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Lewis Acid−Base Studies of Triorganogallium Compounds with Organophosphines

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Summary: The relative Lewis acidities of the series of triorganogallium compounds GaR_3 (R = Me, Et, CH_2CMe_3, CH_2SiMe_3, CH_2CMe_2Ph, $C_6H_2Me_3$) toward the common Lewis base $HPPh_2$ and the relative Lewis basicities of a series of organophosphines which incorporate an acidic hydrogen HPRR′ (PRR′ = PPh_2, $P(C_6H_{11})_2$, PEt_2, $P(H)(C_6H_{11})$) toward the common Lewis acid $Ga(CH_2CMe_3)_3$ 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 ^{31}P 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 $(R_2GaPRR')_2$.

Even though adducts are fundamental to the chemistry of the group 13 elements, suprisingly 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] $(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2$ and $(Me_3SiCH_2)_3Ga{\cdot}P(H)Ph_2$, 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, $Ga(CH_2CMe_3)_3$ was the stronger acid toward $HPPh_2$. The adduct $(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2$ was a crystalline solid at room temperature and was characterized further by an X-ray structural study.[1] The other adduct $(Me_3SiCH_2)_3Ga{\cdot}P(H)Ph_2$ melted at 23.5−24.2 °C but was not characterized in the solid state. Four other adducts of homoleptic organogallium compounds, $Me_3Ga{\cdot}PMe_3$,[2] $Me_3Ga{\cdot}PPh_2C_2H_4PPh_2{\cdot}GaMe_3$,[3] $Ph_3Ga{\cdot}P(SiMe_3)_3$,[4] and $(Me_3SiCH_2)_3Ga{\cdot}P(SiMe_3)_3$,[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, $(Me_3SiCH_2)_3Ga{\cdot}P(SiMe_3)_3$,[5] was investigated by ^1H and ^{13}C NMR spectroscopy and was concluded to be undissociated in benzene solution.

The Lewis acidities of the series of triorganogallium(III) compounds GaR_3 (R = Me, Et, CH_2CMe_3,[1] CH_2SiMe_3,[1] CH_2CMe_2Ph, $C_6H_2Me_3$) toward the common Lewis base $HPPh_2$ have been compared by using cryoscopic molecular weight data and ^{31}P NMR spectroscopy. The cryoscopic molecular weight data for benzene solutions permitted calculations of the equilibrium constant for dissociation of the adduct (K_d, eq 1) (Table 1), and

$$R_3Ga{\cdot}P(H)Ph_2 \rightleftharpoons GaR_3 + HPPh_2 \qquad (1)$$

the percent dissociation of the adduct (α) as a function of concentration, whereas ^{31}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 ($\Delta\delta = [\delta(R_3Ga{\cdot}P(H)Ph_2 - \delta(HPPh_2)]$) and in coupling constants ($^1J_{PH}$) as a function of concentration. All data confirm the existence of an equilibrium for each adduct (eq 1) and are consistent with the following order of Lewis acidity toward $HPPh_2$: $GaMe_3$ (strongest acid) > $GaEt_3$ >> $Ga(CH_2CMe_3)_3$[1] > $Ga(CH_2SiMe_3)_3$[1] > $Ga(CH_2CMe_2Ph)_3$ >> $Ga(C_6H_2Me_3)_3$.

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 (Δδ increased) as the coupling constant $^1J_{PH}$ 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 correlated with the decreased steric effcts of methyl groups. In contrast, the diphenylphosphine adducts of $Ga(CH_2CMe_3)_3$,[1] $Ga(CH_2SiMe_3)_3$,[1] and $Ga(CH_2CMe_2Ph)_3$ are significantly dissociated in solution with ∼0.05 M solutions being more than 50% dissociated. Trimesitylgallium, $Ga(C_6H_2Me_3)_3$, 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 $HPPh_2$,[1] $HP(C_6H_{11})_2$, $HPEt_2$, and $HP(H)(C_6H_{11})$ toward the common Lewis acid $Ga(CH_2CMe_3)_3$ were investigated. The cryoscopic molecular weight data were used to calculate an equilibrium constant for dissociation of each adduct (K_d, eq 1) and the percent dissociation of the adduct (α) 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: $HPEt_2$ (strongest base) > $HP(C_6H_{11})_2$ ≈ HP(H)-

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

adduct system	calcd mol wt	obsd mol wt	α	K_d(av)
$Me_3Ga{\cdot}P(H)Ph_2$	0.0644	0.0672	4.3	1×10^{-4}
	0.0525	0.0550	4.8	
$Et_3Ga{\cdot}P(H)Ph_2$	0.0580	0.0649	12	8×10^{-4}
	0.0422	0.0478	13	
$(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2$[1]	0.0522	0.0828	58	4×10^{-2}
	0.0415	0.0668	61	
$(Me_3SiCH_2)_3Ga{\cdot}P(H)Ph_2$[1]	0.0492	0.0794	62	5×10^{-2}
	0.0376	0.0629	67	
$(PhMe_2CCH_2)_3Ga{\cdot}P(H)Ph_2$	0.0495	0.0823	66	5×10^{-2}
	0.0371	0.0690	67	
$(C_6H_2Me_3)_3Ga{\cdot}P(H)Ph_2$	0.0415	0.0832	100	
	0.0371	0.739	99	

Table 2. ^{31}P NMR Spectral Data for $R_3Ga{\cdot}P(H)Ph_2$ Adduct Systems in Benzene Solution

adduct system	concn (M)	δ (ppm)	Δδ (ppm)	$^1J_{PH}$ (Hz)
PPh_2H		−40.40		215
$Me_3Ga{\cdot}P(H)Ph_2$	0.0689	−33.40	7.00	290
	0.138	−33.17	7.23	292
$Et_3Ga{\cdot}P(H)Ph_2$	0.0689	−35.84	4.56	272
	0.138	−34.00	6.40	296
$(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2$[1]	0.0689	−37.83	2.57	232
	0.138	−36.48	3.92	241
$(Me_3SiCH_2)_3Ga{\cdot}P(H)Ph_2$[1]	0.0689	−38.45	1.95	232
	0.138	−37.74	2.66	240
$(PhMe_2CCH_2)_3Ga{\cdot}P(H)Ph_2$	0.689	−39.17	1.23	224
	0.138	−38.40	2.00	230
$(C_6H_2Me_3)_3Ga{\cdot}P(H)Ph_2$	0.0689	−40.40	0.00	217
	0.138	−40.40	0.00	217

Table 3. Cryoscopic Molecular Weight Studies for $(Me_3CCH_2)_3Ga{\cdot}P(H)RR'$ Adduct Systems in Benzene Solution

adduct system	calcd mol wt	obsd mol wt	α	K_d(av)
$(Me_3CCH_2)_3Ga{\cdot}P(H)Et_2$	0.0541	0.0584	7.9	5×10^{-4}
	0.0460	0.0507	10	
$(Me_3CCH_2)_3Ga{\cdot}P(H)(C_6H_{11})_2$	0.0526	0.0785	49	2×10^{-2}
	0.0413	0.0639	55	
$(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$	0.0552	0.0828	52	3×10^{-2}
	0.0430	0.0663	54	
$(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2$[1]	0.0522	0.0828	58	4×10^{-2}
	0.0415	0.0668	61	

Table 4. ^{31}P NMR Spectral Data for $(Me_3CCH_2)_3Ga{\cdot}P(H)RR$ Adduct Systems in Benzene Solution

compd	concn (M)	δ (ppm)	Δδ (ppm)	$^1J_{PH}$ (Hz)
PEt_2H		−55.13		192
$(Me_3CCH_2)_3Ga{\cdot}P(H)Et_2$	0.0689	−38.29	16.84	271
	0.138	−37.87	17.26	272
$P(C_6H_{11})_2H$		−27.40		193
$(Me_3CCH_2)_3Ga{\cdot}P(H)(C_6H_{11})_2$	0.0689	−25.02	2.38	219
	0.138	−25.80	3.60	230
$P(C_6H_{11})H_2$		−111.4		189
$(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$	0.0689	−98.3	13.1	226
	0.138	−95.9	15.5	227

$(C_6H_{11}) > HPPh_2$. Thus, the least sterically demanding base $HPEt_2$ is the strongest, as expected. The one surprise from our data is that $HP(C_6H_{11})_2$ and $HP(H)(C_6H_{11})$ have similar basicities.

The bulky dicyclohexylphosphine has an apparent base strength which is comparable to that of the less sterically demanding monocyclohexylphosphine. Since $HP(H)(C_6H_{11})$ would have been expected to be more basic than $HP(C_6H_{11})_2$, 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 strengths of $HP(C_6H_{11})_2$ and of $HP(H)(C_6H_{11})$ might be related to solvation effects. If the solvation of free $HP(H)(C_6H_{11})$ 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 π-cloud of benzene, whereas such hindrance would not occur for the free phosphine. It is also noteworthy that although $(Me_3CCH_2)_3Ga{\cdot}P(H)(C_6H_{11})_2$ 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 the hydrocarbon[6] RH and form a phosphide of the type $(R_2GaPR'_2)_n$.

$$GaR_3 + HPR'_2 \rightarrow (1/n)(R_2GaPR'_2)_n + RH \qquad (2)$$

Available ^{31}P NMR spectral data were used to study the relative order of reactivity of different organogallium compounds with $HPPh_2$ and of different phosphines with $Ga(CH_2CMe_3)_3$, all as benzene solutions of the same concentration. The following order was observed for decreasing ease of elimination in benzene solution when the phosphine was $HPPh_2$: $GaEt_3$ (most reactive) $> GaMe_3 > Ga(CH_2SiMe_3)_3 >> Ga(CH_2CMe_3)_3 \approx Ga(C_6H_2Me_3)_3$ (no reaction). 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 the organogallium phosphide $(R_2GaPPh_2)_n$ in benzene solution at room temperature, but both reactions were very slow. The NMR data demonstrated that approximately 45% of the $Et_3Ga{\cdot}P(H)Ph_2$ as a 0.138 M solution was converted to

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(6) Beachley, O. T., Jr.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241.

Et_2GaPPh_2 after 12 days, whereas a benzene solution of $Me_3Ga{\cdot}P(H)Ph_2$ 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 $(Me_2GaPPh_2)_3$ for an X-ray structural study. When no solvent was used, temperatures of 90−110 °C were reported by Coates and Graham[8] to be necessary to initiate the elimination of methane from the adduct $Me_3Ga{\cdot}P(H)Ph_2$ in a sealed tube. When the elimination of $SiMe_4$ from a benzene solution of $(Me_3SiCH_2)_3Ga{\cdot}P(H)Ph_2$ was investigated,[1,9] heating to reflux was necessary to initiate a very slow reaction. In constrast, $(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2$ did not eliminate CMe_4, even upon refluxing a solution for 3 weeks.[1,10] Reactivity studies of $Ga(CH_2CMe_3)_3$ with $HP(H)(C_6H_{11})$ demonstrated that approximately 90% of the CMe_4 was eliminated after a solution of $Ga(CH_2CMe_3)_3$ and $HP(H)(C_6H_{11})$ in benzene had been heated in a 70 °C oil bath for 7 days. However, heating for 18 days was necessary for complete reaction. The two phosphines $HP(C_6H_{11})_2$ and $HPEt_2$ did not undergo elimination reactions with $Ga(CH_2CMe_3)_3$, even upon heating benzene solutions at 70 °C for 3 weeks.

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 $HMe_2Al{\cdot}N(H)(Me)(Ph)$ 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 $HMe_2Al{\cdot}N(H)_2(CH_2Ph)$ system[12] provided additional support for the conclusion that dissociation of the adduct was needed for the elimination reaction to occur. When $HMe_2Al{\cdot}N(H)_2(CH_2Ph)$ was present as a solution in toluene, elimination of H_2 was observed. However, when the adduct precipitated from toluene solution, H_2 was not formed. The temperature was constant for these observations for the $HMe_2Al{\cdot}N(H)_2(CH_2Ph)$ system. Similarly, a benzene or toluene[8] solution of $Me_3Ga{\cdot}P(H)Ph_2$ eliminated methane at room temperature, whereas the pure adduct without solvent[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 $Et_3Ga{\cdot}P(H)Ph_2$ was faster than was the elimination of methane from a solution of $Me_3Ga{\cdot}P(H)Ph_2$, even though $GaMe_3$ is the stronger Lewis acid. Lastly, the extended times necessary for complete reactions for $Et_3Ga{\cdot}P(H)Ph_2$ and $(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$ are also consistent with the occurrence of bimolecular reactions.

The observed reactivity patterns of $GaMe_3$[13] and $Ga(CH_2SiMe_3)_3$[5] with $P(SiMe_3)_3$ also suggest that dissociation of these adducts might be required for the elimination of $SiMe_4$ with formation of $[R_2GaP(SiMe_3)_2]_n$. The reagents $GaMe_3$ and $P(SiMe_3)_3$ reacted smoothly in toluene solution to form $[Me_2GaP(SiMe_2)_2]_2$.[13] In contrast, $Ga(CH_2SiMe_3)_3$ reacted with $P(SiMe_3)_3$ in pentane solution to form only the adduct[5] $(Me_3SiCH_2)_3Ga{\cdot}P(SiMe_3)_3$. ^1H and ^{13}C NMR spectra demonstrated that the adduct did not dissociate in benzene solution. The product of the elimination reaction $[(Me_3SiCH_2)_2Ga{\cdot}P(SiMe_3)_2]_2$ was not formed.[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 $Ga(CH_2CMe_3)_3$,[14] $Ga(CH_2SiMe_3)_3$,[15] $Ga(C_6H_2Me_3)_3$,[16] $Ga(CH_2CMe_2Ph)_3$,[17] $(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2$,[1] and $(Me_3SiCH_2)_3Ga{\cdot}P(H)Ph_2$[1] 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 $SiMe_4$ at 0.00 ppm (δ) and C_6D_6 at 7.15 ppm. The ^{31}P NMR spectra were recorded at 161.9 MHz by using a Varian VXR-400 spectrometer. Proton-decoupled ^{31}P NMR chemical shifts are referenced to 85% H_3PO_4 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 quanity of the nonvolatile component and a known amount of C_6D_6 were placed into a reaction tube which was equipped with a magnetic stirbar 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 adduct 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 values for K_d in the tables have been rounded off to one significant figure to avoid misinterpretation or overinterpretation.

$(Me_3CCH_2)_3Ga{\cdot}P(H)Et_2$. (a) ^1H NMR (0.0689 M, C_6D_6, δ): 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, $^1J_{PH} = 273$ Hz, $-PH$). ^1H NMR (0.138 M, C_6D_6, δ): 0.76 (m, $-CH_3$), 0.91 (s, $Ga-CH_2-$), 1.18 (m, $P-CH_2-$), 1.21 (s, $-CMe_3$), 3.05 (dm, $^1J_{PH} = 273$ Hz, $-PH$). ^{31}P NMR (0.0689 M, C_6D_6, δ): −38.29 (dp, $^1J_{PH} = 271$ Hz,

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${}^3J_{PCCH}$ = 13.4 Hz). ^{31}P NMR (0.138 m, C_6D_6, δ): −37.87 (dp, ${}^1J_{PH}$ = 272 Hz, ${}^3J_{PCCH}$ = 13.4 Hz). Cryoscopic molecular weight (measured upon mixing reagents; formula weight 373.1; calcd mol wt, obsd mol wt, α or percent dissociation, K_d): 0.0541, 0.0584, 7.95%, 3.71 × 10^{-4}; 0.0460, 0.0507, 10.2%, 5.35 × 10^{-4}; 0.0376, 0.0422, 12.2%, 6.41 × 10^{-4}.

(b) A solution to study the elimination reaction was prepared by mixing 0.19 g (0.66 mmol) of $Ga(CH_2CMe_3)_3$, 0.060 g (0.67 mmol) of $HPEt_2$, and 4.82 g of C_6D_6. ^{31}P NMR (0.14 M, 20 °C, δ): initial spectrum, −37.87 (dp, ${}^1J_{PH}$ = 272 Hz, ${}^3J_{PCCH}$ = 13.4 Hz, $(Me_3CCH_2)_3Ga{\cdot}P(H)Et_2$). No change in the spectrum occurred after heating the sample for 3 weeks at an oil bath temperature of 70 °C.

$(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$. (a) ^{1}H NMR (0.0689 M, C_6D_6, δ): 0.90 (s, $-C_6H_{11}$), 0.94 (s, $-C_6H_{11}$), 1.00 (s, $-CMe_3$), 1.07 (s, $Ga-CH_2-$), 1.12 (s, $-CMe_3$), 1.15 (s, $-C_6H_{11}$), 1.18−1.7 (br, C_6H_{11}), 2.75 (dm, ${}^1J_{PH}$ = 225 Hz, −PH). ^{1}H NMR (0.138 M, C_6D_6, δ): 0.90 (s, $-C_6H_{11}$), 0.93 (s, $-C_6H_{11}$), 1.01 (s, $-CMe_3$), 1.06 (s, $Ga-CH_2-$), 1.10 (s, $-CMe_3$), 1.20−1.7 (br, $-C_6H_{11}$), 2.76 (dm, ${}^1J_{PH}$ = 225 Hz, −PH). ^{31}P NMR (0.0689 M, C_6D_6, δ): −98.3 (t, ${}^1J_{PH}$ = 227 Hz). ^{31}P NMR (0.138 M, C_6D_6, δ): −95.9 (t, ${}^1J_{PH}$ = 227 Hz). Cryoscopic molecular weight (measured upon mixing reagents; formula weight 399.3; (calcd mol wt, obsd mol wt, α or percent dissociation, K_d): 0.0552, 0.0828, 51.8%, 2.76 × 10^{-2}; 0.0430, 0.0663, 54.2%, 2.76 × 10^{-2}.

(b) A solution to study the elimination reaction was prepared by using 0.10 g (0.36 mmol) of $Ga(CH_2CMe_3)_3$, 0.042 g (0.36 mmol) of $H_2P(C_6H_{11})$, and 2.69 g of C_6D_6. ^{31}P NMR (0.13 M, 20 °C, δ): initial spectrum, −95.9 (t, ${}^1J_{PH}$ = 227 Hz, $(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$); 3 weeks after mixing reagents, −63.63 (s, 3.9, $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$), −73.29 (s, 4.1, $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$), −105.3 (s, 1.0, $(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$). A second solution was prepared by combining 0.13 g (0.47 mmol) of $Ga(CH_2CMe_3)_3$, 0.054 g (0.47 mmol) of $H_2P(C_6H_{11})$, and 7.2 g of C_6D_6. ^{31}P NMR, (0.065 m, 20 °C, δ): initial spectrum, −98.3 (t, ${}^1J_{PH}$ = 227 Hz, $(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$); 7 days at 70 °C, −63.58 (s, 4.3, $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$),−73.27 (s, 5.3, $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$), −104.8 (s, 1.0, $(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$); 14 days at 70 °C, −63.83 (s, 5.3, $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$), −73.10 (s, 8.2, $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$), −107.3 (s, 1.0, $(Me_3CCH_2)_3Ga{\cdot}P(H)_2(C_6H_{11})$); 18 days at 70 °C, −63.60 (s, 1.0, $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$), −73.31 (s, 1.2, $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$).

Synthesis of $(Me_3CCH_2)_3Ga{\cdot}P(H)(C_6H_{11})_2$. (a) The reagents 0.524 g (1.85 mmol) of $Ga(CH_2CMe_3)_3$ and 0.367 g (1.85 mmol) of $HP(C_6H_{11})_2$, 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 of $(Me_3CCH_2)_3Ga{\cdot}P(H)(C_6H_{11})_2$, 1.69 mmol, 91.6% yield). Mp: 42−43 °C. ^{1}H NMR (0.0689 M, C_6D_6, δ): 0.82 (s, $-C_6H_{11}$), 1.05 (s, $Ga-CH_2-$), 1.11 (s, $-C_6H_{11}$), 1.17 (s, $-CMe_3$), 1.37 (s, $-C_6H_{11}$), 1.54 (s, $-C_6H_{11}$), 1.60 (s, $-C_6H_{11}$), 1.73 (s, $-C_6H_{11}$), 2.98 (dt, ${}^1J_{PH}$ = 215 Hz, ${}^2J_{HCH}$ = 5.3 Hz, −PH). ^{1}H NMR (0.138 M, C_6D_6, δ): 0.90 (s, $-C_6H_{11}$), 1.00 (s, $-C_6H_{11}$), 1.07 (s, $Ga-CH_2-$), 1.08 (s, $-C_6H_{11}$), 1.14 (s, $-C_6H_{11}$), 1.20 (s, $-CMe_3$), 1.41 (s, $-C_6H_{11}$), 1.55 (s, $-C_6H_{11}$), 1.61 (s, $-C_6H_{11}$), 1.74 (s, $-C_6H_{11}$), 1.75 (s, $-C_6H_{11}$), 3.02 (dt, ${}^1J_{PH}$ = 231 Hz, ${}^2J_{HCH}$ = 4.5 Hz, −PH). ^{31}P NMR (0.0689 M, C_6D_6, δ): −25.02 (d, ${}^1J_{PH}$ = 219 Hz). ^{31}P NMR (0.138 M, C_6D_6, δ): −23.80 (d, ${}^1J_{PH}$ = 230 Hz). Anal. Calcd: C, 67.35; H, 11.72. Found: C, 67.27; 11.57. Cryoscopic molecular weight (formula weight 481.50; calcd mol wt, obsd mol wt, α or percent dissociation, K_d): 0.0638, 0.0918, 43.8%, 2.18 × 10^{-2}; 0.0528, 0.0785, 48.8%, 2.46 × 10^{-2}; 0.0413, 0.0639, 54.6%, 2.71 × 10^{-2}.

(b) Equal molar quantities of $Ga(CH_2CMe_3)_3$ and $HP(C_6H_{11})_2$ were combined in C_6D_6 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, ${}^1J_{PH}$ = 219 Hz, $(Me_3CCH_2)_3Ga{\cdot}P(H)(C_6H_{11})_2$). No change in the spectrum occurred after heating the sample for 3 weeks at 70 °C.

$Me_3Ga{\cdot}P(H)Ph_2$: ^{1}H NMR (0.0689 m, C_6D_6, δ): 0.10 (s, $-CH_3$), 5.19 (d, ${}^1J_{PH}$ = 293 Hz, −PH), 6.8−7.4 (m, Ph). ^{1}H NMR (0.138 m, C_6D_6, δ): 0.99 (s, $-CH_3$), 5.20 (d, ${}^1J_{PH}$ = 290 Hz, −PH), 6.8−7.4 (m, Ph). ^{31}P NMR (0.0.0689 M, C_6D_6, δ): −33.40 (dt, ${}^1J_{PH}$ = 290 Hz, ${}^3J_{PCCH}$ = 9.0 Hz). ^{31}P NMR (0.138 M, C_6D_6, δ): −33.17 (dp, ${}^1J_{PH}$ = 292 Hz, ${}^3J_{PCCH}$ = 9.2 Hz). Cryoscopic molecular weight (measured upon mixing reagents; formula weight 301.02; calcd mol wt, obsd mol wt, α or percent dissociation, K_d): 0.0644, 0.0672, 4.34%, 1.27 × 10^{-4}; 0.0542, 0.0567, 4.61%, 1.21 × 10^{-4}; 0.0525, 0.0550, 4.76%, 1.25 × 10^{-4}.

$Et_3Ga{\cdot}P(H)Ph_2$: ^{1}H NMR upon mixing reagents (0.0689 M, C_6D_6, δ): 0.76 (s, $-CH_2-$), 1.41 (t, ${}^2J_{HCH}$ = 8.0 Hz, $-CH_3$), 5.31 (d, ${}^1J_{PH}$ = 276 Hz, −PH), 6.8−7.4 (m, Ph). ^{1}H NMR (0.138 M, C_6D_6, δ): 0.75 (s, $-CH_2-$), 1.40 (t, ${}^2J_{HCH}$ = 8.0 Hz, $-CH_3$), 5.31 (d, ${}^1J_{PH}$ = 294 Hz, −PH), 6.8−7.4 (m, Ph). ^{31}P NMR (1 h after mixing reagents; 0.0689 M, C_6D_6, δ): −35.84 (dp, ${}^1J_{PH}$ = 272 Hz, ${}^3J_{PCCH}$ = 9.4 Hz, 4.3 $Et_3Ga{\cdot}P(H)Ph_2$), −46.32 (s, 1.0, $Et_2Ga{\cdot}PPh_2$). ^{31}P NMR (1 h after mixing reagents; 0.138 M, C_6D_6, δ): −34.00 (dp, ${}^1J_{PH}$ = 296 Hz, ${}^3J_{PCCH}$ = 9.4 Hz, 4.4, $Et_3Ga{\cdot}P(H)Ph_2$), −46.33 (s, 1.0, $Et_2Ga{\cdot}PPh_2$). ^{31}P NMR (3 days after mixing reagents; 0.0689 M, C_6D_6, δ): −35.83 (dp, ${}^1J_{PH}$ = 272 Hz, ${}^3J_{PCCH}$ = 8.4 Hz, 3.9, $Et_3Ga{\cdot}P(H)Ph_2$), −46.24 (s, 1.0, $Et_2Ga{\cdot}PPh_2$). ^{31}P NMR (3 days after mixing reagents, 0.138 M, C_6D_6, δ): −33.98 (dp, ${}^1J_{PH}$ = 294 Hz, ${}^3J_{PCCH}$ = 9.6 Hz, 2.7, $Et_3Ga{\cdot}P(H)Ph_2$), −46.23 (s, 1.0, $Et_2Ga{\cdot}PPh_2$). ^{31}P NMR (12 days after mixing reagents, 0.0689 M, C_6D_6, δ): −36.05 (dp, ${}^1J_{PH}$ = 278 Hz, ${}^3J_{PCCH}$ = 8.0 Hz, 2.6, $Et_3Ga{\cdot}P(H)Ph_2$), −46.39 (s, 1.0, $Et_2Ga{\cdot}PPh_2$). ^{31}P NMR (12 days after mixing reagents, 0.138 M, C_6D_6, δ): −34.14 (dp, ${}^1J_{PH}$ = 295 Hz, ${}^3J_{PCCH}$ = 9.1 Hz, 1.2, $Et_3Ga{\cdot}P(H)Ph_2$), −46.39 (s, 1.0, $Et_2Ga{\cdot}PPh_2$). Cryoscopic molecular weight (measured upon mixing reagents; formula weight 343.10; calcd mol wt, obsd mol wt, α or percent dissociation, K_d): 0.0720, 0.0785, 9.03%, 6.45 × 10^{-4}; 0.0580, 0.0649, 11.9%, 9.32 × 10^{-4}; 0.0422, 0.0478, 13.3%, 8.57 × 10^{-4}.

$(PhMe_2CCH_2)_3Ga{\cdot}P(H)Ph_2$. ^{1}H NMR (0.0689 M, C_6D_6, δ): 0.83 (s, $Ga-CH_2-$), 1.23 (s, $-CMe_2-$), 5.15 (d, ${}^1J_{PH}$ = 219 Hz, −PH), 6.80−7.40 (m, Ph). ^{1}H NMR (0.138 M, C_6D_6, δ): 0.84 (s, $Ga-CH_2-$), 1.24 (s, $-CMe_2-$), 5.13 (d, ${}^1J_{PH}$ = 231 Hz, −PH), 6.82−7.42 (m, Ph). ^{31}P NMR (0.0689 M, C_6D_6, δ): −39.17 (dp, ${}^1J_{PH}$ = 224 Hz, ${}^3J_{PCCH}$ = 7.3 Hz). ^{31}P NMR (0.138 M, C_6D_6, δ): −38.40 (dp, ${}^1J_{PH}$ = 230 Hz, ${}^3J_{PCCH}$ = 7.4 Hz). Cryoscopic molecular weight (formula weight 655.56; calcd mol wt, obsd mol wt, α or percent dissociation, K_d): 0.0495, 0.0823, 66.3%, 6.44 × 10^{-2}; 0.0414, 0.0690, 66.7%, 5.52 × 10^{-2}; 0.0315, 0.0518, 64.4%, 3.68 × 10^{-2}.

Reaction of $Ga(C_6H_2Me_3)_3$ with $HPPh_2$. ^{1}H NMR (0.0689 M of each reagent, C_6D_6, 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). ^{1}H NMR (0.138 m, C_6D_6, 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). ^{31}P NMR (0.0689 M, C_6D_6, δ): −40.40 (dp, ${}^1J_{PH}$ = 217 Hz, ${}^3J_{PCCH}$ = 6.9 Hz). ^{31}P NMR (0.138 M, C_6D_6, δ): −40.40 (dp, ${}^1J_{PH}$ = 217 Hz, ${}^3J_{PCCH}$ = 7.6 Hz). Cryoscopic molecular weight (formula weight 613.46; calcd mol wt, obsd mol wt, α or percent dissociation): 0.0415, 0.0832, 100%; 0.0371, 0.0739, 99.2%.

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