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Reduction of R$_3$Ga with Alkali Metals in Aromatic Solvents—Formation of R$_3$GaAr$^-$ and R$_3$GaH$^-$ [1]

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Reduction of trialkylgallium compounds (R$_3$Ga) in benzene with alkali metals forms R$_3$GaPh$^-$ and R$_3$GaH$^-$ anions in addition to the expected R$_4$Ga$^-$ anions. The portion of the product consisting of R$_3$GaPh$^-$ and R$_3$GaH$^-$ decreases as R is changed in the series *sec*-butyl > isobutyl > ethyl > methyl. Only R$_4$Ga$^-$ is observed when the reducing agent is Li instead of Na/K alloy, K, or Cs. Reductions in a monoalkylbenzene form R$_3$Ga(*m*-alkylphenyl)$^-$ and R$_3$GaH$^-$. ^{1}H and ^{13}C NMR spectra of *s*-Bu$_3$Ga, *s*-Bu$_4$Ga$^-$, *s*-Bu$_3$GaPh$^-$, and *s*-Bu$_3$GaH$^-$ show a discrete absorption for each diastereomer for some groupings.

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Reductions of trialkylgallium compounds by alkali metals in aromatic solvents produce up to three organogallium ions. One is R$_4$Ga$^-$, expected because of reports[2] of the formation of these ions by reduction of R$_3$Ga compounds by alkali metals in other solvents. This paper identifies the two new ions, describes the effect of R, the reducing agent, and the solvent on the product composition, and considers possible mechanisms for their formation.

Results and Discussion

^{1}H NMR spectra of the products from reductions of benzene solutions of *i*-Bu$_3$Ga with either K or Na/K alloy have three sets of isobutyl absorptions, suggesting three components. ^{1}H NMR spectra (Figure 1) of the products from similar reductions of *s*-Bu$_3$Ga have only two sets of *sec*-butyl absorptions. The benzene solutions that result from the reductions are relatively stable for days at ambient temperature. Efforts to isolate individual compounds have been unsuccessful, however. The operations of solvent removal, attempted crystallization of the resulting oils, etc., ultimately seem to cause decomposition. The structures of the products could be established, however, by the comparison of their NMR absorptions to those of compounds prepared by traditional syntheses.

Identification of R$_3$GaPh$^-$. ^{1}H NMR spectra of the product solutions show the absorptions expected for a phenyl group, with the absorption areas relative to those of one of the sets of isobutyl or *sec*-butyl absorptions, indicating one phenyl group per three butyl groups. The inference that R$_3$GaPh$^-$ is one of the products was confirmed by synthesizing the ion, stirring solutions of *i*-Bu$_3$Ga or *s*-Bu$_3$Ga with solid PhK,[4] and finding ^{1}H NMR and (examined for the *s*-Bu case) ^{13}C NMR absorptions identical to those of one of the components of the reductions.

Identification of R$_3$GaH$^-$. ^{1}H NMR spectra of the product solutions show an additional broad and weak absorption (δ 2.31 in the isobutyl case and δ 2.32 in the *sec*-butyl case).[5] The inference that R$_3$GaH$^-$ is one of the products was confirmed by synthesizing the ion, stirring a solution of *i*-Bu$_3$Ga or *s*-Bu$_3$Ga with solid KH.[7] and finding ^{1}H and ^{13}C NMR absorptions identical to those of one of the components of the reductions. Surprisingly, the CH$_2$Ga absorption in the ^{1}H NMR spectrum of *i*-Bu$_3$GaH$^-$ is a doublet of doublets. One of the splittings is due to the expected coupling with the adjoining CH. A decoupling experiment shows the additional splitting ($J = 1.4$ Hz) to be due to coupling with the hydrogen (δ 2.31) bonded to gallium.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.

[1] Much of this work adapted from Tang, H. Ph.D. Dissertation, The Pennsylvania State University, 1997. Some earlier experiments were done by R. Fabicon (some of these are described in Fabicon, R. M. Ph.D. Dissertation, The Pennsylvania State University, 1991).

[2] Wolfrum, R.; Sauermann, G.; Weiss, E. *J. Organomet. Chem.* **1969**, *18*, 27. Weibel, A. T.; Oliver, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 8590. Parman, M. R. D. A. Dissertation, University of Northern Colorado, 1978; *Diss. Abstr. Int. B* **1979**, *39*, 3833. Reference 3. Also see: *Gmelin Handbook of Inorganic Chemistry, Organogallium Compounds*, 8th ed.; Springer-Verlag: Berlin, 1987; part 1.

[3] Gavrilenko, V. V.; Kolesov, V. S.; Chekulaeva, L. A.; Antonovich, V. A.; Zakharkin, L. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1977**, 1127; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 1227.

[4] Reactions of R$_3$Ga and R′M (M is an alkali metal) have been used before to convert R$_3$Ga to R$_3$GaR′$^-$. See, for example: Williams, K. C.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4134. Kovar, R. A.; Derr, H.; Brandau, D.; Callaway, J. O. *Inorg. Chem.* **1975**, *14*, 2809. Gavrilenko, V. V.; Kolesov, V. S.; Zakharkin, L. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1981**, 1937; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 2354.

[5] ^{1}H NMR GaH absorptions were not observed for a benzene solution of (Me$_3$SiCH$_2$)$_3$GaH$^-$K$^+$ (ref 6). For other types of GaH compounds, ^{1}H NMR absorptions of GaH are not seen in some instances but are in others, for example, at δ 3.06 for Me$_2$GaH (Baxter, P. L.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1990**, 2873) and at δ 3.07 for Et$_2$GaH (Grady, A. S.; Mapplebeck, A. L.; Russell, D. K.; Taylorson, M. G. *J. Chem. Soc., Chem. Commun.* **1990**, 929), both in PhCD$_3$.

[6] Hallock, R. B.; Beachley, O. T., Jr.; Li, Y.-J.; Sanders, W. M.; Churchill, M. R.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1983**, *22*, 3683.

[7] Reactions of R$_3$Ga and MH (M is an alkali metal) have been used before to convert R$_3$Ga to R$_3$GaH$^-$. For example, refs 3 and 6. Gavrilenko, V. V.; Fatyushina, N. P.; L'vova, V. A.; Kolesov, V. S.; Karaksin, Yu. N.; Zakharkin, L. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1972**, 122; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 126. Beachley, O. T., Jr.; Tessier-Youngs, C.; Simmons, R. G.; Hallock, R. B. *Inorg. Chem.* **1982**, *21*, 1970.

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Table 1. NMR Absorptions Possible for Organogallium Compounds Containing *sec*-Butyl Groups Bonded to Gallium

no. of *s*-Bu groups	max no. of absorptions	relative intensities
1	1	1
2	2	1:1
3 (planar structure)	3	1:2:1
3 (nonplanar structure)	4	1:1:1:1
4	4	1:3:3:1

Identification of R_4Ga^-. The ^1H NMR spectrum in benzene-d_6 of *i*-Bu_4Ga^- K^+, synthesized from a reaction[4] of *i*-BuK and *i*-Bu_3Ga, is identical to that of one of the products of the reductions of *i*-Bu_3Ga. The same spectrum is produced by reducing *i*-Bu_3Ga in THF with Na/K alloy or K, these reductions in THF producing neither of the additional products that result in benzene. Addition of 18-crown-6 to a benzene solution of the presumed *i*-$Bu_4Ga^-K^+$ leads to formation of a second liquid phase, an indication that the products are ionic since some ionic compounds in benzene form a dense second phase[8] that contains much of the solute. The ^1H NMR spectrum of the lower phase shows one set of isobutyl absorptions and one crown ether absorption, in a position (δ ca. 3.0) expected for a crown ether coordinated to K^+; the absorption intensities indicate a 4:1 ratio of isobutyl groups to crown ether residues.

s-$Bu_4Ga^-Li^+$ was synthesized from *s*-BuLi and *s*-Bu_3Ga.[4] Reduction of *s*-Bu_3Ga in benzene with Li gives a solution having the same ^1H NMR spectrum. *s*-$Bu_4Ga^-K^+$ could not be prepared from a reaction of *i*-Bu_3Ga with *s*-BuK because *s*-BuK rapidly metalated the benzene. A reaction of *s*-Bu_2Hg, *s*-Bu_3Ga, and K was tried in hopes that (1) reduction of *s*-Bu_2Hg to form *s*-BuK would be more rapid than that of *s*-Bu_3Ga to form *s*-Bu_3GaPh^- and *s*-Bu_3GaH^- and (2) *s*-BuK would react more rapidly with *s*-Bu_3Ga than with benzene. The ^1H NMR spectrum of the product indicates the presence of a considerable amount of *s*-$Bu_4Ga^-K^+$ but also of residual *s*-Bu_2Hg and other species. *s*-$Bu_4Ga^-K^+$ was prepared more cleanly from *s*-Bu_3Ga and K in THF.

Other Evidence for Structures of Products. Adding 1 equiv of 18-crown-6 to a solution resulting from the reduction of *i*-Bu_3Ga or *s*-Bu_3Ga with Na/K alloy causes the formation of a second liquid layer, an indication that the products are ionic.[8] ^1H NMR spectra show the lower layer to have essentially all of the solute. The ^1H NMR spectrum of the lower layer from the *s*-Bu_3Ga reaction exhibits two sets of *sec*-butyl absorptions, slightly shifted from those observed before addition of the crown ether, and one crown ether absorption, in a position (δ 2.95) expected for a crown ether coordinated to K^+.

$Me_3NH^+Cl^-$ (approximately 1 equiv per *s*-Bu_3Ga initially used) was added to a solution obtained from reaction of *s*-Bu_3Ga and K. The ^1H NMR spectrum of the solution remaining after centrifugation of a precipitate that formed is the same as that of a solution of equimolar amounts of *s*-Bu_3Ga and Me_3N. This result suggests that both of the products of the reduction have three *sec*-butyl groups bonded to a gallium.

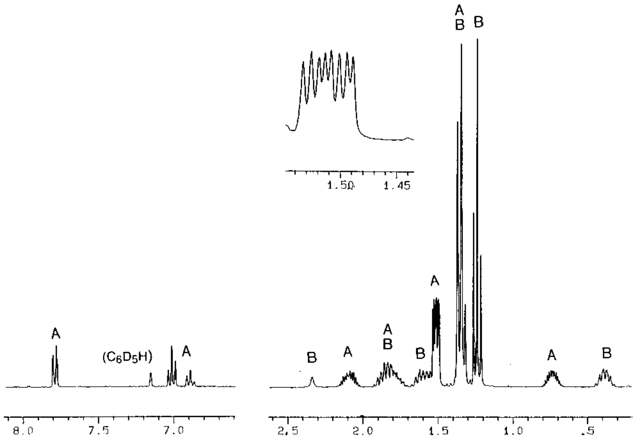

Figure 1. ^1H NMR spectrum (300 MHz, benzene-d_6) of the material obtained from a reaction of *s*-Bu_3Ga and potassium in benzene. Absorptions of *s*-Bu_3GaPh^- are labeled A and those of *s*-Bu_3GaH^- are labeled B.

NMR Observations of Stereoisomers. NMR spectra can indicate the number of alkyl groups bonded to a Ga when the alkyl group is chiral. Although not needed to identify the products in this work, some observations are presented since similar stereochemical behavior will appear in other chemical systems. Because *sec*-butyl groups are chiral, stereoisomeric compounds exist for structures containing them. While NMR spectra of enantiomers are identical (in the absence of chiral influences such as chiral solvents), spectra of diastereomers are inherently different,[9] although differences will not be observed if they are too small or if the exchange of groups or inversion of configuration at the chiral carbon is rapid on the NMR time scale.

A structure with two identically placed *s*-Bu groups should have two sets of NMR absorptions: one for the *RR* and *SS* isomers and the other for the *RS* isomer. Three identically placed groups provide isomers (R_3 and R_2S and their enantiomers), and the R_2S (or S_2R) isomer should have two sets of absorptions since its *R* and *S* groups have different environments. As a further complication, if the structure is nonplanar (certainly the case if a fourth group of any sort is bonded to the gallium), then the two *R* (or *S*) groups of the R_2S (or S_2R) isomer are diastereotopic and may exhibit different absorptions. With four identically placed groups, the *R* and *S* groups in the R_3S (or S_3R) isomer are different. Table 1 lists the maximum number of absorptions (assuming structural placement of the *sec*-butyl groups to be identical) and the relative absorption intensities (assuming *R* and *S* groups to be distributed randomly) for $(s\text{-Bu})_nGa$ structures.

For example, the ^1H NMR spectrum of *s*-Bu_3Ga (Figure 2) shows three triplets having 1:2:1 intensities for $\mathbf{CH_3}CH_2$ and the ^{13}C NMR spectrum (Figure 3) shows three absorptions having 1:2:1 intensities for each of the CH_3 groups and for the CH group. Such groups of absorptions sometimes have essentially equal spacing between the components (the $\mathbf{CH_3}CH_2$ absorptions of

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(8) Atwood, J. L. in *Inclusion Compounds*; Atwood, J. L, Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; Vol. 1, Chapter 9.

(9) For an example of the use of such differences to define structure, see: Hanawalt, E. M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4983.

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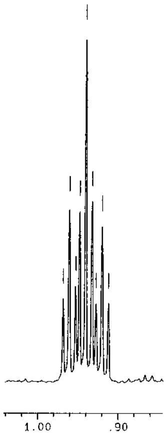

Figure 2. ^1H NMR spectrum (360 MHz, benzene-d_6) of the $C\mathbf{H}_3CH_2$ absorption of s-Bu_3Ga.

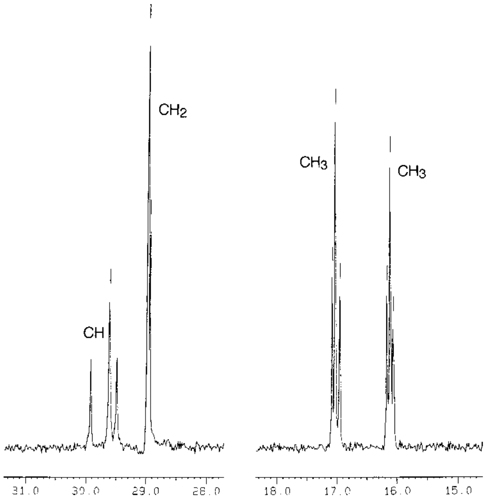

Figure 3. ^{13}C NMR spectrum (75 MHz, proton-decoupled, benzene-d_6) of s-Bu_3Ga.

s-Bu_3Ga are an example) and appear like a first-order multiplet; this is fortuitous, however, since there is no inherent reason for spacings between the absorptions of diastereomers to be equal.

The spectrum of s-Bu_3GaPh^- has a 1:1:1:1 set of doublets for $C\mathbf{H}_3CH$, indicating three *sec*-butyl groups bonded to Ga. The spectrum of s-Bu_3GaH^- has a 1:2:1 set of doublets for $C\mathbf{H}_3CH$, also a possibility when three *sec*-butyl groups are bonded to Ga. Different absorptions for the diastereotopic *sec*-butyl groups in the R_2S (and S_2R) isomers that would lead to the 1:1:1:1 pattern observed for s-Bu_3GaPh^- are not evident. It is reasonable that the differences in NMR environments of the diastereotopic *sec*-butyl groups are less when the fourth group is hydrogen rather than the much larger phenyl. The spectrum of s-$Bu_4Ga^-Li^+$ shows the 1:3:3:1 set of $C\mathbf{H}_3CH$ doublets (Figure 4) possible for a species having four *sec*-butyl groups bonded to gallium. The $C\mathbf{H}_3CH$ absorptions of s-$Bu_4Ga^-K^+$ look like three 1:3:4 doublets, however, since two of the stereoisomers have a similar position for this absorption.

Yields of Products. The oil remaining from the reaction of s-Bu_3Ga and K after filtration and removal of solvent contains only s-$Bu_3GaPh^-K^+$and s-$Bu_3GaH^-K^+$, in equal amounts. Its weight indicates that this oil contains about 87% of the *sec*-butyl groups and gallium atoms of the reactant. Therefore, the reaction in eq 1 is almost quantitative.

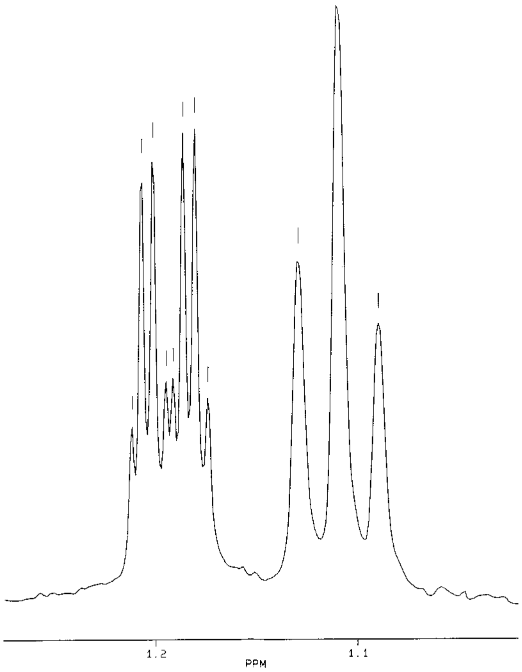

Figure 4. ^1H NMR spectrum (300 MHz, benzene-d_6) of the $C\mathbf{H}_3CH$ (left) and $C\mathbf{H_3}CH_2$ absorptions of s-Bu_4Ga^- Li^+ obtained from a reaction of s-Bu_3Ga and s-BuLi.

$$2R_3Ga + PhH + 2K \rightarrow R_3GaPh^-K^+ + R_3GaH^-K^+ \qquad (1)$$

Effect of R in R_3Ga on Product Composition. ^1H and ^{13}C NMR spectra of solutions obtained from reduction of s-Bu_3Ga with Na/K alloy or K show only absorptions of s-Bu_3GaPh^- and s-Bu_3GaH^- (1:1 ratio). Similar reductions of i-Bu_3Ga give solutions whose ^1H NMR spectra show absorptions of i-Bu_3GaPh^-, i-Bu_3GaH^-, and i-Bu_4Ga^- (1:1:0.8). By contrast, the ^1H NMR spectrum of the solution obtained by reduction of Me_3Ga with K has a single absorption; the lack of absorptions due to a phenyl group or to a hydrogen bonded to gallium indicate this to be Me_4Ga^-. Similarly, reduction of Et_3Ga gives solutions with one principal set of ethyl absorptions, attributed to Et_4Ga^-; small amounts (ca. 5%) of Et_3GaPh^- and Et_3GaH^- are indicated, however, by weak absorptions similar to those of R_3GaPh^- and R_3GaH^- when R is isobutyl or *sec*-butyl. The portion of R_3GaPh^- and R_3GaH^- in the products formed by reduction of R_3Ga, therefore, increases in the series Me < Et < i-Bu < s-Bu.

Effect of Reducing Agent and Solvent on Product Composition. Experiments with s-Bu_3Ga show that identical product mixtures result from reactions using amounts of Na/K alloy containing one, two, or several equivalents of K. The reaction is slower, but the product mixture is identical when K metal is used instead of Na/K alloy. Cs produces a similar product mixture, but Li produces mainly s-Bu_4Ga^-. In contrast to the reactions in benzene, reduction in THF of i-Bu_3Ga or s-Bu_3Ga with K furnishes only R_4Ga^-. Therefore, use of Li instead of a more polar alkali metal and use of THF instead of benzene favor R_4Ga^- formation.

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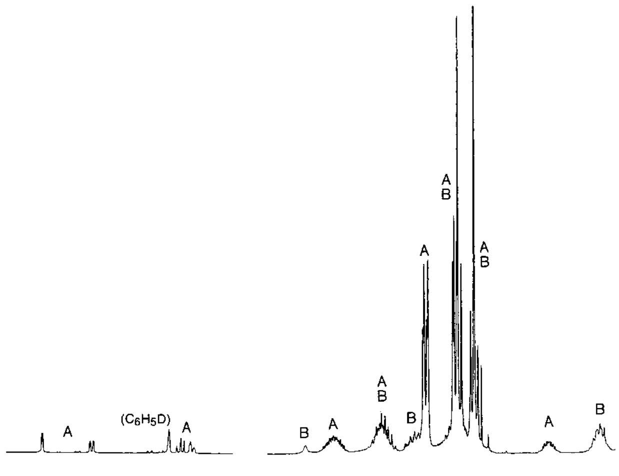
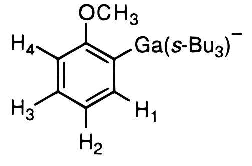


Figure 5. ^{1}H NMR spectrum (300 MHz, benzene-d_6) of the material obtained from a reaction of *s*-Bu_3Ga and potassium in *tert*-butylbenzene. Absorptions of *s*-Bu_3Ga(*m*-*t*-butylphenyl)$^-$ (**2b**) are labeled A and those of *s*-Bu_3GaH^- are labeled B.

Effect of the Aromatic Solvent on Product Structure and Composition. ^{1}H NMR spectra of products obtained from reactions of *s*-Bu_3Ga and K in anisole ($PhOCH_3$) instead of benzene as the solvent also indicate the formation of equal amounts of two products. One is *s*-Bu_3GaH^-; the second is *s*-Bu_3GaAn^- (**1**), the aryl absorptions indicating an ortho-substituted anisyl ring.



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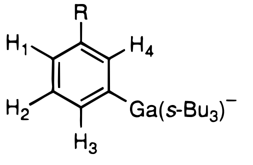


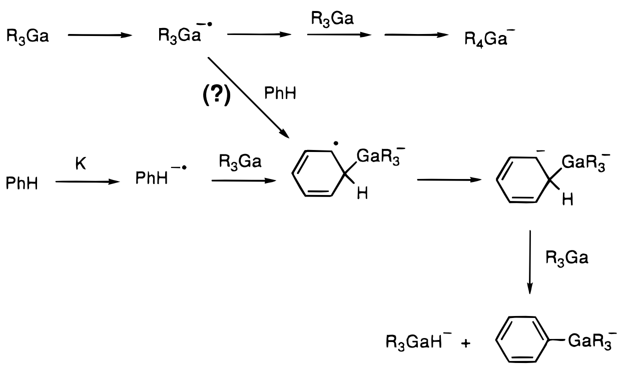
2a R = Me
2b R = *t*-Bu

Similar reactions in toluene and *tert*-butylbenzene also give *s*-Bu_3GaH^- and *s*-Bu_3GaAr^-, but the aryl ^{1}H NMR absorptions (Figure 5) indicate meta-substituted rings (**2**). More than 5 % of the ortho or para isomers should have been detected if they had been present.

The relative reactivities of the aromatic compounds were determined by reducing *s*-Bu_3Ga with K in equimolar mixtures of two aromatic compounds. In anisole–benzene, the *s*-Bu_3GaAn^- to *s*-Bu_3GaPh^- ratio was 2.5. In toluene–benzene or *tert*-butylbenzene–benzene, only *s*-Bu_3GaPh^- absorptions were observed, indicating a preference exceeding 20:1 for benzene incorporation.

Reaction of the Naphthalene Radical Anion with R_3Ga. A likely pathway for R_3GaAr^- and R_3GaH^- formation involves reaction of the radical anion ($Ar^{-\bullet}$) of the aromatic solvent with R_3Ga. If $Ar^{-\bullet}$ is involved, then a solution of it that contains no alkali metal should react with R_3Ga to produce R_3GaAr^- and R_3GaH^-. Such an experiment cannot be done with the aromatic compounds we used since their conversion by alkali metals to radical anions is far from complete, and so the alkali metal remains as an alternate reactant. An experiment with naphthalene is possible, however, since its reaction with K can incorporate all of the metal into K^+ $Naph^{-\bullet}$. In fact, a solution of K^+ $Naph^{-\bullet}$ reacts rapidly with *s*-Bu_3Ga. A ^{1}H NMR spectrum shows one-half of the product to be *s*-Bu_3GaH^-; the other absorptions are reasonable for *s*-$Bu_3Ga(Naph)^-$, but the component responsible for these absorptions did not survive further workup efforts.

Scheme 1



Mechanism. The equal amounts of R_3GaH^- and R_3GaPh^- suggests their formation to be linked. The initial step in likely processes (Scheme 1) is formation of either (1) a reactive organogallium species, such as $R_3Ga^{-\bullet}$, which then attacks the aromatic ring or (2) the radical anion[10] of the aromatic compound which then (or after further reduction) attacks R_3Ga. Either process would lead to a species having an aryl ring attached to gallium, further reaction of which could furnish the products. Further reduction as in Scheme 1, for example, would give a dianion which by transferring a hydride to R_3Ga would produce equal amounts of R_3GaH^- and R_3GaPh^-.

Formation of R_3GaPh^- and R_3GaH^- in reactions with K or Cs but not Li and a report that K and Cs but not Li react with benzene to form a radical anion[11] provide particularly compelling evidence for the radical anion pathway. Li, K, and Cs can produce R_4Ga^-, however, suggesting a different key step in the pathway leading to $R_4Ga^{-\bullet}$. Moreover, a solution of $Naph^{-\bullet}$ K^+ (containing no K metal) reacts with *s*-Bu_3Ga to produce products of the type observed with benzene.

The effects of the substituents on the benzene ring provide clues about the mechanism. Since the effect of methoxyl could be due to coordination[12] of organogallium species to the oxygen rather than to an electronic effect, we will discuss only the alkyl substituents. The effects of a substituent on the benzene ring on the rate and position of attack by a free radical depends on the electrophilic–nucleophilic character of the radical.[13] We are not aware of information about $R_3Ga^{-\bullet}$ species. Somewhat related, however, are $R_3Si^\bullet$ radicals,[14] which attack toluene with only small positional selectivities[15] and at rates[16] similar to attack on benzene. The

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(10) Evidence has been presented for attack by a naphthalene radical anion on $(neopentyl)_2GaCl$ (Beachley, O. T.; Pazik, J. C.; Noble, M. J. *Organometallics* **1994**, *13*, 2885).

(11) Jones, M. T.; Kuechler, T. C. *J. Phys. Chem.* **1977**, *81*, 360.

(12) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.

(13) Nonhebel, D. C.; Walton, J. C. *Free Radical Chemistry*; Cambridge: Cambridge, 1974; Chapter 11. Perkins, M. J. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; Vol. 2, Chapter 16.

(14) For overviews, see: Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; Vol. 2, Chapter 25. Dohmaru, T. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, 1988; Vol. 3, Chapter 16.

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electronegativities of Ga and Si are similar, but the negative charge of $R_3Ga^{-\bullet}$ should enhance nucleophilicity. $R_3Ga^{-\bullet}$, therefore, may exhibit a preference for benzene over alkylbenzenes and for meta substitution of alkylbenzenes. Because the σ values of alkyl groups are small,[17] however, unusually large ρ values would be required to cause the large rate differences and positional selectivities that are observed.

Alkyl substitution makes the reduction[18] of aromatic compounds to radical anions less favorable in a thermodynamic sense and probably slower. Positional selectivity in attachment to a radical anion is probably related to some combination of (1) electron densities of its carbons and (2) stabilities of the intermediates that would result from forming bonds at these carbons. Electron spin densities in toluene and *tert*-butylbenzene are greatest at the meta positions,[19] but overall electron density, available only from calculations, may be more critical.[20] There seems to be little experimental information about the positions at which radical anions react. A recent study finds protonation of the anisole radical anion to have a meta-to-ortho ratio of about 3,[20] but protonation of the toluene radical anion only is known to be ortho or meta (or some combination).[20]

R effects the product composition as expected if the factor favoring R_3GaPh^- and R_3GaH^- over R_4Ga^- is the increasing steric demand of R, increasing stability of $R^\bullet$, or decreasing stability of R^-. Reduction of R_3Ga must initiate R_4Ga^- formation. If this reduction were also the initial step in R_3GaPh^- and R_3GaH^- formation, then product composition would probably be related to the relative rates of loss of R from and attack by $R_3Ga^{-\bullet}$ on the aromatic ring. $R^\bullet$ loss should increase with increasing $R^\bullet$ stability, in contrast to the results.[21] If reduction of the aromatic compound is the initial step in R_3GaPh^- and R_3GaH^- formation, however, then the relative ease of reducing R_3Ga and PhH will influence the product balance (rates of subsequent reactions may also have an effect if the reduction step is reversible). The rate of reduction of R_3Ga by metals probably decreases with the increasing size of R, a prediction consistent with the product compositions.

It may be interesting for someone to investigate reactions of aromatic radical anions with polar, main-group organometallic compounds.

Experimental Section

All NMR spectra were taken in benzene-d_6. ^1H NMR absorptions are reported in parts per million (δ) downfield from internal benzene (C_6D_5H), taken as δ 7.15 ppm, and using the following notations: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions; b, broad. ^{13}C NMR spectra are reported in parts per million (δ) downfield from internal benzene (C_6D_6), taken as δ 128.0 ppm. Some products containing *sec*-butyl groups consist of several stereoisomers; in some instances, discrete absorptions for a particular structural feature, although with only slightly different chemical shifts, are seen for each stereoisomer. These absorptions are described by listing the chemical shift of the most upfield absorption and then the shift downfield from this peak of each of the other absorptions and the approximate relative areas. The NMR tubes had an extension of routine glass tubing to facilitate sealing with a flame after the contents had been added.

The procedures involving the organometallic compounds were performed under a nitrogen atmosphere using Schlenk techniques, a glovebox, and a vacuum line. Nitrogen was purified by passing through columns of manganese oxide oxygen scavenger and molecular sieves (4 Å). Glassware was dried in an oven at 200 °C.

Hydrocarbon solvents, TMEDA (tetramethylethylenediamine), and anisole were distilled from CaH_2 and stored over molecular sieves (4 Å). Diethyl ether and THF (tetrahydrofuran) were distilled from sodium benzophenone ketyl immediately prior to use. Benzene-d_6 was stored over molecular sieves (4 Å). Ga (99.9%), Li, Cs, and NaF were used as obtained (Aldrich). Na and K were ingots in mineral oil (Aldrich). Immediately before use, large pieces were washed repeatedly with hexane and then cut into smaller pieces. KH was a dispersion in mineral oil (Aldrich); it was washed repeatedly with hexane and heated under vacuum (60 °C, 10^{-3} Torr) prior to use.

Preparation of Trialkylgallium Compounds. Trimethylgallium was prepared following a literature procedure.[22] The crude product (bp 55−60 °C) was redistilled (bp 57 °C; lit.[22] bp 55.7 °C) over NaF. The other trialkylgallium compounds were generally prepared from reactions of a Grignard reagent and $GaCl_3$ using the following procedure. In the glovebox, a Et_2O solution of the Grignard reagent (1.0 M, 100 mL, 0.1 mol) was added dropwise to a stirred solution of $GaCl_3$ (freshly sublimed, 5.3 g, 0.03 mol) in Et_2O (20 mL). The reaction was then stirred for 12 h. The products were isolated by fractional distillation. To reduce residual diethyl ether, the distillates then were carefully subjected to a vacuum at 0 °C and then to a vacuum transfer. Et_3Ga still contained 1 equiv of Et_2O. *i*-Bu_3Ga also was prepared by stirring a mixture of *i*-Bu_2Hg (15.7 g, 0.05 mol), Ga (5.6 g, 0.08 mol), and a crystal of $HgCl_2$ at 150−170 °C for 48 h.[23] The mixture was cooled and decanted from the Hg, and the product was distilled (88−90 °C, 10 Torr). Yield: 89% (based on *i*-Bu_2Hg).

Trimethylgallium: ^1H NMR (360 MHz) δ −0.18 (s, CH_3).

Triethylgallium ($Et_3Ga(OEt_2)$): ^1H NMR (200 MHz) δ 0.60 (q, J = 8.1 Hz, 2, CH_2Ga), 1.09 (t, J = 8.0 Hz, 3, $C\mathbf{H_3}CH_2O$), 1.41 (t, J = 8.0 Hz, 3, $C\mathbf{H_3}CH_2Ga$), 3.26 (q, J = 8.1 Hz, 2, CH_2O).

Triisobutylgallium: ^1H NMR (360 MHz) δ 0.74 (d, J = 7.0 Hz, 2, CH_2), 1.00 (d, J = 6.6 Hz, 6, CH_3), 2.06 (sept, J = 6.7 Hz, 1, CH). ^{13}C NMR (75 MHz) δ 27.0 (CH_2), 27.8 (CH_3), 32.8 (CH).

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Tri-*s*-butylgallium: ^{1}H NMR (360 MHz) δ 0.93 (+0.008, +0.015; three triplets, 1:2:1, $J \cong 7.4$ Hz, 9, $C\mathbf{H}_3CH_2$), 1.20−1.22 (c, 4, $CH_3C\mathbf{H}$), 1.69 (m, 2, CH_2), ^{13}C NMR (75 MHz) 16.05 (+0.046, +0.104; three absorptions, 1:2:1, $\mathbf{C}H_3$), 16.94 (+0.065, +0.127; three absorptions, 1:2:1, $\mathbf{C}H_3$), 28.94 (+0.031; two absorptions, 1:2, CH_2), 29.62 (the larger of three 1:2:1 absorptions, CH).

Preparation of Phenylpotassium. This compound was prepared by metalation of benzene by EtK.[24] K (0.4 g, 0.01 mol), Et_2Hg (1.5 g, 0.006 mol), and benzene (8 g) were stirred under nitrogen for 48 h. The solvent and any residual Et_2Hg were removed at reduced pressure (0.1 Torr, ambient temperature) from the suspension, leaving a gray-blue solid. One equivalent of TMEDA was used to make the PhK sufficiently soluble in benzene-d_6 for a routine ^{1}H NMR spectrum (200 MHz): δ 2.10 (s, 6, CH_3 of TMEDA), 2.34 (s, 4, CH_2 of TMEDA), 7.06 (d, $J = 7.2$ Hz, 2, *o*-H), 7.10 (t, $J = 7.3$ Hz, 1, *p*-H), 7.31 (t, $J = 7.6$ Hz, 2, *m*-H).

Reactions of R_3Ga with Alkali Metals in Benzene or THF. The alkali metal (0.6−0.8 mmol) was added to a solution of the organogallium compound (0.3 mmol) in the solvent (0.6 mL), and the mixture was stirred for 24 h. When Na/K alloy was used, the K content was 2−3 times the amount of organogallium compound. Then the solution was filtered, the solvent was removed at reduced pressure, and the remaining oil was dissolved in benzene-d_6 for NMR spectroscopy.

***s*-Bu_3Ga and K in Benzene.** The ^{1}H and ^{13}C NMR spectra were essentially identical to the superposition of the spectra of *s*-$Bu_3GaPh^-K^+$ and *s*-$Bu_3GaH^-K^+$. The fact that particular *s*-Bu absorptions belong to the same *s*-Bu group was verified by decoupling experiments. The weight remaining after thorough removal of the solvent from a reaction corresponded to incorporation of 87% of the *sec*-butyl groups and Ga atoms of the reactant into the two products; the ^{1}H NMR spectrum then verified that solvent removal had been complete and that *s*-Bu_3GaPh^- and *s*-Bu_3GaH^- were the only significant components present. Addition to the benzene-d_6 solution obtained from a typical reaction of $Me_3NH^+Cl^-$ (freshly sublimed at 80 °C, 10 Torr, approximately 1 mol/mol of *s*-Bu_3Ga used) led to the formation of a precipitate. ^{1}H NMR spectrum of the solution remaining (300 MHz): δ 0.71 (m, 3, CH), 1.15 (t, 9, $J = 6.9$ Hz, $C\mathbf{H}_3CH_2$), 1.33 (d, $J = 6.9$ Hz, 9, $C\mathbf{H}_3CH$), 1.55 (m, 3, $C\mathbf{H}H$), 1.81 (s, 9, CH_3N), 1.88 (m, 3 $CH\mathbf{H}$). In a reaction using only 1 mol of K/mol of *s*-Bu_3Ga, all of the metal dissolved but the NMR spectrum of the product was identical to those of the products of reactions using more K.

***s*-Bu_3Ga and Na/K Alloy (60% K by Weight) in Benzene.** The ^{1}H NMR spectrum of the product was identical to the superposition of the spectra of *s*-$Bu_3GaPh^-K^+$ and *s*-$Bu_3GaH^-K^+$.

***s*-Bu_3Ga and Cs in Benzene.** ^{1}H NMR (360 MHz): *s*-Bu_3GaH^- absorptions δ 0.55 (m, 3, CH), 1.34 (t, $J = 7.3$ Hz, 9, $C\mathbf{H}_3CH_2$), 1.48 (+0.003, +0.007, +0.010; four doublets, 1:1:1:1, $J \cong 7.5$ Hz, 9, $C\mathbf{H}_3CH$), 1.69 (m, 3, $C\mathbf{H}H$), 1.90 (m, 3, $CH\mathbf{H}$), 3.78 (bs, <1, GaH); *s*-Bu_3GaPh^- absorptions δ 0.87 (m, 3, CH), 1.42 (t, $J = 7.2$ Hz, 9, $C\mathbf{H}_3CH_2$), 1.60 (+0.004, +0.012, +0.016; four doublets, 1:1:1:1, $J \cong 7.4$ Hz, 9, $C\mathbf{H}_3CH$), 1.98 (m, 3, $C\mathbf{H}H$), 2.20 (m, 3, $CH\mathbf{H}$), 6.92 (t, $J = 7.2$ Hz, 1, *p*-H), 7.05 (t, $J = 7.2$ Hz, 2, *m*-H), 7.89 (d, $J = 7.2$ Hz, 2, *o*-H).

***s*-Bu_3Ga and Li in Benzene; Preparation of Li^+*s*-Bu_4Ga^-.** Lithium metal powder (5−6 equiv) was used. ^{1}H NMR (300 MHz): δ 0.05 (m, 1, CH), 1.13 (t, $J = 7.2$ Hz, 3, $C\mathbf{H}_3CH_2$), 1.22 (+0.007, +0.013, +0.017; four doublets, 1:1:1:1, $J \cong 7.6$ Hz, 3, $C\mathbf{H}_3CH$), 1.45 (m, 1, $C\mathbf{H}H$), 1.77 (m, 1, $CH\mathbf{H}$). ^{13}C NMR (75 MHz): δ 15.04 ($\mathbf{C}H_3CH_2$), 18.48 ($\mathbf{C}H_3CH$), 20.07 (b, CH), 29.69 (CH_2).

***s*-Bu_3Ga and K in THF; Preparation of *s*-$Bu_4Ga^-K^+$.** ^{1}H NMR (300 MHz): δ 0.23 (m, 1, CH), 1.32 (t, $J = 7.2$ Hz, 3, $C\mathbf{H}_3CH_2$), 1.52 (+0.004, +0.011; three doublets, 4:3:1, $J \cong 7.5$ Hz, 3, $C\mathbf{H}_3CH$), 1.81 (m, 1, $C\mathbf{H}H$), 2.14 (m, 1, $CH\mathbf{H}$).

***i*-Bu_3Ga and K in Benzene.** The ^{1}H NMR spectrum was essentially identical to the superposition of the spectra of *i*-$Bu_3GaPh^-K^+$, *i*-$Bu_3GaH^-K^+$, and *i*-$Bu_4Ga^-K^+$ in 1:1:0.8 portions. The fact that particular *i*-Bu absorptions belong to the same *i*-Bu group was verified by decoupling experiments.

***i*-Bu_3Ga and K or Na/K Alloy (72% K by Weight) in THF; Preparation of K^+*i*-Bu_4Ga^-.** ^{1}H NMR of the product from the reaction with K (300 MHz): δ −0.07 (d, $J = 6.9$ Hz, 2, CH_2), 1.24 (d, $J = 6.5$ Hz, 6, CH_3), 2.08 (sept, $J = 6.5$ Hz, 1, CH). An identical spectrum resulted from using Na/K alloy.

$Et_3Ga(OEt_2)$ and K in Benzene. ^{1}H NMR (200 MHz): δ 0.11 (q, $J = 8.0$ Hz, 2, CH_2), 1.44 (t, $J = 8.0$ Hz, 3, CH_3); these absorptions constituted most of the total absorption, but there were additional weak absorptions similar to the Ph and GaH absorptions of R_3GaPh^- and R_3GaH^- when R is *i*-Bu or *s*-Bu.

Me_3Ga and K in Benzene. ^{1}H NMR (200 MHz): δ −0.50 (s, CH_3).

Reactions of R_3Ga with PhK and KH; Preparations of $R_3GaPh^-K^+$ and $R_3GaH^-K^+$. A typical procedure to prepare R_3GaPh^- was to stir R_3Ga (0.3 mmol) with PhK (0.4 mmol) in benzene-d_6 (0.6 mL) for 24 h. The mixture then was filtered to remove excess PhK and transferred to an NMR tube. The procedure to prepare R_3GaH^- was similar except that a larger excess of KH (1.0 mmol) was used.

***i*-$Bu_3GaPh^-K^+$:** ^{1}H NMR (300 MHz) δ 0.31 (d, $J = 6.9$ Hz, 6, CH_2), 1.37 (d, $J = 6.5$ Hz, 18, CH_3), 2.30 (sept, $J = 6.6$ Hz, 3, CH of *i*-Bu), 6.97 (t, $J = 7.3$ Hz, 1, *p*-H), 7.08 (t, $J = 7.5$ Hz, 2, *m*-H), 7.74 (d, $J = 7.6$ Hz, 2, *o*-H).

***s*-$Bu_3GaPh^-K^+$:** ^{1}H NMR (360 MHz) δ 0.81 (m, 3, CH of *s*-Bu), 1.39 (t, $J = 7.5$ Hz, 9, CH_3), 1.55 (+0.005, +0.011, +0.019; four doublets, 1:1:1:1, $J \cong 7.5$ Hz, 9, $C\mathbf{H}_3CH$), 1.86 (m, 3, $C\mathbf{H}H$), 2.16 (m, 3, $CH\mathbf{H}$), 6.83 (t, $J = 7.3$ Hz, 1, *p*-H), 6.97 (t, $J = 7.2$ Hz, 2, *m*-H), 7.81 (d, $J = 7.6$ Hz, 2, *o*-H); ^{13}C NMR (90 MHz) δ 15.9 ($\mathbf{C}H_3CH_2$), 20.3 ($\mathbf{C}H_3CH$), 21.5 (CH), 31.2 (CH_2), 124.0 (*p*-C), 126.9 (*m*-C), 139.7 (*o*-C), 171.2 (CGa).

***i*-$Bu_3GaH^-K^+$:** ^{1}H NMR (300 MHz) δ 0.13 (d of d, $J = 6.9$ and 1.4 Hz, 6, CH_2), 1.22 (d, $J = 6.5$ Hz, 18, CH_3), δ 2.00 (sept, $J = 6.6$ Hz, 3, CH), 2.49 (bs, <1, GaH).

***s*-$Bu_3GaH^-K^+$:** ^{1}H NMR (300 MHz) δ 0.39 (m, 3, CH of *s*-Bu), 1.24 (t, $J = 7.2$ Hz, 9, $C\mathbf{H}_3CH_2$), 1.34 (+0.008, +0.017; three doublets, 1:2:1, $J \cong 7.5$ Hz, 9, $C\mathbf{H}_3CH$), 1.60 (m, 3, $C\mathbf{H}H$), 1.86 (m, 3, $CH\mathbf{H}$), 2.31 (bs, <1, GaH); ^{13}C NMR (90 MHz) δ 15.6 ($\mathbf{C}H_3CH_2$), 21.1 ($\mathbf{C}H_3CH$), 21.3 (CH), 31.8 (CH_2).

Reactions of R_3Ga with RK or RLi; Preparations of $R_4Ga^-K^+$ and $R_4Ga^-\ Li^+$. *i*-$Bu_4Ga^-K^+$. *i*-BuK was prepared in situ from stirring *i*-Bu_2Hg (0.4 mmol) and K (0.8 mmol) in benzene-d_6 (0.5 mL) for 12 h. Excess K was removed using a spatula, *i*-Bu_3Ga (0.3 mmol) was added, and the mixture was stirred for 12 h and then filtered and transferred to an NMR tube. The ^{1}H NMR spectrum was identical to that of the product of the reaction of *i*-Bu_3Ga and K in THF. Upon addition of 18-crown-6, a second layer formed. The ^{1}H NMR spectrum of the lower layer showed one set of isobutyl absorptions and one crown ether absorption, the intensities indicating a 4:1 ratio.

***s*-$Bu_4Ga^-Li^+$.** The procedure was similar to that used with *i*-Bu_3Ga. The ^{1}H NMR spectrum was identical to that of the product of the reaction of *s*-Bu_3Ga and Li in benzene.

Reactions of *s*-Bu_3Ga and K in Other Aromatic Solvents. The typical procedure was to add K (0.5 mmol) to a solution of *s*-Bu_3Ga (0.24 mmol) in the aromatic compound (0.5 mL) and stir the mixture for 24 h. Equimolar amounts (5.0 mmol of each) were used in reactions involving two aromatic compounds. The mixture then was filtered, the solvent was removed under reduced pressure, and the remaining viscous oil was dissolved in benzene-d_6 for NMR spectroscopy.

Anisole. The ^{1}H NMR spectrum (300 MHz) shows the characteristic absorptions of *s*-$Bu_3GaH^-K^+$ and absorptions assigned to *s*-$Bu_3Ga(o\text{-}C_6H_4OCH_3)^-K^+$ (**1**): δ 0.53 (m, 3, CH),

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1.33 (t overlapping with t of *s*-Bu_3GaH^-, 9, $\mathbf{CH_3}CH_2$), 1.49 (+0.010, +0.014, +0.022; four doublets, 1:1:1:1, $J \cong 7.4$ Hz, 9, $C\mathbf{H_3}CH$), 1.78 (m, 3, CH**H**), 2.07 (m, 3, CH**H**), 3.38 (s, 3, CH_3O), 6.50 (d, $J = 7.9$ Hz, 1, H_4), 6.81 (t, $J = 6.8$ Hz, 1, H_3), 6.95 (t, $J = 7.6$ Hz, 1, H_2), 7.81 (d, $J = 6.8$ Hz, 1, H_1).

***tert*-Butylbenzene.** The ^{1}H NMR spectrum (300 MHz) shows the characteristic absorptions of *s*-$Bu_3GaH^-K^+$ and absorptions assigned to *s*-$Bu_3Ga(m\text{-}C_6H_4CMe_3)^-K^+$ (**2b**): δ 0.78 (m, 3, CH of *s*-Bu), 1.25 (s overlapping with a t of *s*-Bu_3GaH^-, 9, $C(CH_3)_3$), 1.36 (t overlapping with a d of *s*-Bu_3GaH^-, 9, $C\mathbf{H_3}CH_2$), 1.56 (+0.005, +0.009; three doublets, 2:1:1, $J \cong 7.5$ Hz, 9, $C\mathbf{H_3}CH$), 1.86 (m overlaps with CH**H** of *s*-Bu_3GaH^-, 3, C**H**H), 2.12 (m, 3, CH**H**), 7.00 (d, $J = 7.8$ Hz, 1, H_1), 7.07 (t, $J = 7.2$ Hz, 1, H_2), 7.66 (d, $J = 6.7$ Hz, 1, H_3), 7.99 (s, 1, H_4).

Toluene. The ^{1}H NMR spectrum (300 MHz) shows the characteristic absorptions of *s*-$Bu_3GaH^-K^+$ and absorptions assigned to *s*-$Bu_3Ga(m\text{-}C_6H_4Me)^-$ K^+ (**2a**): δ 0.80 (m, 1, CH of *s*-Bu), 1.38 (t overlapping with a d of *s*-Bu_3GaH^-, 9, $C\mathbf{H_3}CH_2$), 1.61 (+0.006, +0.007, +0.016; four doublets, 1:1:1:1, $J \cong 7.4$ Hz, 9, $C\mathbf{H_3}CH$), 1.86 (m overlapping with a m of CH**H** of *s*-Bu_3GaH^-, C**H**H), 2.11 (s, $m\text{-}C_6H_4C\mathbf{H_3}$), 2.19 (m, 3, CH**H**), 6.60 (d, $J = 6.8$ Hz, 1, H_1), 6.84 (t, $J = 7.2$ Hz, 1, H_2), 7.61 (d, $J = 6.9$ Hz, 1, H_3), 7.71 (s, 1, H_4).

Anisole−Benzene. The ^{1}H NMR spectrum shows only the absorptions of *s*-$Bu_3GaH^-K^+$ and in 2.5:1 ratio of *s*-$Bu_3Ga(o\text{-}C_6H_4OCH_3)^-K^+$ and *s*-$Bu_3GaPh^-K^+$.

***tert*-Butylbenzene−Benzene.** The ^{1}H NMR spectrum shows only the absorptions of *s*-$Bu_3GaH^-K^+$ and *s*-$Bu_3GaPh^-K^+$.

Toluene−Benzene. The ^{1}H NMR spectrum shows only the absorptions of *s*-$Bu_3GaH^-K^+$ and *s*-$Bu_3GaPh^-K^+$.

Reaction of *s*-Bu_3Ga and Potasssium Naphthalenide. Naphthalene (70 mg, 0.55 mmol) and K (20 mg, 0.51 mmol) were stirred in THF (0.6 g) for 12 h. *s*-Bu_3Ga (60 mg, 0.25 mmol) was added, and the solution was stirred for an additional 24 h. The ^{1}H NMR spectrum (300 MHz) shows the characteristic absorptions of *s*-$Bu_3GaH^-K^+$ and absorptions that can be attributed to *s*-$Bu_3Ga(Naph)^-K^+$: δ −0.02 (m, 3, CH of *s*-Bu), 1.25 (t overlapping with a t of *s*-Bu_3GaH^-, $C\mathbf{H_3}CH_2$), 1.32 (d overlapping with a d of *s*-Bu_3GaH^-, $C\mathbf{H_3}CH$), 1.46 (m, 3, C**H**H), 1.92 (m overlapping with a m of *s*-Bu_3GaH^-, CH**H**), 7.00−7.80 (bc, 7, Naph H's).

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