20% of total ionization. Small amounts (~0.5%) of $C_6H_5InC_6H_4^+$ present, 70 eV. Abundance of $C_6H_5^+$ corrected for 15% contribution from $C_6H_6^+$. Second value = % of 5 metal-containing ions. Values in parentheses from ref. 12. $(C_6H_5)_3Ga$, 80—170° C. $(C_6H_5)_3In$, 120—200° C.

larly for $(C_6H_5)_3In$ for which hydrocarbon ions were reported to carry 99% of the total ion current [12]. In our "best" spectrum of $(C_6H_5)_3In$, the sum of all hydrocarbon ions was less than 10% of the total ionization. Consequently, we feel that $(C_6H_5)_3In$ is approximately as thermally stable as $(C_6H_5)_3Ga$.

A comparison of the spectrum of $(C_6H_5)_3Ga$ with the spectrum of $(n\text{-}C_4H_9)_3$-Ga [13] shows a greater abundance of molecular ions for the triaryl compound, 2.8% vs. 0.4%, in general agreement with most hydrocarbon systems. The same ionic species are dominant, GaR_2^+, GaR^+, and Ga^+; however the ratios of these three species are very different: 1/0.03/0.5 for triphenylgallium and 1/0.4/1 for tributylgallium. There is no obvious explanation for this difference. There are significant abundances of ions involving C—C cleavage in the spectrum of tributylgallium, but none of this type of ion in the spectrum of triphenylgallium. Hydrocarbon ions comprise about 20% of the ionic abundance in the spectrum of tributylgallium, but comparisons cannot be made because of the likelihood of hydrocarbon ions being formed by direct ionization of neutral hydrocarbons for both compounds.

The greater abundances of M^+ and to a lesser extent of $(C_6H_5)_2M^+$ from $(C_6H_5)_3In$ compared with $(C_6H_5)_3Ga$ agree with observations on the *EI* spectra of the metal tris(acetylacetonates) [11]. This difference was attributed to the greater stability of the +1 oxidation state of In compared with Ga and the suggestion that the decompositions may involve changes in oxidation states of the metals [11]:

$$M^{III}(C_6H_5)_2^+ \rightarrow M^{I}C_6H_5^{+\cdot} + C_6H_5^{\cdot} \qquad (1)$$

Comparisons between $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ are difficult to make because of the absence of reliable thermochemical data. However, the smaller abundance of $(C_6H_5)_3In^+$ than $(C_6H_5)_3Ga^+$ and the larger abundance of In^+ than Ga^+ suggest that the ionic $In—C_6H_5$ bonds are weaker than the ionic $Ga—C_6H_5$ bonds as indicated by appearance potential data [12].

As with most organometallic compounds the dominant ions are those in

$$(C_6H_5)_3M^{+\cdot} \begin{cases} \rightarrow (C_6H_5)_2M^+ + C_6H_5^{\cdot} & (2a) \\ \rightarrow (C_6H_5)_2M^{\cdot} + C_6H_5^+ & (2b) \end{cases}$$

which the positive charge is retained on the metallic species. Reaction 2a has been confirmed by metastable decompositions and reaction 2b may occur to a small extent. It has been well established in organic mass spectrometry that the ion resulting from the lower energy path will be in greater abundance unless it decomposes further [14,15]. The much greater abundances of $(C_6H_5)_2Ga^+$ and $(C_6H_5)_2In^+$ than $C_6H_5^+$ in these spectra indicate that $IP[(C_6H_5)_2M^{\cdot}] < IP(C_6H_5^{\cdot}) = 9.2$ eV [15]. No better upper limit can be obtained from these experiments.

Spectra of $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ obtained at even higher temperatures than those indicated in Table 2 showed higher mass ions which contained two metal atoms. Digallium species, $(C_6H_5)_5Ga_2^+$ and $(C_6H_5)_4Ga_2^+$, were reported previously [12] and are confirmed in our experiments. In addition, we observed significant amounts of $(C_6H_5)_3Ga_2^+$ ions which were not observed in earlier work. In order to establish that these ions result from ionization and fragmentation of $[(C_6H_5)_3Ga]_n$, $n \geqslant 2$ and not ion/molecule reactions with $(C_6H_5)_3$-Ga, the spectra were obtained at different repeller voltages. The ratio, $(C_6H_5)_5$-$Ga_2^+/(C_6H_5)_2Ga^+$, was independent of repeller voltage. The two species are therefore both formed by direct electron impact since an increase in repeller voltage would cause a decrease in this ratio if $(C_6H_5)_5Ga_2^+$ were the product of any ion/molecule reaction.

Similar observations were made for $(C_6H_5)_3In$ at high temperatures. Although no diindium ions were observed at 200° C, significant amounts of $(C_6H_5)_3In_2^+$ and $(C_6H_5)_5In_2^+$ were observed at ~225° C. In our best spectrum of $(C_6H_5)_3In$ at high temperatures, the sum of ion currents at 78 and 154 (benzene and biphenyl) were about 3% of the total ionization and the dominant ions were those which contained metal atoms. The other ions were $(C_6H_5)_5In_2^+$ (8%), $(C_6H_5)_4In_2^+$ (1%), $(C_6H_5)_3In_2^+$ (22%), $(C_6H_5)_3In^+$ (2%), $(C_6H_5)_2In^+$ (20%), C_6H_5In (0.4%), In^+ (7%), and $C_6H_5^+$ (4%). Although no $(C_6H_5)_6In_2^+$ ions were observed, these data provide clear evidence for stable neutral species $[(C_6H_5)_3$-$In]_n$, $n \geqslant 2$ in the gas phase. A significant stability is indicated for the In—C_6H_5—In bond because of the large abundance of the ions which contain two In atom. No $(C_6H_5)_5In^+$ ions were observed in any of our experiments, although these ions were reported previously [12]. Experiments of mixtures of $(C_6H_5)_3$-In and $C_6H_5C_6H_5$ gave no indication of the formation of $(C_6H_5)_5In^+$ from ion/molecule reactions of $(C_6H_5)_3In^+$ with $C_6H_5C_6H_5$. However, the pressures may have been too low in our experiments for such reactions to occur.

Our experiments and those reported previously [12] clearly indicate the presence of at least dimers of $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ in the gas phase at relatively high temperatures: $T \gtrsim 150°C$ for $(C_6H_5)_3Ga$ and $T \gtrsim 260°C$ for $(C_6H_5)_3In$. Quantitation is not possible from our experiments, but from the relatively large abundances of dimetallic ions, we feel that significant amounts of the dimer (or higher) molecules are formed by vaporization. No evidence was found for trimers in our experiments, but it is possible that such could be found at higher temperatures, and that low abundances of such ions were not detected under our conditions.

The presence of substantial ion current in the form of ions containing two metal atoms is not contradictory to the evidence that monomers exist in solution. Molecular weight determinations of $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$ in benzene and dioxane are consistent with monomeric molecules [17], as are the ^{13}C NMR spectra of $CDCl_3$ [1]. However, these solution studies probably can not detect a small percent of dimers, say less than 5%, if such were to exist. The absence of enthalpy of solvation in the mass spectral experiment permits some dimer formation. The same can be said for the solid state where significant intermolecular association takes place [18] in the absence of solvent molecules.

Methane chemical ionization, CH_4 *CI*, mass spectra were also obtained for $(C_6H_5)_3Ga$ and $(C_6H_5)_3In$. The CH_4 *CI* spectra of both compounds were similar under the different experimental conditions. At the lower temperatures, the spectra contained essentially only one peak, $(C_6H_5)_2M^+$. Small amounts of In^+ (1—2%) may be formed. $(C_6H_5)_3Ga^+$ and $(C_6H_5)_3In^+$ are present only as traces, less than 1%. No $(C_6H_5)_3MH^+$ ions are observed in the spectra, nor are significant amounts of $(C_6H_5)_2M(C_6H_4)^+$ ions formed by hydride transfer. These results are compatible with protonation of the phenyl group followed by essentially complete loss of neutral benzene.

$$\begin{array}{l} CH_5^+ \\ \\ C_2H_5^+ \end{array} + (C_6H_5)_3M \rightarrow [(C_6H_5)_2M(C_6H_6)]^{+*} \rightarrow (C_6H_5)_2M^+ + C_6H_6 \qquad (3)$$

At higher temperatures $(C_6H_5)_5M_2^+$ (~10%), $(C_6H_5)_3M_2^+$ (~2%), and small amounts of $(C_6H_5)_3M^+$ (~1%) are present, but the dominant ionic species is still $(C_6H_5)_2M^+$ (85%). The protonated dimer ions would be expected to decompose readily.

$$\begin{array}{l} CH_5^+ \\ \\ C_2H_5^+ \end{array} + (C_6H_5)_6M_2 \rightarrow [(C_6H_5)_5M_2(C_6H_6)]^{+*} \left\{ \begin{array}{ll} \rightarrow (C_6H_5)_5M_2^+ + C_6H_6 & (4a) \\ \rightarrow (C_6H_5)_2M^+ + (C_6H_5)_3M + C_6H_6 & (4b) \end{array} \right.$$

The existence of at least neutral dimers in relatively abundant concentrations is confirmed by these experiments.

Table 3 shows partial *EI* spectra of a series of substituted triarylgallium compounds. Hydrocarbon ions are not included in this tabulation, only the five major metal-containing species in the spectrum of $(C_6H_5)_3Ga$. Low abundances of other metal-containing ions may be present in some of the spectra, but their presence could not be confirmed by precise mass measurement and the isotopic abundances were complicated by the presence of other species. For the compounds reported in this table, these five ions comprise about 70% of the total ion current.

No fragment ions were observed which involved the transfer of the substituent from the aromatic ring to the metal, although such ions have been observed in the spectra of $M(C_6F_5)_4$ and π-bonded compounds like $Cr(CO)_3C_6H_5X$ and $C_5H_5FeC_5H_4X$ [19—21]. Substituted phenyl ions were observed in all cases, but the relative abundances of these ions were low. It was difficult to estimate the extent of formation from the triarylmetal ion decomposition because of the relatively extensive amount of hydrocarbon ions present from decomposition products. In no cases, even for the alkylphenyl species, were the substituted phenyl ions major ionic species.

The most striking observation which can be made about these spectra is their similarity. With the exception of the larger abundance of the parent ion for the *p*-methoxy compound, the relative abundances of these major ionic species are independent of substituent and are the same as the relative abundances of the major ions in $(C_6H_5)_3Ga$ reported in Table 2. The variation in the ratio of $(\text{Parent} - H)^+$ to $(\text{Parent})^+$ is perhaps real, but the differences in actual ionic abundances are small. The temperatures at which the spectra were obtained were different because of the different volatilities of the compounds and some variation may result from the changes in this experimental parameter.

Table 4 shows partial *EI* mass spectra of a series of substituted triarylindium compounds. These ions constitute the major In-containing ions in the spectra. It is possible that low abundances of other In-containing species are present, but their elemental compositions could not be established unambiguously. Because the triarylindium compounds are more susceptible to hydrolysis, these

TABLE 3

PARTIAL *EI* MASS SPECTRA OF $(XC_6H_4)_3Ga$ [a]

Ion	Metal containing ions (%)							
	X = *p*-F	X = *m*-F [b]	X = *m*-Cl	X = *p*-CH_3 [c]	X = *m*-CH_3 [c]	X = *p*-C_2H_5 [d]	X = *p*-t-C_4H_9 [e]	X = *p*-CH_3O [f]
$(XC_6H_4)_3Ga$	1.6	1.7	3.4	1.5	2.8	1.4	1.1	7.5
$(XC_6H_4)_2Ga(C_6H_3X)$	0.7	0.6	0.5	1.8	2.2	1.9	3.1	1.6
$(XC_6H_4)_2Ga$	59.5	59.5	62.7	60.3	57.7	64.4	67.4	59.1
$(XC_6H_4)Ga$	3.2	2.3	1.9	<0.5	<0.5	<0.5	<0.5	0.9
Ga	35.0	35.9	31.5	36.4	37.3	32.4	26.5	30.9

[a] 70 eV, single spectra, 100—140° C. Calculated as % of these 5 species only. These five species comprise 70—80% of the total ion current unless otherwise noted. Digallium ions observed at higher temperatures for some of these compounds. [b] Low abundances of probable Ga species at 275—279, ~4% of total ion current. [c] Low abundances of probable Ga species at 255—257, ~3% of total ion current. [d] 1% probable (Parent — C_2H_5)$^+$; 1% probable (Parent — $C_6H_5C_2H_5$ — CH_3)$^+$ and (Parent — $C_6H_5C_2H_5$ — C_2H_5)$^+$. Large amounts of hydrocarbons from hydrolysis products. [e] Possibly low abundances of Ga species with ring rupture, ~5%. Extensive formation of hydrocarbon ions, primarily hydrolysis products. [f] Possibly low abundances of other Ga species, ~3%.

TABLE 4

PARTIAL *EI* MASS SPECTRA OF $(XC_6H_4)_3In$ [a]

Ion	X						
	p-F [b]	*m*-F [b]	*m*-Cl [c]	*p*-CH_3 [d]	*p*-C_2H_5 [e]	*p*-t-C_4H_9 [f]	*p*-CH_3O
$(XC_6H_4)_3In$	0.6	1.0	0.8	0.9	1.1	1.1	1.7
$(XC_6H_4)_2In(C_6H_3X)$	0.9	0.8	0.8	1.7	2.0	1.6	2.0
$(XC_6H_4)_2In$	50.7	42.7	39.6	41.9	50.8	46.5	42.2
$(XC_6H_4)In$	2.0	2.1	2.1	1.7	1.0	0.7	1.2
In	45.8	53.1	56.8	53.8	44.7	50.0	52.9

[a] 150—250° C, 70 eV, single spectra. Calculated as % of these five species only. These five species comprise 40—60% of the total ion current. $(XC_6H_4)_3In_2{}^+$ observed at high temperature. [b] Possible (Parent — C_6H_5F — F)$^+$, ~0.2%. [c] Possible other ClIn-containing ions, ~2%. [d] Possible (Parent — CH_3)$^+$, (Parent — $C_6H_5CH_3$ — H^+), ~0.5%. [e] Possible (Parent — $C_6H_5C_2H_5$ — CH_3)$^+$, ~1%. [f] Possible low abundances of In-containing species with ring rupture.

spectra contained more hydrocarbon ions, about half of the total ionization. Table 4 is based only on the five major In-containing species found in the best spectrum of $(C_6H_5)_3In$. Small amounts of substituted phenyl ions were found in these spectra, but they are not included in this tabulation because of the large correction for the formation from the neutral hydrocarbons that are present as impurities in the samples as they are introduced into the mass spectrometer. In no cases were substituted phenyl ions major ionic decomposition products. No evidence was found for transfer of a substituent from the ring to In.

Like the spectra of the triarylgallium compounds, the spectra of these compounds are remarkably similar. Making a reasonable allowance for the reproducibility of the decomposition pattern under somewhat different conditions, we consider that these spectra are the same. There appears to be no effect of aromatic substituent on the decomposition reactions. The ratio, $In^+/(XC_6H_4)_2In^+$, in these compounds may be slightly smaller than the ratio in $(C_6H_5)_3In$, but even this effect is small. The $(XC_6H_4)_3In$ spectra are very similar to the analogous $(XC_6H_4)_3Ga$ spectra. The major difference between the spectra of these compounds of the two elements is the larger abundance of the In^+ ion than of Ga^+ and a lower abundance of $(XC_6H_4)_2In^+$ than of $(XC_6H_4)_2Ga^+$.

For both sets of these compounds, spectra obtained at high temperatures contained $(XC_6H_4)_5M_2^+$ and $(XC_6H_4)_3M_2^+$ ions, although systematic studies were not made. Gaseous neutral dimers appear to be generally formed for these compounds.

One other item about these spectra that appears worthy of comment is the general appearance of the small amount of (Parent — H)$^+$ ions in the spectra of all of the $(XC_6H_4)_3Ga$ and $(XC_6H_4)_3In$ compounds. It is possible that this unexpected ion is one in which the metal is bonded to benzyne after a rearrangement. However, other structures are possible and no evidence is available for any particular structure.

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