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Organometallic Compounds of Group III. II. The Reaction of Gallium Alkyls and Alkyl Hydrides with Unsaturated Hydrocarbons[1a]

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An investigation of the reactivity and mode of reaction of gallium alkyls and dialkylgallium hydrides toward olefins, acetylenes, oxygen and protic solvents has been made. The requisite dialkylgallium hydride was obtained from the exchange reaction between a dialkylgallium chloride and dialkylaluminum hydride in the presence of potassium chloride. This hydride was found to add readily both to olefins and acetylenes to yield unsymmetrical gallium alkyls which tended to disproportionate upon attempted distillation. Gallium alkyls and olefins, on the other hand, underwent either an olefin displacement reaction or a "growth" reaction, but with less facility than has been observed with aluminum alkyls. In the case of gallium alkyls and terminal acetylenes addition to the triple bond was not observed, but rather the acetylene behaved as a pseudoacid, cleaving one alkyl–gallium bond. In Ziegler polymerization experiments triethylgallium showed a high degree of activity, far superior to that of triethylindium. Finally, in both solvolysis and oxidation studies gallium alkyls showed a marked tendency to undergo transformation to rather stable R_2GaZ types ($Z = OH, OR$). The differences in the kind and degree of reactivity between gallium alkyls and aluminum alkyls are discussed in terms of bond polarity and Lewis acidity variations.

Introduction

The behavior of aluminum alkyls and alkylaluminum hydrides toward olefins and acetylenes has brought to light many novel facets of organometallic chemistry which are of both theoretical and practical significance.[2] In order that a better understanding of the electronic factors involved in this recently uncovered organoaluminum chemistry might be obtained, it seemed fruitful to examine the reactions of other Group III metal alkyls with unsaturated hydrocarbons. As new methods have been developed recently for the preparation of gallium alkyls from the readily accessible aluminum alkyls,[3] the purpose of this study was to consider the behavior of the little-known gallium alkyls and hydrides toward such unsaturated organic compounds.

Unfortunately, the preparation of the requisite hydride and alkyl hydrides of gallium has been reported in the literature only in a fragmentary or dubious fashion. Aside from two unsubstantiated reports on the preparation of traces of gallium hydride,[4] Wiberg and Johannsen[5] have claimed the first successful synthesis of gallium hydride by the hydrogenolysis of trimethylgallium. Passage of a trimethylgallium–molecular hydrogen mixture through an electric glow discharge at low pressure resulted in the formation of tetramethyldigallane. Upon treatment with triethylamine the latter alkyl hydride disproportionated into the trimethylgallium–triethylamine complex and the unstable digallane, Ga_2H_6.[6] Syntheses of gallium hydride complexes, on the other hand, have been realized by various workers. Thus the unstable etherate $GaH_3 \cdot (C_2H_5)_2O$, prepared from lithium hydride and gallium(III) chloride in ether solution, was found to decompose rapidly into metallic gallium and hydrogen upon warming or to deposit polymeric gallane, $(GaH_3)_x$, from the unheated solution.[7] The recently prepared trimethylamine complex of gallane, $GaH_3 \cdot (CH_3)_3N$, seems to be more stable.[8] Finally, various mixed hydrides of gallium, such as $LiGaH_4$, have been characterized.[9] Since an alkylgallium hydride in an uncomplexed state was required for the investigation of the reactivity of such types toward olefins and acetylenes, none of the foregoing gallium hydride syntheses seemed appropriate for the synthesis of diethylgallium hydride. Consequently, the first phase of the present investigation consisted in devising a feasible synthesis of the unknown diethylgallium hydride in the absence of donor solvents such as amines or ethers.

Results

Preparation of Diethylgallium Hydride.—In order to prepare this compound in the absence of complexing solvents and in a convenient fashion, an exchange reaction between a gallium halide and an aluminum hydride seemed appealing. This approach suggested itself on the basis of previous success in obtaining gallium alkyls from gallium(III) halides and aluminum alkyls.[3] The necessary diethylgallium chloride was prepared readily by means of an exchange reaction between triethylgallium and gallium(III) chloride[10]

$$2Ga(C_2H_5)_3 + GaCl_3 \xrightarrow[\Delta]{} \underset{\text{I}}{3Ga(C_2H_5)_2Cl} \qquad (1)$$

To test the proposed chloride–hydride exchange reaction between gallium halides and aluminum hydrides, gallium(III) chloride and gallium(III)

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(1) (a) This work constitutes a part of the results presented at the Organometallic Symposium, sponsored by the Cincinnati Section, A.C.S., October 29, 1958. (b) Department of Chemistry, University of Michigan, Ann Arbor, Mich.

(2) *Cf.* K. Ziegler and co-workers, *Ann.*, **629**, 1 (1960), for a comprehensive treatment of recent developments in organoaluminum chemistry.

(3) Paper I of this series: J. J. Eisch, *J. Am. Chem. Soc.*, **84**, 3605 (1962).

(4) (a) E. Tomkinson, *Chem. News*, **122**, 238 (1921) [*Chem. Zentr.*, **93**, I, 401 (1922)], reported evidence of gallium hydride traces in the electrolysis of gallium-containing solutions; (b) E. Pietsch, *et al.*, *Z. Elektrochem.*, **39**, 577 (1933), heated gallium and hydrogen at 100–170° for 15 hours and claimed to have obtained a "hydride salt."

(5) E. Wiberg and T. Johannsen, *Naturwissenschaften*, **29**, 320 (1941).

(6) Attempts by several research groups to reproduce this reported synthesis of digallane have hitherto been unsuccessful.

(7) E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 172 (1951); **7b**, 577 (1952).

(8) D. Shriver and R. W. Parry, University of Michigan, unpublished studies.

(9) (a) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947); (b) E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 171 (1951); (c) **6b**, 335 (1951); (d) E. Wiberg and W. Henle, *Z. Naturforsch.*, **7b**, 575 (1952); and (e) T. Wartik and H. I. Schlesinger, *J. Am. Chem. Soc.*, **75**, 835 (1953).

(10) The dimeric or polymeric character of the metal halides and alkyls is ignored in the reaction formulas.

bromide were treated separately with three equivalents of diethylaluminum hydride at room temperature in the hope of preparing Ga_2H_6

$$2GaX_3 + 6Al(C_2H_5)_2H \longrightarrow \underset{\text{II}}{Ga_2H_6} + 6Al(C_2H_5)_2X \quad (2)$$

However, in both cases a prompt evolution of hydrogen gas and the deposition of metallic gallium were observed. Therefore, if digallane (II) were formed transitorily, it decomposed rapidly at room temperature. This is in fair accord with the report[5] that II decomposes slowly at ordinary temperatures and rapidly at 130°. Significant, nevertheless, was the fact that gallium metal was recoverable to the extent of 90–100% from such reactions. This indicated that chloride–hydride exchange had predominated over chloride–ethyl exchange. Consequently, the following reaction scheme for the synthesis of diethylgallium hydride appeared feasible

$$\underset{\text{I}}{Ga(C_2H_5)_2Cl} + Al(C_2H_5)_2H + KCl \longrightarrow \underset{\text{III}}{Ga(C_2H_5)_2H} + K[Al(C_2H_5)_2Cl_2] \quad (3)$$

The use of potassium chloride in reaction 3 served to bring about the formation of a complex with the resulting diethylaluminum chloride and thus permitted the separation of the diethylgallium hydride by decantation and distillation. The procedure was found to be satisfactory for the preparation of the hydride if the temperature was not allowed to exceed 80° and if the concurrently formed triethylgallium was removed by reduced pressure distillation. The triethylgallium (*ca.* 50%) seemed to arise either from chloride–ethyl exchange between I and diethylaluminum hydride or from the disproportionation–decomposition of III

$$\begin{tikzcd}
\underset{\text{III}}{3Ga(C_2H_5)_2H} \arrow[r] & 2Ga(C_2H_5)_3 + GaH_3 \arrow[d] & (4) \\
& Ga + 1.5H_2 &
\end{tikzcd}$$

Although the yield of III was low (25–30%), the procedure is amenable to the preparation of considerable quantities. The purity attained for the isolated hydride was approximately 95%; by suitable treatment with additional $Ga(C_2H_5)_2Cl$ or $Al(C_2H_5)_2H$, impurities of $Al(C_2H_5)_2H$ or $Ga(C_2H_5)_2Cl$, respectively, could be decreased even more. The main impurity was triethylgallium. Therefore, this two-step synthesis of diethylgallium hydride (eq. 1 and 3) should be a general, convenient source of this reactive organometallic type. Unlike diethylgallium chloride, which neither burns in air nor shows any explosive hydrolytic action with water, the hydride III is a pyrophoric substance which reacts vigorously with water. Complete hydrolytic cleavage to Ga^{+3}, however, requires warming with dilute acid.

Although feasible preparative procedures could not be found, the transitory formation of alkylgallium hydrides seems reasonable for two other reactions of gallium alkyls. Admixing three equivalents of diethylaluminum hydride with one equivalent of triethylgallium liberated heat to form a system which upon heating at 120–130° evolved a mixture of hydrogen and ethane (*ca.* 4:1) and deposited gallium metal. The hydrogen can be viewed as arising from hydride–ethyl exchange and the disproportionation–decomposition of diethylgallium hydride (III), as in eq. 4

$$Al(C_2H_5)_2H + Ga(C_2H_5)_3 \rightleftarrows Al(C_2H_5)_3 + \underset{\text{III}}{Ga(C_2H_5)_2H} \quad (5)$$

Alternatively, a 1:3 complex may be formed between triethylgallium and diethylaluminum hydride[11]; this could dissociate into gallium hydride or decompose directly

$$\begin{tikzcd}
& 3Al(C_2H_5)_3 + Ga + \frac{3}{2}H_2\uparrow & \\
Ga(C_2H_5)_3 + 3Al(C_2H_5)_2H \arrow[r] & Ga[Al(C_2H_5)_3H]_3 \arrow[u] \arrow[d] & (6) \\
& \frac{3}{2}Al(C_2H_5)_3 + \frac{3}{2}Al(C_2H_5)_2H + Ga + \frac{3}{2}C_2H_6\uparrow &
\end{tikzcd}$$

The latter decomposition scheme would account for the formation of some ethane.

A second reaction in which alkylgallium hydrides seemed to be formed was the hydrogenolysis of triethylgallium by hydrogen at temperatures ranging from 85° to 140° and pressures of 90 to 100 atm. Cleavage in the sense

$$Ga(C_2H_5)_3 + H_2 \longrightarrow Ga(C_2H_5)_2H + C_2H_6 \quad (7)$$

was extremely slow, and at the temperatures required only a trace of hydride survived the ready decomposition depicted in eq. 4.

Dialkylgallium Hydride with Olefins and Acetylenes.—Diethylgallium hydride was found to add promptly to carbon–carbon unsaturation at moderate temperatures. Treatment of 1-decene with this hydride at 65° led to the unsymmetrical adduct, *n*-decyldiethylgallium (eq. 8). At 100° this product was converted into an equilibrium mixture containing the symmetrical gallium alkyls (eq. 9)

$$Ga(C_2H_5)_2H + H_2C{=}CHC_8H_{17} \longrightarrow Ga(C_2H_5)_2C_{10}H_{21} \quad (8)$$

$$3Ga(C_2H_5)_2C_{10}H_{21} \xrightarrow{100^\circ} 2Ga(C_2H_5)_3\uparrow + Ga(C_{10}H_{21})_3 \quad (9)$$

The triethylgallium was drawn off under reduced pressure and identified by oxidation to ethoxydiethylgallium (*cf. infra*). Similarly, 3-hexyne and diethylgallium hydride reacted smoothly at 65° to form 3-hexenyldiethylgallium. Therefore, the interaction of this dialkylgallium hydride with such unsaturated hydrocarbons furnishes an excellent route to unsymmetrical GaR_2R' types. However, attempted distillation of such compounds at higher temperatures encounters the difficulty of disproportionation (eq. 9).

Another approach to dialkylgallium hydride additions is the generation of R_2GaH *in situ* from

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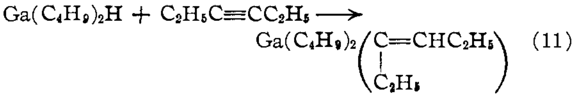
[11] *Cf.* Paper I of this series for evidence favoring a 1:3 complex between gallium(III) chloride and diethylaluminum chloride.

suitable R_3Ga types by thermal elimination of olefin. It already has been reported[3] that triisobutylgallium and α-olefins yield the higher trialkylgallium and isobutylene at 150–160°. The analogous reaction with 3-hexyne at 140° furnished one equivalent of isobutylene and subsequent hydrolysis yielded only 3-hexene

$$Ga(C_4H_9)_3 \underset{\Delta}{\longrightarrow} Ga(C_4H_9)_2H + C_4H_8\uparrow \quad (10)$$



$$Ga(C_4H_9)_2H + C_2H_5C\equiv CC_2H_5 \longrightarrow Ga(C_4H_9)_2\left(\begin{array}{l}C{=}CHC_2H_5\\ |\\ C_2H_5\end{array}\right) \quad (11)$$

Gallium Alkyls with Olefins and Acetylenes.—As with aluminum alkyls, the behavior of gallium alkyls with olefins was found to take two forms: first, a displacement reaction in the case of 1-alkenes and branched gallium alkyls[3]

$$Ga(i\text{-}C_4H_9)_3 + 3CH_2{=}CHR \xrightarrow{150\text{–}160°} Ga(CH_2CH_2R)_3 + 3i\text{-}C_4H_8\uparrow \quad (12)$$

and second, a "growth" reaction in the case of ethylene and triethylgallium

$$Ga(C_2H_5)_3 + 3nCH_2{=}CH_2 \xrightarrow[170°]{100\text{–}125\text{ atm.}} Ga[(CH_2CH_2)_nC_2H_5]_3 \quad (13)$$

It is noteworthy, however, that the feasible temperature ranges necessary to achieve these reactions with gallium alkyls are considerably higher than with aluminum alkyls. With triisobutylaluminum, for example, the olefin displacement (eq. 12) proceeds readily at 100–110° [12] and with triethylaluminum the "growth" reaction (eq. 13) can be realized under ethylene pressures of 50–100 atm. and temperatures of 100–120°.[13]

A more striking difference in the behavior of gallium alkyls *versus* aluminum alkyls came to light in the case of terminal acetylenes. Wilke and Müller[14] have observed not only that triethylaluminum can add to the triple bond in acetylene (eq. 14) more readily than to the double bond in ethylene, but that there is no interference from the "acidic" hydrogens (eq. 15)

$$Al(C_2H_5)_3 + HC\equiv CH \xrightarrow{40\text{–}60°} Al(C_2H_5)_2(CH{=}CHC_2H_5) \quad (14)$$

$$Al(C_2H_5)_3 + HC\equiv CH \xrightarrow[\text{observed}]{\text{not}} Al(C_2H_5)_2(C\equiv CH) + C_2H_6\uparrow \quad (15)$$

On the other hand, triethylgallium and terminal acetylenes (ethyne and 1-hexyne) reacted with each other mainly according to eq. 15

$$Ga(C_2H_5)_3 + HC\equiv CR \xrightarrow{50°} \underset{\text{IV}}{Ga(C_2H_5)_2(C\equiv CR)} + C_2H_6\uparrow \quad (16)$$

In the reaction with 1-hexyne the resulting 1-hexynyldiethylgallium (IV) was found to disproportionate and decompose upon distillation

$$\begin{array}{l} \underset{\text{IV}}{3Ga(C_2H_5)_2(C\equiv CC_4H_9)} \underset{\Delta}{\rightleftarrows} \\ \qquad 2Ga(C_2H_5)_3 + Ga(C\equiv CC_4H_9)_3 \quad (17) \\ \qquad \Big\downarrow O_2 \\ \qquad 2Ga(C_2H_5)_2(OC_2H_5) \end{array}$$

Finally, the reactivity of catalytic amounts of triethylgallium and titanium(IV) chloride toward ethylene was compared with the triethylindium–titanium(IV) chloride system in the Ziegler polyethylene polymerization process.[15] Although a careful comparison with triethylaluminum was not made, triethylgallium possessed a high degree of co-catalytic activity which was far superior to that of triethylindium.

Oxidation and Solvolysis of Gallium Alkyls.—In correlating the behavior of gallium alkyls toward unsaturated compounds with cleavage by oxygen and protic sources, and in identifying the products of such unsaturated hydrocarbon–gallium alkyl interactions, it was appropriate to study the oxidation and solvolysis of these alkyls. It has been observed previously that gallium alkyls burn in air[16] and undergo cleavage of one alkyl group with water at room temperature[16] or two alkyl groups with aqueous base at 100°.[16b,17] Warm dilute sulfuric acid is necessary to cleave all three alkyl groups and liberate the Ga^{+3} ion.[16a] In this study it was shown that gallium alkyls can be smoothly oxidized to the alkoxydialkylgallium (V). The latter type is quite stable toward further oxidation at ordinary temperatures and is hydrolyzed only slowly in moist air to R_2Ga–OH. The structure of V was proved in the triethylgallium case by obtaining the oxidation product, ethoxydiethylgallium, *via* an independent route involving the monoethanolysis of triethylgallium

$$2Ga(C_2H_5)_3 + O_2 \longrightarrow \underset{\text{V}}{2Ga(C_2H_5)_2(OC_2H_5)} \xleftarrow[-C_2H_6]{} 2Ga(C_2H_5)_3 + 2C_2H_5OH \quad (18)$$

The characteristically sweet odors detected when traces of gallium alkyls are entrained in air therefore are due to the stable oxidation products of type V.

The inertness of the second and third alkyl groups in the solvolysis of triethylgallium is emphasized by the high yield of the monoethoxy derivative obtained when this gallium alkyl was heated with an excess of ethanol (eq. 18). Cleavage of gallium alkyls by water at room temperature has been shown by previous workers[16a,17] to involve the formation of dialkylgallium hydroxide. In the present work it was observed that the initially formed diethylgallium hydroxide gave rise to polymeric ethylgallium oxide at higher temperatures (*cf.* ref. 17)

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[12] K. Ziegler, W.-R. Kroll, W. Larbig and O. W. Steudel, *Ann.*, **629**, 53 (1960).

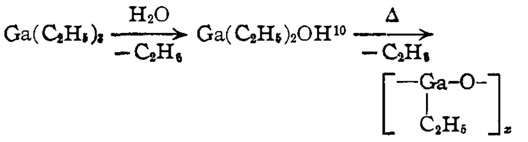
[13] K. Ziegler, H.-G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll and W.-R. Kroll, *ibid.*, **629**, 121 (1960).

[14] G. Wilke and H. Müller, *ibid.*, **629**, 222 (1960).

[15] K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, **67**, 426 (1955).

[16] (a) L. M. Dennis and W. Patnode, *J. Am. Chem. Soc.*, **54**, 182 (1932); (b) C. A. Kraus and F. E. Toonder, *Proc. Natl. Acad. Sci.*, **19**, 292 (1933) [*C. A.*, **27**, 2646 (1933)].

[17] M. E. Kenney and A. W. Laubengayer, *J. Am. Chem. Soc.*, **76**, 4839 (1954).



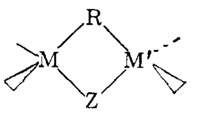
$$Ga(C_2H_5)_3 \xrightarrow[-C_2H_6]{H_2O} Ga(C_2H_5)_2OH^{10} \xrightarrow[-C_2H_6]{\Delta} \left[\begin{matrix}—Ga\text{-}O— \\ | \\ C_2H_5\end{matrix}\right]_x \quad (19)$$

The foregoing results point up the marked tendency of gallium alkyls to undergo oxidation and solvolysis of only one alkyl group under moderate conditions. In marked contrast, all three alkyl groups of organoaluminum compounds can be readily cleaved by oxygen and protic solvents under comparable conditions.

Discussion

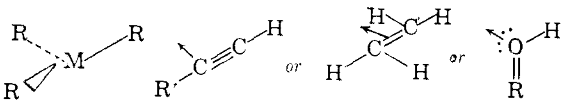
Though the gallium and aluminum atoms are congeners of Group III because of their common outermost electronic configuration of ns^2np^1, gallium's electronic arrangement is attained by filling its underlying or 3d- and 3p-orbitals, while its nuclear charge is increasing by 18 protons. As a consequence the covalent radii of aluminum and gallium are the same (1.26 Å.). The heightened effective nuclear charge of gallium seems responsible also for the slightly greater electronegativity of gallium compared with that of aluminum (Ga = 1.6; Al = 1.5, on the Pauling scale). This should mean a lower carbon–metal bond polarity in gallium alkyls ($\overset{\delta-}{C}$–$\overset{\delta+}{Ga}$) than in aluminum alkyls ($\overset{\delta-}{C}$–$\overset{\delta+}{Al}$). Despite the greater electronegativity of gallium, however, there are several lines of evidence which demonstrate that gallium alkyls are less effective Lewis acids than aluminum alkyls.[18] This may be related to the unfavorable electronic repulsions encountered between the 3d-electrons of the gallium atom in gallium alkyls and the donor electron pair of the Lewis base.

This decrease in bond polarity and Lewis acid character seems the explanation for the decreased reactivity and the differences in mode of reaction of gallium alkyls compared with aluminum alkyls. The Lewis acid character of Group III metal alkyls seems significant in two general reaction types: first, in exchange reactions between metal alkyls and metal halides, hydrides or dissimilar metal alkyls (VI); and, second, in the behavior of metal alkyls toward potential Lewis base substrates, such as olefins, acetylenes, alcohols and oxygen (VII)



VI

R = CH_3CH_2, H, $CH_3(CH_2)_3C{\equiv}C$
Z = Cl, CH_3CH_2O
M,M′ = Ga, Al



VII

R = CH_3CH_2, H; R′ = $CH_3CH_2CH_2CH_2$; M = Ga, Al

From the known dimeric or trimeric bridge structures of many organoaluminum compounds[19] and from the recent findings of Köster and Bruno[20] concerning exchange reactions between boron and aluminum alkyls, it seems appealing to view a generalized configuration such as VI as an intermediate or as a transition state through which actual group exchange takes place. In this conception the greater the tendency of a group to act as a bridging group, the greater the tendency for exchange. Although further work is needed to establish the generality of this hypothesis, two examples support this view: the predominance of hydride–halide over ethyl–halide exchange in the reaction between gallium(III) halides and diethylaluminum hydride (eq. 2); and the nearly quantitative yield of diethylgallium chloride obtained from gallium(III) chloride and triethylgallium, underlining the inability of ethylgallium dichloride and triethylgallium to resist a net chloride exchange (eq. 1). Thus the course of these reactions can be understood if the superior bridging tendencies of hydride and chloride groups, compared with that of the ethyl group, are borne in mind.

In a parallel fashion for metal alkyl interactions with unsaturated hydrocarbons, complexes such as VII may be important reaction intermediates. This would also call upon the Lewis acid character of the metal alkyl. The lessened reactivity of triethylgallium toward ethylene, compared with triethylaluminum, becomes reasonable in this light. One of the most striking differences in *degree* of reactivity of organogallium *versus* organoaluminum compounds is the pronounced resistance of the R_2GaZ types (Z = Cl, F, OH, OR) to further oxidation and hydrolysis (*cf.* the reactive properties of $(C_2H_5)_2AlCl$). Although the degree of association of many R_2GaZ types is unknown, evidence at hand[21] strongly suggests their existence as intermolecular complex structures which are at least dimeric. Hence, it may be that such autocomplexation (*cf.* VI, where R and Z = Cl, OR, and M and M′ = Ga) reduces their Lewis acid activity even further and thus their reactivity toward olefins, alcohols and oxygen markedly. Although R_2AlZ types are also strongly associated and hence do not react with olefins in the usual manner,[22] they do undergo ready oxidation and solvolysis.

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(18) (a) G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, 3351 (1956), have established the order of decreasing Lewis acidity for Group III metal alkyls as B < Al > Ga > In > Tl by comparing the heats of dissociation of $R_3M \leftarrow NR_3$ complexes; (b) W. Strohmeier and K. Hümpfner, *Z. Elektrochem.*, **61**, 1010 (1951), have arrived at the same order of Lewis acidity by correlating dipole moments of solutions of Group III metal alkyls in donor solvents; and (c) Paper I of this series reports that whereas $Al(C_2H_5)_3$ complexes with NaF or KF in a 1:1 fashion, $Ga(C_2H_5)_3$ complexes with KF, but not with NaF. Finally, $In(C_2H_5)_3$ complexes neither with NaF nor with KF.

(19) *Cf.* (a) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953), for X-ray crystallographic evidence for the structure of $[Al(CH_3)_3]_2$; (b) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942); (c) E. G. Hoffmann, *Ann.*, **629**, 104 (1960).

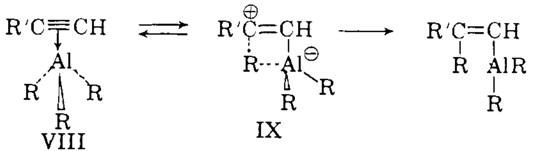
(20) R. Köster and G. Bruno, *ibid.*, **629**, 89 (1960).

(21) (a) G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 3907 (1959), have shown that dimethylgallium hydroxide is a tetramer in the crystalline state; (b) G. E. Coates and R. G. Hayter, in G. E. Coates, "Organo Metallic Compounds," Methuen and Co., London, 1960, p. 151, state that dimethylgallium chloride is a dimer in the vapor state.

(22) K. Ziegler and W.-R. Kroll, *Ann.*, **629**, 167 (1960), have shown that only when a catalytic amount of R_3Al is added does one observe a growth reaction with R_2AlZ types and ethylene.

Presumably the greater polarity of the Al–C bond *versus* the Ga–C bond is important in understanding the pyrophoric and easily hydrolyzable character of $(C_2H_5)_2AlCl$ *versus* the inertness of $(C_2H_5)_2GaCl$.

The most striking difference in *kind* of behavior between gallium alkyls and aluminum alkyls lies in their interaction with terminal acetylenes. That aluminum alkyls add to the triple bond[14] and that gallium alkyls provoke the pseudoacidic character of the terminal acetylene can be brought into consonance with bond polarity and Lewis acidity differences. Considering an initial complex formation analogous to VII one would obtain π-complexes



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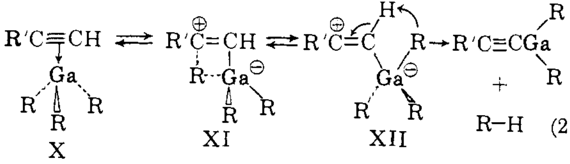
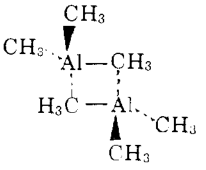


(21)

such as VIII and X, the former being the stronger of the two. Structures IX and XI would be considered as possible transition states in which the complexes are beginning to develop the character of a σ-complex. It is reasonable to assume that in IX the R group should find it easier to bridge between the aluminum and the positively polarized β-carbon atom than the R group in XI can bridge between the gallium and β-carbon atom. This view finds support in the fact that trimethylaluminum has a dimeric bridge structure in the vapor state (XIII),[19] while trimethylgallium exists as a monomer in the vapor state.[16b] The bridging of the alkyl group between the two electron-deficient atoms (C_β and Al) in IX would resemble the known



XIII

situation in XIII. As suggested earlier, the greater the bridging tendency, the greater the exchange tendency. In the case of IX, of course, the result would be addition. The decrease in bond polarity and in bridging tendency with gallium alkyls would mean that XI would be less favored and consequently the gallium system would find it more advantageous to assume σ-complex character as in XII. Nucleophilic attack of the negatively polarized R group on hydrogen then would lead to the observed product.

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Experimental

General Techniques and Starting Materials.—The reactions and transfers of moisture- and oxygen-sensitive gallium and aluminum compounds were conducted under an atmosphere of ultra-pure nitrogen or argon. Techniques for the handling, preparation and analysis of starting materials employed in this study are described in a previous paper.[3]

Diethylgallium Chloride.—To 8.81 g. (0.050 mole) of solid gallium(III) chloride was added dropwise 15.7 g. (0.10 mole) of triethylgallium over a period of 20 minutes. A strongly exothermic reaction accompanied the formation of an almost colorless solution. (Despite the apparent vigor of the reaction it was found necessary to heat the resulting solution for some time at 100°. Omission of the heating prior to distillation resulted in very non-uniform distillation fractions.) The clear reaction mixture was heated at 90–100° for 1 hour and then distilled under reduced pressure. With little fore- or after-run the colorless main fraction was collected at 60–62° (2 mm.), 98% yield, d^{20}_{20} 1.35. In contrast to the pyrophoric and moisture-sensitive character of diethylaluminum chloride the gallium analog did not burn in air or react vigorously with water. The product was fractionally redistilled before analysis (oxine method for gallium and the Mohr method for chloride on hydrolyzed samples).

Anal. Calcd. for $C_4H_{10}ClGa$: Cl, 21.71; Ga, 42.70. Found: Cl, 21.61; Ga, 42.76.

Diethylgallium Fluoride.—A mixture of 16.3 g. (0.10 mole) of diethylgallium chloride and 11.6 g. (0.20 mole) of ignited and powdered potassium fluoride was heated at 100–105° for 2 hours with frequent shaking. The reaction product was then distilled under mercury diffusion pump vacuum (10^{-4} mm.). After a forerun of unreacted chloride the main fraction (70%) boiled at 50–80°. This fraction was reheated at 100° with 2.0 g. of fresh potassium fluoride for 1 hour and then distilled at oil-pump pressure. The product boiled at 80–81° under 1 mm. as a colorless, viscous liquid.

Anal. Calcd. for $C_4H_{10}FGa$: Ga, 47.48. Found: Ga, 47.76.

Reaction between Diethylaluminum Hydride and Gallium(III) Halides. a. Gallium(III) Bromide.—A suspension of 28.9 g. (0.094 mole) of gallium(III) bromide in 100 ml. of dry pentane was treated dropwise with 23.5 g. of 90% pure diethylaluminum hydride (21.1 g., 0.245 mole) at room temperature over a period of 45 minutes. Ten minutes after the addition had started, the system became gray and gas evolution set in. After gas evolution had ceased, a shiny globule of gallium metal was filtered from the reaction mixture, washed with pentane and water, dried and weighed. In this manner 5.2 g. (91%, based upon the available $(C_2H_5)_2AlH$) of gallium metal was recovered. The evolved gas contained only hydrogen and pentane vapor.

b. **Gallium(III) Chloride.**—In a similar fashion the slow addition of 2.8 g. (0.033 mole) of pure diethylaluminum hydride to 1.76 g. (0.010 mole) of solid gallium(III) chloride gave a mixture which turned gray and began to evolve hydrogen. At the end of the reaction 0.7 ± 0.05 g. (100%) of gallium metal was recovered.

Diethylgallium Hydride.—A mixture of 70.2 g. (0.43 mole) of diethylgallium chloride and 54 g. (0.72 mole) of ignited and powdered potassium chloride was treated with 37.8 g. (0.43 mole) of diethylaluminum hydride during a 50-minute period. The exothermic reaction raised the internal temperature to 40–45°, and the mixture was agitated frequently to dissipate the heat and to suspend the potassium chloride. After 2 hours three distinct phases were in evidence: an upper liquid layer containing the diethylgallium hydride and triethylgallium; a lower semi-solid layer of $K[Al(C_2H_5)_2Cl_2]$; and a solid layer of excess potassium chloride. The upper liquid layer was pipetted into a Claisen distillation flask under an inert atmosphere. After 6 g. of powdered potassium chloride (scavenger for $Al(C_2H_5)_2Cl$) and 1 g. of mercury (gallium metal scavenger) were introduced, the mixture was thoroughly shaken and then subjected to mercury diffusion pump vacuum (10^{-4} mm.) without heating. The volatile triethylgallium was collected in the trap cooled with liquid air during a 1-hour period. Thereupon the distillation residue was warmed to 60° for an additional hour. During this period decomposition began—formation of a gray precipitate and increased pressure (10^{-2} mm.) in the vacuum system. The bath temperature was raised to 72–73° and the distillation of the residue began: after 1 ml. of fore-run the main fraction was collected between 47° (10^{-3} mm.) and 51° (5×10^{-2} mm.). This product amounted to 13.5 g. (24%) of impure diethylgallium hydride. From the cold trap 32 g. (47%) of mainly triethylgallium was recovered. Redistillation of the hydride provided a clear, colorless, rather mobile liquid, b.p. 40–42° (10^{-4} mm.), which burned spontaneously in air and reacted violently with water. The product contained 53.45% gallium and a trace of chlorine (*ca.* 0.1%). Diethylgallium hydride should contain 54.11% gallium. Contamination by triethylgallium (44.44% Ga) and diethylaluminum hydride ("44.03%," ash calculated as Ga_2O_3) were responsible for the low value; the product was approximately 95% pure. Further purification by redistillation was not successful. A 0.309-g. sample was decomposed first with 2-ethylhexanol and then with warm dilute sulfuric acid. The collected gas amounted to 166 ml. at 19° and 759 mm. (96% of the theoretical quantity), consisting of ethane and hydrogen (1.8:1.0).

Diethylgallium Hydride and 1-Decene.—In a preliminary trial a 1-ml. sample of the hydride was heated with 2 ml. of anhydrous 1-decene for 3 hours at 80°. A sample was withdrawn and hydrolyzed in the usual gas analysis apparatus. Only ethane was found by mass spectrometric analysis; hydrogen was not detectable.

A mixture of 3.9 g. (0.030 mole) of diethylgallium hydride and 4.2 g. (0.030 mole) of 1-decene was heated at 65° for 7 hours. A clear, weakly fluorescent solution resulted. Since it was felt that the unsymmetrical alkyl, diethyl-*n*-decylgallium, should have a tendency to disproportionate into triethylgallium and tri-*n*-decylgallium, the reaction product was heated for 3 hours at 100° under 3 mm. pressure. The Dry Ice–acetone trap was found to contain 3.2 g. of liquid (expected quantity = 0.02 mole or 3.1 g.). This product was shown to be triethylgallium by oxidizing it with dry air to yield ethoxydiethylgallium, $n^{20}D$ 1.450, which has a characteristic sweet, vanilla-like odor. The viscous liquid residue in the original reaction vessel was analyzed for gallium. Decomposition of the sample by acid resulted in some gas evolution (ethane). The sample contained 16.0% gallium. Since $Ga(C_{10}H_{21})_3$ would contain 14.12% Ga and $Ga(C_{10}H_{21})_2(C_2H_5)$ 18.28% Ga, disproportionation of the original $Ga(C_2H_5)_2(C_{10}H_{21})$, containing 25.91% Ga, had taken place to a great extent.

Diethylgallium Hydride and 3-Hexyne.—Mixing 3.8 g. (0.029) mole of diethylgallium hydride and 3.7 g. (0.045 mole) of anhydrous 3-hexyne resulted in a clear, colorless solution without the evolution of heat. After 10 minutes at 65° the solution became yellow-green. The colored solution was maintained at 65° for 2.5 hours and then the excess 3-hexyne was drawn off under oil pump vacuum (recovered 3-hexyne: 1.5 g., $n^{20}D$ 1.4155, containing traces of GaR_3; calculated excess, 1.3 g.). The residual yellow diethyl-3-hexenylgallium was analyzed. The product still fumed in air.

Anal. Calcd. for $C_{10}H_{21}Ga$: Ga, 33.04. Found: Ga, 32.77.

Decomposition of the product first with methanol and then with warm dilute sulfuric acid evolved a gas containing only ethane and 3-hexene. No 3-hexyne was found.

Triethylgallium and Acetylene.—A 250-ml. two-necked, round-bottomed flask, fitted with a three-way stopcock and containing 3.2 g. (0.020 mole) of triethylgallium, was cooled in a Dry Ice–acetone-bath, evacuated at the oil-pump and refilled with anhydrous acetylene at room temperature. (After usual purification the acetylene was bubbled through AlR_3 and passed through a −78° condensing trap.) A slight rise in temperature and a rose coloration were observed. After 15 hours a colorless precipitate had separated from the red liquid. However, no partial vacuum existed in the vessel. Mass spectrometric analysis of the reaction mixture's gas phase showed the presence of 62.4% acetylene, 37.2% ethane, 0.3% 1-butene and 0.1% *n*-butane. The flask was evacuated again, refilled with acetylene and allowed to stand for an additional 24 hr. Pentane was added and the insoluble white solid was collected. The product was insoluble in water but completely soluble in dilute hydrochloric acid. In air the solid was oxidized with charring.

Triethylgallium and 1-Hexyne.—To confirm the above reaction, a monosubstituted acetylene was chosen for further study. The addition of 7.2 g. (0.088 mole) of anhydrous 1-hexyne to 5.4 g. (0.034 mole) of triethylgallium resulted in a warm, pale yellow solution and the slow evolution of gas (collected in a gas buret). The solution thereupon was heated at 50–55° for 1.5 hours. The evolved gas (calcd. for 1 equiv. C_2H_6, 840 ml. at 21° and 749 mm.; found, 820 ml.) was shown to be ethane and corresponded to the loss of one ethyl group. The excess 1-hexyne was removed from the reaction product at 55° and 2 mm. pressure (calculated excess, 4.5 g.; recovered excess, 4.2 g.). The viscous, pale yellow residue in the flask gave satisfactory analysis for diethyl-1-hexynylgallium.

Anal. Calcd. for $C_{10}H_{19}Ga$: Ga, 33.37. Found: Ga, 33.29.

The compound was oxidized readily in air, emitting a heavy, fruity odor, and was hydrolyzed violently to yield ethane and 1-hexyne. Attempted distillation at 120–150° and 2 mm. pressure changed the yellow diethyl-1-hexynylgallium into a viscous, dark-brown mass. From the cold trap *ca.* 1 g. of liquid was obtained, which yielded ethoxydiethylgallium, $n^{20}D$ 1.450, when treated with dry air. Hence, disproportionation to triethylgallium and tri-1-hexynylgallium seemed to occur upon heating.

Triisobutylgallium and 3-Hexyne.—Addition of 2.8 g. (0.034 mole) of anhydrous 3-hexyne to 8.0 g. (0.033 mole) of triisobutylgallium resulted in the formation of a warm, yellow solution accompanied by gas evolution. The mixture was heated at 140° under reflux for 48 hours, while the evolved gas was collected in a gas buret; calcd. for 1 equiv. of *iso*-C_4H_8, 830 ml. at 20° and 755 mm.; found, 820 ml. containing 90.2% isobutylene, 7.9% isobutane, 1.2% 3-hexene and 0.7% 3-hexyne. The viscous, dark-brown adduct was hydrolyzed in the usual manner to yield only isobutane (85%) and 3-hexene (15%).

Oxidation of Triethylgallium.—A current of dry air (previously passed through a drying tower of Molecular Sieves, Linde Division, Union Carbide Corp.) was passed over a stirred 6.3-g. (0.040 mole) sample of triethylgallium. During the 2-hour reaction period the temperature rose to 50–60° and fell as the oxidation rate slackened. The colorless product distilled almost quantitatively at 78–79° (1 mm.). Although this product slowly was changed into a white, semi-solid material by atmospheric moisture, it was sufficiently stable for a refractive index measurement, $n^{20}D$ 1.449. The ethoxydiethylgallium (*cf. infra*) had the characteristic vanilla odor associated with traces of triethylgallium in air.

Anal. Calcd. for $C_6H_{15}GaO$: Ga, 40.32. Found: Ga, 40.36.

Alcoholysis of Triethylgallium.—To a solution of 6.3 g. (0.040 mole) of triethylgallium in 35 ml. of pentane was added dropwise 4.6 g. (0.10 mole) of freshly prepared absolute ethanol. After the vigorous gas evolution had ceased, the solution was heated under reflux for 30 minutes. The pentane was drawn off under reduced pressure and the somewhat turbid residue was distilled. The ethoxydiethylgallium distilled at 86–87° (3 mm.) and comprised an 87% yield. The infrared spectrum of this product was superimposable with that obtained from the oxidation of triethylgallium ($n^{20}D$ 1.448, $d^{20}{}_4$ 1.158).

Anal. Calcd. for $C_6H_{15}GaO$: Ga, 40.32. Found: Ga, 40.25.

Hydrolysis of Triethylgallium.—To a solution of 4.2 g. (0.027 mole) of triethylgallium in 25 ml. of pentane was added 0.5 g. (0.028 mole) of water. After the vigorous gas evolution had ceased, a clear solution of supposedly $Ga(C_2H_5)_2OH$ was obtained. Heating the solution at the reflux temperature for 1 hour caused further gas evolution and the deposition of a colorless solid. The suspension was filtered off and washed with pentane. The semisolid product was heated at 100° for 1 hour, during which time more gas was evolved. In this manner 2.91 g. of a white solid was obtained. Upon heating, the product did not melt, but charred with the evolution of a flammable gas. Solution in warm sulfuric acid also evolved gas. Based upon polymeric ethylgallium oxide, the yield was 94%.

Anal. Calcd. for C_2H_5GaO: Ga, 60.75. Found: Ga, 59.98; 60.07; 60.38.

Oxidation of Triisobutylgallium.—Similarly to the oxidation of triethylgallium, this compound was oxidized quantitatively to isobutoxydiisobutylgallium, b.p. 161–163° (3 mm.), n^{20}D 1.458, possessing an apricot-like odor.

Anal. Calcd. for $C_{12}H_{27}GaO$: Ga, 27.12. Found: Ga, 27.15.

Oxidation of Tri-*n*-decylgallium.—The non-distillable *n*-decoxydi-*n*-decylgallium could be prepared in an identical fashion. This product had a heavy, higher alcohol-like odor, n^{20}D 1.463.

Anal. Calcd. for $C_{30}H_{63}GaO$: Ga, 13.68. Found: Ga, 13.81.

Triethylgallium and Diethylaluminum Hydride. a. Equivalent Quantities.—Mixing 6.8 g. (0.079 mole) of diethylaluminum hydride with 4.2 g. (0.027 mole) of triethylgallium caused a noticeable evolution of heat. The clear, colorless solution was heated at 120–130° and the evolved gas was collected. During the first (16-hour) heating period the solution deposited a gray solid and 175 ml. of gas was evolved (at 20° and 755 mm.: 72% hydrogen, 18% ethane and 10% butane–butene). The second (12-hour) period produced 150 ml. of gas (66% hydrogen, 22% ethane, 7% 1-butene and 5% *n*-butane). The gray reaction mixture was distilled at the mercury diffusion pump and 70° to remove the organometallic products. The residue consisted of 0.18 g. of gallium metal (29%, based upon 0.027 mole of GaH_3).

b. Excess of Diethylaluminum Hydride.—A mixture of 4.2 g. (0.027 mole) of triethylgallium and 30 ml. of diethylaluminum hydride (90% hydride and 10% triethylaluminum was heated at 120–130° for 125 hours. Only 160 ml. of gas (20° and 759 mm.) was collected: 82% hydrogen and 18% ethane.

Hydrogenolysis of Triethylgallium.—In a 250-ml. steel autoclave 10.6 g. (0.067 mole) of triethylgallium was heated with hydrogen (80 atm., cold) for 20 hours at 85–100°. Gas analysis of the atmosphere of the autoclave indicated the presence of 96% hydrogen and 4% ethane. A further 20 hours at 120–125° (after refilling to 80 atm.) resulted in a similar analysis: 95% hydrogen and 5% ethane. A final 20 hours at 135–140° caused little change: 94:6. The contents of the autoclave now consisted of a gray suspension weighing 7.1 g. A sample of clear, supernatant liquid (precipitate was gallium) was hydrolyzed and the evolved gas was analyzed: 99.3% ethane and 0.7% hydrogen.

Growth Experiments with Ethylene. a. Triethylgallium.—A 250-ml., steel autoclave, fitted with a glass insert, was charged with 2.1 g. (0.013 mole) of triethylgallium and 22 g. (0.78 mole) of ethylene (50 atm.). The autoclave was heated with agitation for various periods, the ethylene released from the cooled autoclave and the autoclave tared to obtain any weight increase due to liquid olefin formation (see table). After the liquid in the autoclave (11 g.) was hydrolyzed, dried and distilled, about 3 ml. of hydrocarbon boiling from 48° (14 mm.) to 165° (2 mm.) was obtained. Volatile olefinic materials were caught in the cold trap. Infrared analysis showed these fractions resembled a mixture of higher 1-alkenes, internal alkenes and alkanes. The autoclave atmosphere contained mostly ethylene and butylenes.

Temp., °C.	Time, hr.	Pressure, atm.	Wt. increase, g.
110	20	90	0
130	20	97	0
170	20	115	2
210	30	120 (90, final)	7

b. Triethylindium.—In a similar manner 2.0 g. (0.010 mole) of triethylindium was heated with ethylene under pressure. No drop in the pressure (120 atm., warm) was noted until 170° was reached. After 40 hours at 170° and 24 hours at 195° only a maximum of 2 g. of ethylene was taken up. The resulting gray suspension recovered from the autoclave pointed to indium alkyl decomposition.

c. Triethylgallium at Higher Pressures.—In a 200-ml. steel autoclave 7.4 g. (0.047 mole) of triethylgallium and 42 g. (1.5 moles) of ethylene were heated at 140° for 24 hours. (An initial, 3-hour period at 125° caused no drop in pressure.) The initial pressure of 170 atm. (warm) fell to 160 atm. After an additional 30 hours at 170° the autoclave was vented to yield 33 g. of gas consisting of 52% ethylene, 22% *trans*-2-butene, 14% ethane, 9% *cis*-2-butene and 3% 1-butene. The yellow liquid product (12 g.) showed no sign of gray suspended gallium metal. However, about 2 g. of polyethylene was found in the autoclave. Distillation of the liquid residue allowed the recovery of 4.2 g. of triethylgallium. The fore-run and after-run consisted of olefinic material.

Polymerization Experiments.[23] **a. Triethylgallium.**—A 500-ml., three-necked cylindrical flask, equipped with a wide gas-inlet tube, stirrer and a thermometer dipping into the solvent, was flushed with nitrogen and then charged with 250 ml. of dry diesel oil (b. range 180–240°, from sodium) and 1.32 g. (0.0084 mole) of triethylgallium. With stirring 0.52 g. (0.0027 mole) of titanium(IV) chloride was introduced; a dark brown suspension thereupon was formed. The pure and dry ethylene was bubbled into the stirred catalyst suspension at such a rate that the internal temperature rose to 60° within 10 minutes. The reaction temperature was held between 60–70° during the polymerization by means of a compressed-air stream. After 45 minutes the reaction mixture consisted of a light brown, mealy suspension which was almost unstirrable. The polyethylene was isolated by the addition of 25 ml. of *n*-butyl alcohol and then water. The white polymer was collected by filtration, triturated several times with water, warm hydrochloric acid and ether, and finally dried at 80°. The completely white polyethylene weighed 47 g.

b. Triethylindium.—In a manner strictly comparable to section a, a solution of 1.70 g. (0.0084 mole) of triethylindium in 250 ml. of dry diesel oil was treated with 0.52 g. (0.0027 mole) of titanium(IV) chloride to produce a black suspension. Introduction of ethylene gas caused only a slight rise in temperature (18–33°) and only 6 g. of ethylene gas was taken up in a 90-minute reaction period. The customary work-up gave 5 g. of polyethylene.

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[23] K. Ziegler and H. Martin, *Makromol. Chem.*, **18-19**, 186 (1956).