Title: Lewis Acid-Base Studies of Triorganogallium Compounds with Organophosphines

Author(s): O.T. Beachley, Jr. and John D. Maloney

Performing Organization: Department of Chemistry, State University of New York at Buffalo, NSM Complex, Buffalo, NY 14260-3000

Sponsoring Agency: Office of Naval Research, 800 N. Quincy Street, Arlington, VA 22217-5000

Abstract:

The relative Lewis acidities of a series of triorganogallium compounds GaR₃ (R = Me, Et, CH₂CMe₃, CH₂SiMe₃, CH₂CMe₂Ph and C₆H₄Me₃) toward a common Lewis base HPPh₂ and the relative Lewis basicities of a series of organophosphines which incorporate an acidic hydrogen HPRR' (PRR' = PPh₂, P(C₆H₄H₁₂), PET₂ and P(H)(C₆H₁₂)) toward a common Lewis acid Ga(CH₂CMe₃)₃ have been investigated and compared. Cryoscopic molecular weight data permitted an evaluation of the equilibrium constant for the dissociation of each of the adducts. The ³¹P NMR spectral data which were consistent with the molecular weight data were also used to study the relative rates of hydrocarbon elimination reactions to form (R₂GaP RR').

Subject Terms:
Organogallium-phosphorus adducts, Lewis acidity and basicity, elimination reactions
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O. T. Beachley, Jr. and John D. Maloney

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State University of New York at Buffalo
Department of Chemistry
Buffalo, New York 14260-3000

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O. T. Beachley, Jr.* and John D. Maloney
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14260-3000

ABSTRACT

The relative Lewis acidities of a series of triorganogallium compounds GaR₃ (R = Me, Et, CH₂CMₑ₂, CH₂SiMe₃, CH₂CMe₂Ph and C₆H₅Me₃) toward a common Lewis base HPPh₂ and the relative Lewis basicities of a series of organophosphines which incorporate an acidic hydrogen HPR'R' (PR'R' = PPh₂, P(C₆H₁₁)₂, PPh₂ and P(H)(C₆H₁₁)) toward a common Lewis acid Ga(CH₂CMe₂)₃ have been investigated and compared. Cryoscopic molecular weight data permitted an evaluation of the equilibrium constant for the dissociation of each of the adducts. The ³¹P NMR spectral data which were consistent with the molecular weight data were also used to study the relative rates of hydrocarbon elimination reactions to form (R₂GaPR'R')₂.
Even though adducts are fundamental to the chemistry of the group 13 elements, surprisingly few investigations have focused on the characterization of the adducts of homoleptic triorganogallium compounds with phosphorus bases in order to understand if these compounds exist as single species in solution or whether they are partially dissociated or even fully dissociated in benzene solution. Only two of these types of adducts\(^1\) \((\text{Me}_3\text{CCH}_2)_3\text{Ga} \cdot \text{P(H)Ph}_2\) and \((\text{Me}_3\text{SiCH}_2)_3\text{Ga} \cdot \text{P(H)Ph}_2\) have been characterized in benzene solution by both cryoscopic molecular weight and NMR spectroscopic studies to our knowledge and both were found to be extensively dissociated in benzene solution. Of these two Lewis acids, \(\text{Ga(CH}_2\text{CMe}_3\text{)}_3\) was the stronger acid toward \(\text{HPPh}_2\). The adduct \((\text{Me}_3\text{CCH}_2)_3\text{Ga} \cdot \text{P(H)Ph}_2\) was a crystalline solid at room temperature and was characterized further by an X-ray structural study.\(^1\) The other adduct \((\text{Me}_3\text{SiCH}_2)_3\text{Ga} \cdot \text{P(H)Ph}_2\) melted at 23.5 - 24.2 °C but was not characterized in the solid state. Four other adducts of homoleptic organogallium compounds \(\text{Me}_3\text{Ga} \cdot \text{PMe}_3\)^2, \(\text{Me}_3\text{Ga} \cdot \text{PPh}_2\text{C}_2\text{H}_4\text{PPh}_2 \cdot \text{GaMe}_3\)^3, \(\text{Ph}_3\text{Ga} \cdot \text{P(SiMe}_3\text{)}_3\)^4 and \((\text{Me}_3\text{SiCH}_2)_3\text{Ga} \cdot \text{P(SiMe}_3\text{)}_3\)^5 have been structurally characterized but no data permitted a determination of the extent of dissociation of the first three of these adducts in solution. The last adduct \((\text{Me}_3\text{SiCH}_2)_3\text{Ga} \cdot \text{P(SiMe}_3\text{)}_3\)^5 was investigated by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy and was concluded to be undissociated in benzene solution.

The Lewis acidities of a series of triorganogallium(III) compounds \(\text{GaR}_3\) (\(\text{R} = \text{Me, Et, CH}_2\text{CMe}_3\)^1, \(\text{CH}_2\text{SiMe}_3\)^1, \(\text{CH}_2\text{CMe}_2\text{Ph}\) and \(\text{C}_6\text{H}_5\text{Me}_3\)) toward a common Lewis base \(\text{HPPh}_2\) have been compared by using cryoscopic molecular weight data and \(^{31}\text{P}\) NMR spectroscopy. The cryoscopic molecular weight data for benzene solutions permitted calculations of the equilibrium constant for dissociation of the adduct \((K_d, \text{Equation } 1)\) (Table 1), and the percent dissociation of the adduct \((\alpha)\) as a function of concentration, whereas \(^{31}\text{P}\) NMR spectral data (Table 2) were used to calculate changes in chemical shifts between that observed for the solution which contained the adduct and the solution of the pure phosphine \((\Delta\delta = [\delta (\text{R}_3\text{Ga} \cdot \text{P(H)Ph}_2) - \delta (\text{HPPh}_2)])\) and in coupling constants \((^{1}J_{\text{PH}})\) as
a function of concentration. All data confirm the existence of an equilibrium for each
adduct (Equation 1) and are consistent with the following order of Lewis acidity toward

$$R_3Ga\cdot P(H)Ph_2 \leftrightarrow GaR_3 + HPPH_2$$ (1)

$HPPH_2, GaMe_3$ (strongest acid) $> GaEt_3 \gg Ga(CH_2CMe_3)_3 \gg Ga(CH_2SiMe_3)_3 \gg Ga(CH_2CMe_2Ph)_3 \gg Ga(C_6H_2Me_3)_3$.

A comparison of the $^{31}P$ NMR spectroscopic data revealed significant differences
between the chemical shifts and coupling constants of resonances for solutions of the
adducts at the same concentration in comparison to the value observed for a solution of
pure $HPPH_2$. Furthermore, as the concentration of the adduct increased, the chemical shift
of the observed $^{31}P$ NMR line moved downfield or away from the chemical shift of the line
for pure $HPPH_2$ in benzene solution ($\Delta \delta$ increased) as the coupling constant $^{1}J_{pp}$ increased
(Table 2). Thus, the NMR and cryoscopic molecular weight data indicate that
$Me_3Ga\cdot P(H)Ph_2$ and $Et_3Ga\cdot P(H)Ph_2$ are only slightly dissociated in benzene solution but
$GaMe_3$ is a stronger Lewis acid than is $GaEt_3$ toward $HPPH_2$. These observations may be
be correlated with the decreased steric effects of methyl groups. In contrast, the
diphenylphosphine adducts of $Ga(CH_2CMe_3)_3$, $Ga(CH_2SiMe_3)_3$ and $Ga(CH_2CMe_2Ph)_3$
are significantly dissociated in solution with $<0.05$ m solutions being more than 50 %
dissociated. Timesitylgallium $Ga(C_6H_2Me_3)_3$ is so weak a Lewis acid that it does not
appear to form significant concentrations of adduct even when the concentrations of the
Lewis acid and base are 0.138 m, the highest concentrations studied.

The Lewis basicities of the phosphines $HPPH_2$, $HP(C_6H_11)_2$, $HPEt_2$ and
$HP(H)(C_6H_11)$ toward a common Lewis acid $Ga(CH_2CMe_3)_3$ were investigated. The
cryoscopic molecular weight data was used to calculate an equilibrium constant for
dissociation of each adduct ($K_d$, Equation 1) and the percent dissociation of the adduct ($\alpha$)
as a function of concentration. All data (Table 3) confirm the existence of an equilibrium
for each adduct and the following order of relative Lewis basicity for the phosphine, HPEt₂ (strongest base) > HP(C₆H₁₁)₂ ≈ HP(H)(C₆H₁₁) > HPPH₂. Thus, the least sterically demanding base HPEt₂ is the strongest, as expected. The one surprise from our data is that HP(C₆H₁₁)₂ and HP(H)(C₆H₁₁) are of similar basicity.

The bulky dicyclohexylphosphine has an apparent base strength which is comparable to that of the less sterically demanding monocyclohexylphosphine. Since HP(H)(C₆H₁₁) would have been expected to be more basic than HP(C₆H₁₁)₂, steric effects cannot be the only important factor influencing the Lewis basicity of these two phosphines. One possible explanation for the observation of similar base strength of HP(C₆H₁₁)₂ and of HP(H)(C₆H₁₁) might be related to solvation effects. If the solvation of free HP(H)(C₆H₁₁) is more favorable than is the solvation of the adduct, dissociation of the adduct would be favored. Molecular models suggest that the P-H protons in the adduct might be protected by the three neopentyl groups on gallium from an interaction with the pi-cloud of benzene whereas such hindrance would not occur for the free phosphine. It is also noteworthy that although (Me₂CCH₂)₃Ga·P(H)(C₆H₁₁)₂ is significantly dissociated in benzene solution (~ 50%), the adduct has been isolated as a colorless crystalline solid with a sharp melting point (42-43 °C). A partial elemental (C/H) analysis of a sublimed sample was consistent with the empirical formula of the adduct. This observation is consistent with the existence of a pure, single compound in the solid state. It is regrettable that attempts to characterize this adduct in the solid state by an X-ray structural study were unsuccessful.

All of the phosphines used in these investigations have acidic protons with the potential to eliminate a hydrocarbon⁶ RH and form a phosphide of the type (R₂GaPR’₂)ₙ.

\[
\text{GaR₃} + \text{HPR’₂} \rightarrow \frac{1}{n} \text{(R₂GaPR’₂)}ₙ + \text{RH} \quad (2)
\]

Available ³¹P NMR spectral data were used to study the relative order of reactivity of different organogallium compounds with HPPH₂ and of different phosphines with
Ga(CH$_2$CMe$_3$)$_3$, all as benzene solutions of the same concentration. The following order for decreasing ease of elimination in benzene solution when the phospine was HPPh$_2$, GaEt$_3$ (most reactive) > GaMe$_3$ > Ga(CH$_2$SiMe$_3$)$_3$ >> Ga(CH$_2$CMe$_3$)$_3$ = Ga(C$_6$H$_2$Me$_2$)$_3$ (no reaction), was observed. It should be noted that this order is not the same order as was observed for the relative Lewis acidities toward HPPh$_2$ as the order for GaEt$_3$ and GaMe$_3$ are reversed. Both GaEt$_3$ and GaMe$_3$ eliminated an alkane and formed an organogallium phosphide (R$_2$GaPPh$_2$)$_4$ in benzene solution at room temperature but both reactions were very slow. The NMR data demonstrated that approximately 45% of the Et$_2$Ga-P(H)Ph$_2$ as a 0.138 m solution was converted to Et$_2$GaPPh$_2$ after 12 d whereas a benzene solution of Me$_3$Ga-P(H)Ph$_2$ eliminated methane much more slowly. It is noteworthy that Robinson, Burns and Pennington$^7$ described the use of a toluene (10 mL) solution of GaMe$_3$ (5 mmol) and HPPh$_2$ (5 mmol) to prepare (Me$_2$GaPPh$_2$)$_3$ for an X-ray structural study. When no solvent was used, temperatures of 90 - 110$^\circ$C were reported by Coates and Graham$^8$ to be necessary to initiate the elimination of methane from the adduct Me$_3$Ga•P(H)Ph$_2$ in a sealed tube. When the elimination of SiMe$_4$ from a benzene solution of (Me$_3$SiCH$_2$)$_3$Ga-P(H)Ph$_2$ was investigated,$^{1,9}$ heating to reflux was necessary to initiate a very slow reaction. In contrast, (Me$_3$CCH$_2$)$_3$Ga-P(H)Ph$_2$ did not eliminate CMe$_4$, even upon refluxing a solution for 3 wk.$^{1,10}$ Reactivity studies of Ga(CH$_2$CMe$_3$)$_3$ with HP(H)(C$_6$H$_{11}$) demonstrated that approximately 90% of the CMe$_4$ was eliminated after a solution of Ga(CH$_2$CMe$_3$)$_3$ and HP(H)(C$_6$H$_{11}$) in benzene had been heated in a 70 °C oil bath for 7 d. However, heating for 18 d was necessary for complete reaction. The two phosphines HP(C$_6$H$_{11}$)$_2$ and HPEt$_2$ did not undergo elimination reactions with Ga(CH$_2$CMe$_3$)$_3$, even upon heating benzene solutions at 70 °C for 3 wk.

These observations of the relative rates of elimination reactions in gallium phosphorus chemistry are consistent with the mechanism proposed for the elimination reaction in aluminum nitrogen chemistry.$^{11,12}$ Kinetic studies for the HMe$_2$Al-N(H)(Me)(Ph) system supported a bimolecular reaction between the Lewis acid and base.$^{11}$
Formation of the adduct was suggested to be a "dead-end path" for elimination. Furthermore, studies of the HMe₂Al-N(H)₂(CH₂Ph) system\textsuperscript{12} provided additional support for the conclusion that dissociation of the adduct was needed for the elimination reaction to occur. When HMe₂Al‧N(H)₂(CH₂Ph) was present as a solution in toluene, elimination of H₂ was observed. However, when the adduct precipitated from toluene solution, H₂ was not formed. The temperature was constant for these observations for the HMe₂Al-N(H)₂(CH₂Ph) system. Similarly, a benzene or toluene\textsuperscript{8} solution of Me₃Ga-P(H)Ph₂ eliminated methane at room temperature whereas the pure adduct without solvent\textsuperscript{7} required 90 - 110 °C. If the adduct had been the active species for elimination, the solution would have been expected to be less reactive. Second, the elimination of ethane from a benzene solution of Et₃Ga-P(H)Ph₂ was faster than was the elimination of methane from a solution of Me₃Ga-P(H)Ph₂ even though GaMe₃ is the stronger Lewis acid. Lastly, the extended times necessary for complete reactions for Et₃Ga-P(H)Ph₂ and (Me₃CCH₂)₃Ga-P(H)₂(C₆H₁₁) are also consistent with the occurrence of bimolecular reactions.

The observed reactivity patterns of GaMe₃\textsuperscript{13} and Ga(CH₂SiMe₃)₅\textsuperscript{5} with P(SiMe₃)₃ also suggest that dissociation of these adducts might be required for the elimination of SiMe₄ with formation of [R₂GaP(SiMe₃)₂]₄. The reagents GaMe₃ and P(SiMe₃)₃ reacted smoothly in toluene solution to form [Me₂GaP(SiMe₃)₂]₂.\textsuperscript{13} In contrast, Ga(CH₂SiMe₃)₃ reacted with P(SiMe₃)₃ in pentane solution to form only the adduct\textsuperscript{5} (Me₃SiCH₂)₃Ga‧P(SiMe₃)₃. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra demonstrated that the adduct did not dissociate in benzene solution. The product of the elimination reaction [(Me₃SiCH₂)₂Ga‧P(SiMe₃)₃]₂ was not formed.\textsuperscript{5}

**Experimental Section**

All compounds described in this section were extremely sensitive to oxygen and water and were manipulated in a standard vacuum line or under a purified argon atmosphere. The compounds Ga(CH₂CMe₃)₃\textsuperscript{14}, Ga(CH₂SiMe₃)₃\textsuperscript{15}, Ga(C₆H₂Me₃)₃\textsuperscript{16},
Ga(CH₂CMe₂Ph)₃, (Me₃CCH₂)₃Ga•P(H)Ph₂ and (Me₃SiCH₂)₃Ga•P(H)Ph₂ were prepared and purified by literature methods. Dicyclohexylphosphine, cyclohexylphosphine and diethylphosphine were purchased from Alfa Products whereas diphenylphosphine, trimethylgallium and triethylgallium were purchased from Strem Chemicals, Inc. All phosphines were purified by distillation prior to use. Solvents were dried by conventional procedures. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. ¹H NMR spectra were recorded at 300 MHz by using a Varian Gemini-300 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to SiMe₄ at 0.00 ppm (δ) and C₆D₆ at 7.15 ppm. The ³¹P NMR spectra were recorded at 161.9 MHz by using a Varian VXR-400 spectrometer. Proton decoupled ³¹P NMR chemical shifts are referenced to 85% H₃PO₄ at δ 0.00 ppm. All samples for NMR spectra were contained in tubes sealed by fusion of the glass. Melting points were observed in sealed capillaries and are uncorrected.

In a typical NMR spectroscopic study, the volatile component, either the phosphine or the triorganogallium compound, was vacuum distilled into a tared tube equipped with a Teflon valve and a standard tapered joint and weighed. Then, a stoichiometric quantity of the nonvolatile component and a known amount of C₆D₆ were placed into a reaction tube which was equipped with a magnetic stir bar and attached to an NMR tube and a Teflon valve adapter. After the volatile component was vacuum distilled into the reaction tube, the reaction mixture was stirred for 20 min at room temperature. The resulting solution was then poured into the NMR tube, the tube was cooled to -196 °C and flame sealed.

The adducts systems for cryoscopic molecular weight studies were prepared by using a procedure similar to that described previously for the NMR studies. Freezing point depressions were measured by using an instrument similar to that described by Shriver and Drezdzon.¹⁸ Since the error typical of these types of measurements is approximately 10 %, the data in the experimental section for each compound give the actual calculated result,
whereas the corresponding value for \( K_d \) in the tables have been rounded off to one significant figure to avoid misinterpretation or over interpretation.

**\((\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P(H)}\text{Et}_2\).** (a) \(^1\)H NMR (0.0689 m, \( \text{C}_6\text{D}_6 \), \( \delta \)): 0.75 (m, -CH\(_3\)), 0.92 (s, Ga-CH\(_2\)), 1.18 (m, P-CH\(_2\)), 1.21 (s, -CMe\(_3\)), 3.04 (dm, \(^1\)J\(_{\text{PH}}\) = 273 Hz, -PH); (0.138 m, \( \text{C}_6\text{D}_6 \), \( \delta \)): 0.76 (m, -CH\(_2\)), 0.91 (s, Ga-CH\(_2\)), 1.18 (m, P-CH\(_2\)), 1.21 (s, -CMe\(_3\)), 3.05 (dm, \(^1\)J\(_{\text{PH}}\) = 273 Hz, -PH). \(^{31}\)P NMR (0.0689 m, \( \text{C}_6\text{D}_6 \), \( \delta \)): -38.29 (dp, \(^1\)J\(_{\text{PH}}\) = 271 Hz, \(^3\)J\(_{\text{PCCH}}\) = 13.4 Hz); (0.138 m, \( \text{C}_6\text{D}_6 \), \( \delta \)): -37.87 (dp, \(^1\)J\(_{\text{PH}}\) = 272 Hz, \(^3\)J\(_{\text{PCCH}}\) = 13.4 Hz). Cryoscopic molecular weight (measured upon mixing reagents), formula weight 373.1 (calcd m, obsd m, \( \alpha \) or percent dissociation, \( K_d \): 0.0541, 0.0584, 7.95 \%, 3.71 \times 10^{-4}; 0.0460, 0.0507, 10.2 \%, 5.35 \times 10^{-4}; 0.0376, 0.0422, 12.2 \%, 6.41 \times 10^{-4}.

(b) A solution to study the elimination reaction was prepared by mixing 0.19 g (0.66 mmol) of Ga(CH\(_2\)CMe\(_3\))\(_3\), 0.060 g (0.67 mmol) of HPEt\(_2\) and 4.82 g of \( \text{C}_6\text{D}_6 \). Initial spectrum, \(^{31}\)P NMR (0.14 m, 20 \( ^\circ \)C, \( \delta \)): -37.87 (dp, \(^1\)J\(_{\text{PH}}\) = 272 Hz, \(^3\)J\(_{\text{PCCH}}\) = 13.4 Hz, (Me\(_3\)CCH\(_2\))\(_3\)Ga\cdot\text{P(H)}\text{Et}_2). No change in the spectrum occurred after heating the sample for 3 wk at an oil bath temperature of 70 \( ^\circ \)C.

**\((\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P(H)}_2(\text{C}_6\text{H}_{11})\).** (a) \(^1\)H NMR (0.0689 m, \( \text{C}_6\text{D}_6 \), \( \delta \)): 0.90 (s, -C\(_6\)H\(_{11}\)), 0.94 (s, -C\(_6\)H\(_{11}\)), 1.00 (s, -CMe\(_3\)), 1.07 (s, Ga-CH\(_2\)), 1.12 (s, -CMe\(_3\)), 1.15 (s, -C\(_6\)H\(_{11}\)), 1.18 - 1.7 (br, C\(_6\)H\(_{11}\)), 2.75 (dm, \(^1\)J\(_{\text{PH}}\) = 225 Hz, -PH); (0.138 m, \( \text{C}_6\text{D}_6 \), \( \delta \)): 0.90 (s, -C\(_6\)H\(_{11}\)), 0.93 (s, -C\(_6\)H\(_{11}\)), 1.01 (s, -CMe\(_3\)), 1.06 (s, Ga-CH\(_2\)), 1.10 (s, -CMe\(_3\)), 1.20 - 1.7 (br, -C\(_6\)H\(_{11}\)), 2.76 (dm, \(^1\)J\(_{\text{PH}}\) = 225 Hz, -PH); \(^{31}\)P NMR (0.0689 m, \( \text{C}_6\text{D}_6 \), \( \delta \)): -98.3 (t, \(^1\)J\(_{\text{PH}}\) = 227 Hz); (0.138 m, \( \text{C}_6\text{D}_6 \), \( \delta \)): -95.9 (t, \(^1\)J\(_{\text{PH}}\) = 227 Hz). Cryoscopic molecular weight (measured upon mixing reagents), formula weight 399.3 (calcd m, obsd m, \( \alpha \) or percent dissociation, \( K_d \): 0.0552, 0.0828, 51.8 \%, 2.76 \times 10^{-2}; 0.0430, 0.0663, 54.2 \%, 2.76x \times 10^{-2}.

(b) A solution to study the elimination reaction was prepared by using 0.10 g (0.36 mmol) of Ga(CH\(_2\)CMe\(_3\))\(_3\), 0.042 g (0.36 mmol) of H\(_2\)P(C\(_6\)H\(_{11}\)), and 2.69 g of \( \text{C}_6\text{D}_6 \). \(^{31}\)P NMR, initial spectrum, (0.13 m, 20 \( ^\circ \)C, \( \delta \)): -95.9 (t, \(^1\)J\(_{\text{PH}}\) = 227 Hz, (Me\(_3\)CCH\(_2\))\(_3\)Ga\cdot\text{P(H)}_2(\text{C}_6\text{H}_{11})); 3 wk after mixing reagents: -63.63 (s, 3.9,
(Me₃CCH₂)₂GaP(H)(C₆H₁₁), -73.29 (s, 4.1, (Me₃CCH₂)₂GaP(H)(C₆H₁₁)), -105.3 (s, 1.0, (Me₃CCH₂)₂GaP(H)(C₆H₁₁)). A second solution was prepared by combining 0.13 g (0.47 mmol) of Ga(CH₂CMe₃)₃, 0.054 g (0.47 mmol) of H₂P(C₆H₁₁), and 7.2 g of C₆D₆. ³¹P NMR, initial spectrum, (0.065 m, 20 °C, δ): -98.3 (t, JPH = 227 Hz).

(Me₃CCH₂)₂Ga·P(H₂)(C₆H₁₁); 7 d at 70 °C: -63.58 (s, 4.3, (Me₃CCH₂)₂GaP(H)(C₆H₁₁)), -73.27 (s, 5.3, (Me₃CCH₂)₂GaP(H)(C₆H₁₁)), -104.8 (s, 1.0, (Me₃CCH₂)₂Ga·P(H₂)(C₆H₁₁)); 14 d at 70 °C: -63.83 (s, 5.3, (Me₃CCH₂)₂GaP(H)(C₆H₁₁)), -73.10 (s, 8.2, (Me₃CCH₂)₂GaP(H)(C₆H₁₁)), -107.3 (s, 1.0, (Me₃CCH₂)₂Ga·P(H₂)(C₆H₁₁)); 18 d at 70 °C: -63.60 (s, 1.0, (Me₃CCH₂)₂GaP(H)(C₆H₁₁)), -73.31 (s, 1.2, (Me₃CCH₂)₂GaP(H)(C₆H₁₁)).

**Synthesis of (Me₃CCH₂)₂Ga·P(H)(C₆H₁₁)₂.** The reagents, 0.524 g (1.85 mmol) of Ga(CH₂CMe₃)₃ and 0.367 g (1.85 mmol) of HP(C₆H₁₁)₂, contained in screw-cap vials were transferred quantitatively to a Schlenk flask with repeated washing with dry pentane. After the solution was stirred for 2 h, the pentane was removed by vacuum distillation to leave a colorless solid which was purified by sublimation (0.995 g (Me₃CCH₂)₂Ga·P(H)(C₆H₁₁)₂, 1.69 mmol, 91.6 % yield). Mp 42 - 43 °C. ¹H NMR (0.0689 m, C₆D₆, δ): 0.82 (s, -C₆H₁₁), 1.05 (s, Ga-CH₂-), 1.11 (s, -C₆H₁₁), 1.17 (s, -CMe₃), 1.37 (s, -C₆H₁₁), 1.54 (s, -C₆H₁₁), 1.60 (s, -C₆H₁₁), 1.73 (s, -C₆H₁₁), 2.98 (dt, JPH = 215 Hz, JHCH = 5.3 Hz, -PH): 0.90 (s, -C₆H₁₁), 1.00 (s, -C₆H₁₁), 1.07 (s, Ga-CH₂-), 1.08 (s, -C₆H₁₁), 1.14 (s, -C₆H₁₁), 1.20 (s, -CMe₃), 1.41 (s, -C₆H₁₁), 1.55 (s, -C₆H₁₁), 1.61 (s, -C₆H₁₁), 1.74 (s, -C₆H₁₁), 1.75 (s, -C₆H₁₁), 3.02 (dt, JPH = 231 Hz, JHCH = 4.5 Hz, -PH). ³¹P NMR (0.0689 m, C₆D₆, δ): -25.02 (d, JPH = 219 Hz); 0.138 m, C₆D₆, δ): -23.80 (d, JPH = 230 Hz). Anal. Calcd: C, 67.35; H, 11.72. Found: C, 67.27; 11.57. Cryoscopic molecular weight, formula weight 481.50 (calcd m, obsd m, α or percent dissociation, Kd): 0.0638, 0.0918, 43.8 %, 2.18 x 10⁻², 0.0528, 0.0785, 48.8 %, 2.46 x 10⁻², 0.0413, 0.0639, 54.6 %, 2.71 x 10⁻². (b) Equal mol quantities of Ga(CH₂CMe₃)₃ and HP(C₆H₁₁)₂ were combined in C₆D₆ in order to test for
the occurrence of an elimination reaction. Initial $^{31}$P NMR spectrum (0.14 m, 20 °C, δ):

-25.02 (d, $^1$J$_{PH}$ = 219 Hz, (Me$_3$CCH$_2$)$_3$Ga•P(H)(C$_6$H$_{11}$)$_2$). No change in the spectrum occurred after heating the sample for 3 wk at 70 °C.

**Me$_3$Ga•P(H)Ph$_2$:** $^1$H NMR (0.0689 m, C$_6$D$_6$, δ): 0.10 (s, -CH$_3$), 5.19 (d, $^1$J$_{PH}$ = 293 Hz, -PH), 6.8-7.4 (m, Ph); (0.138 m, C$_6$D$_6$, δ): 0.99 (s, -CH$_3$), 5.20 (d, $^1$J$_{PH}$ = 290 Hz, -PH), 6.8-7.4 (m, Ph). $^{31}$P NMR (0.0689 m, C$_6$D$_6$, δ): -33.40 (dt, $^1$J$_{PH}$ = 290 Hz, $^3$J$_{PCH}$ = 9.0 Hz). (0.138 m, C$_6$D$_6$, δ): -33.17 (dp, $^1$J$_{PH}$ = 292 Hz, $^3$J$_{PCH}$ = 9.2 Hz).

Cryoscopic molecular weight (measured upon mixing reagents), formula weight 301.02 (calcd m, obsd m, α or percent dissociation, K$_d$): 0.0644, 0.0672, 4.34 %, 1.27 x 10$^{-4}$; 0.0542, 0.0567, 4.61 %, 1.21 x 10$^{-4}$; 0.0525, 0.0550, 4.76 %, 1.25 x 10$^{-4}$.

**Et$_3$Ga•P(H)Ph$_2$:** $^1$H NMR upon mixing reagents (0.0689 m, C$_6$D$_6$, δ): 0.76 (s, -CH$_2$-), 1.41 (t, $^1$J$_{HCH}$ = 8.0 Hz, -CH$_3$), 5.31 (d, $^1$J$_{PH}$ = 276 Hz, -PH), 6.8-7.4 (m, Ph); (0.138 m, C$_6$D$_6$, δ): 0.75 (s, -CH$_2$-), 1.40 (t, $^1$J$_{HCH}$ = 8.0 Hz, -CH$_3$), 5.31 (d, $^1$J$_{PH}$ = 294 Hz, -PH), 6.8-7.4 (m, Ph); $^{31}$P NMR (1 h after mixing reagents; 0.0689 m, C$_6$D$_6$, δ): -35.84 (dp, $^1$J$_{PH}$ = 272 Hz, $^3$J$_{PCH}$ = 9.4 Hz), 4.3, Et$_3$Ga•P(H)Ph$_2$, -46.32 (s, 1.0, Et$_2$Ga•PPh$_2$); (1 h after mixing reagents; 0.0.138 m, C$_6$D$_6$, δ): -34.00 (dp, $^1$J$_{PH}$ = 296 Hz, $^3$J$_{PCH}$ = 9.4 Hz, 4.4, Et$_3$Ga•P(H)Ph$_2$, -46.33 (s, 1.0, Et$_2$Ga•PPh$_2$); (3 d after mixing reagents; 0.0689 m, C$_6$D$_6$, δ): -35.83 (dp, $^1$J$_{PH}$ = 272 Hz, $^3$J$_{PCH}$ = 8.4 Hz, 3.9, Et$_3$Ga•P(H)Ph$_2$, -46.24 (s, 1.0, Et$_2$Ga•PPh$_2$); (3 d after mixing reagents, 0.138 m, C$_6$D$_6$, δ): -33.98 (dp, $^1$J$_{PH}$ = 294 Hz, $^3$J$_{PCH}$ = 9.6 Hz, 2.7, Et$_3$Ga•P(H)Ph$_2$, -46.23 (s, 1.0, Et$_2$Ga•PPh$_2$); (12 d after mixing reagents, 0.0689 m, C$_6$D$_6$, δ): -36.05 (dp, $^1$J$_{PH}$ = 278 Hz, $^3$J$_{PCH}$ = 8.0 Hz, 2.6, Et$_3$Ga•P(H)Ph$_2$, -46.39 (s, 1.0, Et$_2$Ga•PPh$_2$); (12 d after mixing reagents, 0.138 m, C$_6$D$_6$, δ): -34.14 (dp, $^1$J$_{PH}$ = 295 Hz, $^3$J$_{PCH}$ = 9.1 Hz, 1.2, Et$_3$Ga•P(H)Ph$_2$, -46.39 (s, 1.0, Et$_2$Ga•PPh$_2$). Cryoscopic molecular weight (measured upon mixing reagents), formula weight 343.10 (calcd m, obsd m, α or percent dissociation, K$_d$): 0.0720, 0.0785, 9.03 %, 6.45 x 10$^{-4}$; 0.0580, 0.0649, 11.9 %, 9.32 x 10$^{-4}$; 0.0422, 0.0478, 13.3 %, 8.57 x 10$^{-4}$.
(PhMe₂CCH₂)₃Ga·P(H)Ph₂. ¹H NMR (0.0689 m, C₆D₆, δ): 0.83 (s, Ga-CH₂-), 1.23 (s, -CMe₂-), 5.15 (d, ¹J_PH = 219 Hz, -PH) 6.80-7.40 (m, Ph); (0.138 m, C₆D₆, δ): 0.84 (s, Ga-CH₂-), 1.24 (s, -CMe₂-), 5.13 (d, ¹J_PH = 231 Hz, -PH), 6.82-7.42 (m, Ph).
³¹P NMR (0.0689 m, C₆D₆, δ): -39.17 (dp, ¹J_PH = 224 Hz, ³J_PCC = 7.3 Hz); (0.138 m, C₆D₆, δ): -38.40 (dp, ¹J_PH = 230 Hz, ³J_PCC = 7.4 Hz). Cryoscopic molecular weight, formula weight 655.56 (calcd m, obsd m, α or percent dissociation, K₉): 0.0495, 0.0823, 66.3 %, 6.44 x 10⁻²; 0.0414, 0.0690, 66.7 %, 5.52 x 10⁻²; 0.0315, 0.0518, 64.4%, 3.68 x 10⁻².

**Reaction of Ga(C₆H₂Me₃)₃ with HPh₂.** ¹H NMR (0.0689 m of each reagent, C₆D₆, δ): 2.13 (s, p-Me), 2.32 (s, o-Me), 5.17 (d, ¹J_PH = 216 Hz, -PH), 6.73 (s, m-H), 6.9-7.4 (m, Ph). (0.138 m, C₆D₆, δ): 2.13 (s, p-Me), 2.32 (s, o-Me), 5.17 (d, ¹J_PH = 216 Hz, -PH), 6.73 (s, m-H), 6.9-7.4 (m, Ph). ³¹P NMR (0.0689 m, C₆D₆, δ): -40.40 (dp, ¹J_PH = 217 Hz, ³J_PCC = 6.9 Hz); (0.138 m, C₆D₆, δ): -40.40 (dp, ¹J_PH = 217 Hz, ³J_PCC = 7.6 Hz). Cryoscopic molecular weight, formula weight 613.46 (calcd m, obsd m, α or percent dissociation): 0.0415, 0.0832, 100 %; 0.0371, 0.0739, 99.2 %.

**Acknowledgements.** This work was supported in part by the Office of Naval Research. We thank Matthew J. Noble for preparing the Ga(CH₂CMe₂Ph)₃ which was used in this study.
References

1. Banks, M. A.; Beachley, O. T., Jr.; Maloney, J. D.; Rogers; R. D. *Polyhedron* 1990, 9, 335.


Table 1. Cryoscopic Molecular Weight Studies of $R_3Ga\cdot P(H)Ph_2$ Adduct Systems in Benzene Solution.

<table>
<thead>
<tr>
<th>Adduct System</th>
<th>Calcd. (m)</th>
<th>Obsd. (m)</th>
<th>$\alpha$</th>
<th>$K_a$(Ave)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Me_3Ga\cdot P(H)Ph_2$</td>
<td>0.0644</td>
<td>0.0672</td>
<td>4.3</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.0525</td>
<td>0.0550</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>$Et_2Ga\cdot P(H)Ph_2$</td>
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<td>0.0649</td>
<td>12</td>
<td>$8 \times 10^{-4}$</td>
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<tr>
<td></td>
<td>0.0422</td>
<td>0.0478</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>$(Me_3CCH_2)_3Ga\cdot P(H)Ph_2^1$</td>
<td>0.0522</td>
<td>0.0828</td>
<td>58</td>
<td>$4 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>0.0415</td>
<td>0.0668</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>$(Me_3SiCH_2)_3Ga\cdot P(H)Ph_2^1$</td>
<td>0.0492</td>
<td>0.0794</td>
<td>62</td>
<td>$5 \times 10^{-2}$</td>
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<tr>
<td></td>
<td>0.0376</td>
<td>0.0629</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>$(PhMe_2CCH_2)_3Ga\cdot P(H)Ph_2$</td>
<td>0.0495</td>
<td>0.0823</td>
<td>66</td>
<td>$5 \times 10^{-2}$</td>
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<tr>
<td></td>
<td>0.0371</td>
<td>0.0690</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>$(C_6H_2Me_3)_3Ga\cdot P(H)Ph_2$</td>
<td>0.0415</td>
<td>0.0832</td>
<td>100</td>
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<tr>
<td></td>
<td>0.0371</td>
<td>0.739</td>
<td>99</td>
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Table 2. $^{31}$P NMR Spectral Data for $\text{R}_3\text{Ga}\cdot\text{P(H)Ph}_2$ Adduct Systems in Benzene Solution.

<table>
<thead>
<tr>
<th>Adduct System</th>
<th>Conc. (m)</th>
<th>$\delta$ (ppm)</th>
<th>$\Delta \delta$ (ppm)</th>
<th>$^{1}J_{PH}$ (Hz)</th>
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<tr>
<td>Me$_3$Ga•P(H)Ph$_2$</td>
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<td>-33.40</td>
<td>7.00</td>
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<tr>
<td></td>
<td>0.138</td>
<td>-33.17</td>
<td>7.23</td>
<td>292</td>
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<tr>
<td>Et$_3$Ga•P(H)Ph$_2$</td>
<td>0.0689</td>
<td>-35.84</td>
<td>4.56</td>
<td>272</td>
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<td></td>
<td>0.138</td>
<td>-34.00</td>
<td>6.40</td>
<td>296</td>
</tr>
<tr>
<td>(Me$_3$CCH$_2$)$_3$Ga•P(H)Ph$_2$$^1$</td>
<td>0.0689</td>
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</tr>
<tr>
<td>(Me$_3$SiCH$_2$)$_3$Ga•P(H)Ph$_2$$^1$</td>
<td>0.0689</td>
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<td>1.95</td>
<td>232</td>
</tr>
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<td>0.138</td>
<td>-37.74</td>
<td>2.66</td>
<td>240</td>
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<tr>
<td>(PhMe$_2$CCH$_2$)$_3$Ga•P(H)Ph$_2$</td>
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<td>-39.17</td>
<td>1.23</td>
<td>224</td>
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<td>2.00</td>
<td>230</td>
</tr>
<tr>
<td>(C$_6$H$_2$Me$_3$)$_3$Ga•P(H)Ph$_2$</td>
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<td>-40.40</td>
<td>0.00</td>
<td>217</td>
</tr>
<tr>
<td></td>
<td>0.138</td>
<td>-40.40</td>
<td>0.00</td>
<td>217</td>
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Table 3. Cryoscopic Molecular Weight Studies for 
(Me$_3$CCH$_2$)$_3$Ga•P(H)RR' Adduct Systems in Benzene Solution.

<table>
<thead>
<tr>
<th>Adduct System</th>
<th>Calcd. (m)</th>
<th>Obsd. (m)</th>
<th>α</th>
<th>$K_d$(Ave)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me$_3$CCH$_2$)$_3$Ga•P(H)Et$_2$</td>
<td>0.0541</td>
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<tr>
<td>(Me$_3$CCH$_2$)$_3$Ga•P(H)(C$<em>6$H$</em>{11}$)$_2$</td>
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<td>0.0785</td>
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<td>2 x 10$^2$</td>
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<tr>
<td></td>
<td>0.0413</td>
<td>0.0639</td>
<td>55</td>
<td></td>
</tr>
<tr>
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<td>52</td>
<td>3 x 10$^2$</td>
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<tr>
<td></td>
<td>0.0430</td>
<td>0.0663</td>
<td>54</td>
<td></td>
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<tr>
<td>(Me$_3$CCH$_2$)$_3$Ga•P(H)Ph$_2^1$</td>
<td>0.0522</td>
<td>0.0828</td>
<td>58</td>
<td>4 x 10$^2$</td>
</tr>
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<td></td>
<td>0.0415</td>
<td>0.0668</td>
<td>61</td>
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<tr>
<td>Compound</td>
<td>Conc. (m)</td>
<td>δ (ppm)</td>
<td>Δδ (ppm)</td>
<td>$^1J_{PH}$ (Hz)</td>
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<td>PEt$_2$H</td>
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<td>-55.13</td>
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<td>(Me$_3$CCH$_2$)$_3$Ga·P(H)Et$_2$</td>
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<td>-38.29</td>
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<td>P(C$<em>6$H$</em>{11}$)$_2$H</td>
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<td>-27.40</td>
<td>---</td>
<td>193</td>
</tr>
<tr>
<td>(Me$_3$CCH$_2$)$_3$Ga·P(H)(C$<em>6$H$</em>{11}$)$_2$</td>
<td>0.0689</td>
<td>-25.02</td>
<td>2.38</td>
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<tr>
<td>P(C$<em>6$H$</em>{11}$)H$_2$</td>
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<tr>
<td>(Me$_3$CCH$_2$)$_3$Ga·P(H)$_2$(C$<em>6$H$</em>{11}$)</td>
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<td></td>
<td>0.138</td>
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</table>

Table 4. $^{31}$P NMR Spectral Data for (Me$_3$CCH$_2$)$_3$Ga·P(H)RR Adduct Systems in Benzene Solution.
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