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Use of $Me_2Ga(C_5H_5)$ To Prepare $(Me_2GaERR')_n$ (E = N, P) at or below Room Temperature and the Crystal and Molecular Structure of $[Me_2GaP(Me)(Ph)]_3$

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Summary: The organogallium compound, $Me_2Ga(C_5H_5)$ *has been observed to react at room temperature or below with primary and secondary amines and phosphines to form* $[Me_2GaNH_2]_3$, $[Me_2GaN(H)(Me)]_3$, $[Me_2GaN(H)(t\text{-}Bu)]_2$, $[Me_2GaN(H)(C_6H_{11})]_2$, $[Me_2GaNEt_2]_2$, $[Me_2GaN(Me)(C_6H_{11})]_2$, $[Me_2GaN(Me)(Ph)]_2$, $[Me_2GaN(Et)(Ph)]_2$, $[Me_2GaP(C_6H_{11})_2]_2$, $[Me_2GaP(Me)(Ph)]_3$, *or* $[Me_2GaPPh_2]_2$ *and cyclopentadiene. All new compounds have been fully characterized by their melting points, partial elemental analyses (C and H),* ^1H *NMR,* ^{31}P *NMR (as appropriate), and IR spectroscopic data, and cryoscopic molecular weight studies. The compound* $[Me_2GaP(Me)(Ph)]_3$ *crystallizes in the trigonal space group R3 with a = 16.526(5) Å, c = 10.242(2) Å, V = 2421(1) Å*^{3}*, and Z = 3 (trimeric molecules). The molecule contains a* Ga_3P_3 *ring in the chair conformation with phenyl groups in axial positions. The Ga–P distances range from 2.407(4) to 2.413(6) Å.*

Compounds of the type $R_2MER'_2$ (M = group 13 element, E = group 15 element) are being investigated as single-source precursors for the preparation of group 13–15 materials.[2] The best precursors should be volatile liquids which can be prepared in very high purity. The typical synthetic routes to these types of compounds are either hydrocarbon elimination reactions or metathesis reactions. The major source of impurities in precursors prepared by elimination reactions originates with the high temperatures needed to initiate the elimination reaction between the pure starting materials, the organo group 13 compound, and the group 15 compound.

$$MR_3 + HER'_2 \xrightarrow[\text{reaction}]{\text{elimination}} R_2MER'_2 + RH$$

Typically, elimination reactions in gallium–nitrogen systems[3–5] require 100–130 °C whereas gallium–phosphorus compounds[4,5] need 110–150 °C. For example, the compounds $[Me_2GaNH_2]_3$,[3] $[Me_2GaN(H)(Me)]_3$,[3] Me_2GaNMe_2,[3] $[Me_2GaN(H)(t\text{-}Bu)]_2$,[4] and $(Me_2GaNPh_2)_2$[5] were prepared from the neat reagents, $GaMe_3$, and the corresponding amine, at 90, 125, 125, 110, and 120 °C, respectively, whereas $(Me_2GaNHPh)_2$,[6] $[Me_2GaN(H)Ad]_2$[6] (Ad = 1-adamantyl), $[Me_2GaN(H)Dipp]_2$[6] (Dipp = 2,6-$i\text{-}Pr_2C_6H_3$) were formed from $GaMe_3$ and the corresponding amine in refluxing toluene (bp 110 °C). The gallium–phosphorus compounds, $(Me_2GaPMe_2)_3$,[7] $(Me_2GaPEt_2)_2$,[7] and $[Me_2GaPPh_2]_2$,[5] required heating the corresponding neat reagents to 150, 160, and 110 °C, respectively. It is noteworthy that when $GaMe_3$ and H_2NMes[6] (Mes = 2,4,6-$Me_3C_6H_2$) were combined in refluxing toluene and then heated neat at 190 °C, products indicative of orthometalation rather than a simple product from an elimination reaction were observed. On the other hand, metathesis reactions

$$R_2MCl + LiER'_2 \xrightarrow[\text{reaction}]{\text{metathesis}} R_2MER'_2 + LiCl(s)$$

require more reagents with multistep syntheses and typically require the use of ether solvents. Since each new reagent or solvent introduces the possibility of impurities, the simplest reaction should give the purest product. Thus, one goal of our interest has been to discover new elimination reactions which occur at the lowest possible temperature.

The reaction between $Me_2Ga(C_5H_5)$ and the primary and/or secondary amine and phosphine occurs at or below room temperature (eq 2) and provides a convenient, low-temperature route to gallium–nitrogen and gallium–phosphorus compounds of high purity. The compounds $[Me_2GaNH_2]_3$,[3] $[Me_2GaN(H)(Me)]_3$,[3,8] $[Me_2GaN(H)(t\text{-}Bu)]_2$,[4,10] $[Me_2GaN(H)(C_6H_{11})]_2$, $[Me_2GaNEt_2]_2$, $[Me_2GaN(Me)(C_6H_{11})]_2$, $[Me_2GaN(Me)(Ph)]_2$,[9] $[Me_2GaN(Et)(Ph)]_2$, $[Me_2GaP(C_6H_{11})_2]_2$, $[Me_2GaP(Me)(Ph)]_3$, and $[Me_2GaPPh_2]_2$[5] have been prepared by this route and have been characterized by partial elemental analyses (C and H), melting points, ^1H NMR, ^{31}P NMR, and IR spectroscopy, and cryoscopic molecular weight studies, when appropriate and when data were not available from previous studies. In addition, a crystal of $[Me_2GaP(Me)(Ph)]_3$ has been characterized by an X-ray structural study.

$$Me_2Ga(C_5H_5) + HERR' \rightarrow 1/n[Me_2GaERR']_n + C_5H_6 \quad (1)$$

The reaction between $Me_2Ga(C_5H_5)$ and $HN(H)(C_6H_{11})$ in pentane goes to completion in approximately 5 h at −78 °C, as observed by the disappearance of the initially insoluble $Me_2Ga(C_5H_5)$. The low temperature needed for

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the cyclopentadiene elimination reaction reduces the potential for unwanted side reactions and/or decomposition reactions. The facility of the C_5H_6 elimination reaction might arise from the observation that a proton can be added to the cyclopentadienyl moiety at any of five carbon atoms. Addition of a proton to C_5H_5 would in turn facilitate breakage of the gallium–carbon (cyclopentadienyl) bond. In the corresponding alkane elimination reactions between $GaMe_3$ and group 15 compounds, the hydrogen from the group 15 compound must be added to the unique α-carbon atom bonded to gallium. It is also of interest to note that $Me_2Ga(C_5H_5)$[11] is believed to exist in benzene solution as an equilibrium mixture of $GaMe_3$, $Me_2Ga(C_5H_5)$, $MeGa(C_5H_5)_2$, and $Ga(C_5H_5)_3$. Thus, the elimination of C_5H_6 in benzene solution has the potential to lead to the formation of a mixture of products including $Me_3Ga{\cdot}E(H)RR'$, Me_2GaERR', $(Me)(C_5H_5)GaERR'$, and $(C_5H_5)_2GaERR'$. However, our observation that only pure products of the type Me_2GaERR' are isolated suggests that either ligand redistribution reactions between the various potential products must occur rapidly or the mixtures of products are never formed.

The driving force for the C_5H_6 elimination reaction must be related to the association of monomeric Me_2GaERR' species to form dimers to trimers. A simple acid–base equilibrium (eq 2) can be envisioned to occur as the first

$$Me_2Ga(C_5H_5) + HERR' \rightleftharpoons Me_2GaERR' + C_5H_6 \quad (2)$$

step. Since cyclopentadiene is a stronger acid than HERR′, one might expect the equilibrium constant for eq 2 to be less than 1 and the reaction to be useless. However, if monomeric Me_2GaERR' species rapidly associate to form stable dimers or trimers, the reverse reaction cannot occur. Base sites would not be available for removal of a proton from C_5H_6. In fact, the acidity of C_5H_6 has been used to prepare other cyclopentadienylmetal compounds. For example, $Fe(NEt_2)_2$ reacts with C_5H_6 to form $Fe(C_5H_5)_2$ and $HNEt_2$.[12] Similarly, Me_3SnNEt_2 reacts with C_5H_6 to form $Me_3Sn(C_5H_5)$ and $HNEt_2$.[13] Both of these reactions are the apparent reverse of the reactions observed in gallium–nitrogen and gallium–phosphorus chemistry and take advantage of the high acidity of C_5H_6.

The range of bases which react with $Me_2Ga(C_5H_5)$ to form species of the type $[Me_2GaERR']_n$ has been examined. Three amines with bulky substituents, $HN(C_6H_{11})_2$, $HN(N)(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ (2,4,6-tri-*tert*-butylaniline (HTBA)), and $HN(2,2,4,4\text{-}Me_4C_5H_6)$ (2,2,4,4-tetramethylpiperidine (HTMP)), did not undergo apparent reactions to form the desired gallium–nitrogen products. Since cyclohexylamine and dicyclohexylamine have similar basicities, but cyclohexylamine formed the desired product and dicyclohexylamine did not, steric effects appear to be an exceedingly important factor. It is also noteworthy that dicyclohexylphosphine reacted to form $[Me_2GaP(C_6H_{11})_2]_2$. The longer phosphorus–carbon and/or phosphorus–hydrogen bonds in $HP(C_6H_{11})_2$ in comparison to those to nitrogen in $HN(C_6H_{11})_2$ are sufficient to permit reaction to occur. It is regrettable but we do not know at the present time whether steric effects prevent the elimination reaction from occurring or whether steric effects prevent the association of the monomeric product, Me_2GaERR'. If association of the product does not occur, the high acidity of C_5H_6 would favor the reformation of reactants, the reverse of eq 2, and prevent the isolation of the desired product.

Table I. Cis/Trans Isomer Ratios in C_6H_6 and CH_2Cl_2 Solutions

compd	C_6H_6 % cis	C_6H_6 % trans	CH_2Cl_2 % cis	CH_2Cl_2 % trans
$[Me_2GaN(Me)(Ph)]_2$	70	30	71	29
$[Me_2GaN(H)(C_6H_{11})]_2$	69	31	43	57
$[Me_2GaN(Me)(C_6H_{11})]_2$	48	52	100	0
$[Me_2GaN(H)(t\text{-}Bu)]_2$	0	100	0	100

The degrees of association of all products in benzene solution not previously reported were determined by cryoscopic molecular weight studies. All compounds were either dimers or trimers. None of the compounds exhibited molecular weight data in which the observed molecular weight decreased as the concentration decreased. Thus, no equilibria between species of different degrees of association are proposed. The trimers were $[Me_2GaNH_2]_3$, $[Me_2GaN(Me)]_3$, and $[Me_2Ga(Me)(Ph)]_3$. It is noteworthy that Me_2GaNH_2[3] and $Me_2GaN(H)(Me)$[3] have been previously prepared by elimination reactions between $GaMe_3$ and the amine. Gas phase molecular weight studies[3] of these products revealed the presence of the dimers rather than the trimers observed in solution in the current study.

The ^1H and ^{31}P NMR and IR spectra of compounds, as appropriate, were consistent with the degree of association of the compound in solution and with the nature of the substituents on the group 15 element. Thus, all unsymmetrically substituted species $[Me_2GaERR']_n$ had spectra which could be interpreted best by the presence of mixtures of geometrical isomers. Those dimeric compounds which had the general formula $[Me_2GaERR']_2$ typically exhibited three ^1H NMR lines which can be assigned to Ga–Me protons. Two lines of equal intensity were due to the cis isomer whereas the trans isomer exhibited only one Ga–Me line. The unsymmetrically substituted trimers, $[Me_2GaN(H)(Me)]_3$[8] and $[Me_2GaP(Me)(Ph)]_3$, exhibited multiple (many more than three) gallium–methyl lines. These multiple lines (closely spaced) are consistent with the presence of a number of geometrical isomers. It is noteworthy that even though multiple isomers were observed for the solutions of the unsymmetrically substituted compounds, the melting points of the solids were sharp, less than 2 °C. Sharp melting points might suggest the presence of single isomers in the solid phase. Thus, isomerization reactions would have had to occur upon dissolution of the solid. All infrared bands related to N–H stretching motions were sharp and well-defined. No interactions of the hydrogen bonded to nitrogen with other atoms[14] were suggested by the spectroscopic data.

The cis/trans isomer ratio (Table I) of four unsymmetrically substituted dimers were calculated from ^1H NMR data for C_6H_6 and CH_2Cl_2 solutions. The cis/trans ratio for $[Me_2GaN(Me)(Ph)]_2$ and $[Me_2GaN(H)(t\text{-}Bu)]_2$ did not change significantly between the two solvents, whereas it did for $[Me_2GaN(H)(C_6H_{11})]_2$ and $[Me_2GaN(Me)(C_6H_{11})]_2$. Thus, isomerization reactions must occur in solution. It is also noteworthy that there is no clear trend in the cis/trans ratio with the nature of substituents. Thus, these

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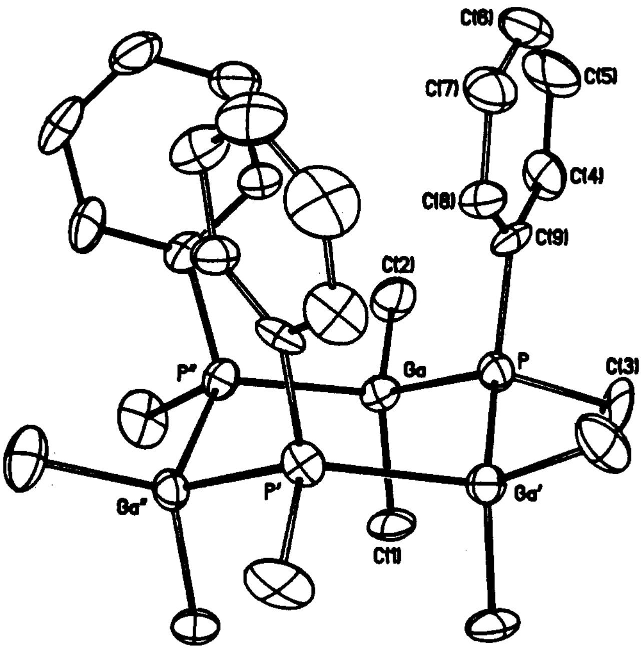

Figure 1. $[Me_2GaP(Me)(Ph)]_3$ with all C-bonded hydrogen atoms omitted.

Table II. Selected Bond Distances and Bond Angles for $[Me_2GaP(Me)(Ph)]_3$

	Bond Distances (Å)		
Ga–P	2.413(6)	Ga–P′	2.407(4)
Ga–C(1)	1.963(16)	Ga–C(2)	1.998(20)
P–C(3)	1.906(25)	P–C(9)	1.824(13)
	Bond Angles (deg)		
P–Ga–C(1)	105.5(8)	P–Ga–C(2)	113.0(8)
C(1)–Ga–C(2)	117.6(8)	P–Ga–P′	105.0(2)
C(1)–Ga–P′	105.6(6)	C(2)–Ga–P′	109.2(8)
Ga–P–C(3)	103.8(10)	Ga′–P–C(3)	104.5(8)
Ga–P–C(9)	112.0(5)	Ga′–P–C(9)	112.2(4)
C(3)–P–C(9)	104.7(8)	Ga–P–Ga′	118.1(2)
P–C(9)–C(4)	120.6(3)	P–C(9)–C(8)	119.4(3)

data suggest that solvent effects might be an important factor.

A crystal of dimethylgallium methyl phenyl phosphide consists of discrete trimeric units with the formula $[Me_2GaP(Me)(Ph)]_3$. There are no abnormally close contacts in the unit cell. The labeling in the molecule is depicted in Figure 1. Selected interatomic distances and angles are collected in Table II.

The Ga_3P_3 six-membered ring has a typical chair conformation with all three phenyl groups in axial positions. The only other structure of an unsymmetrically substituted gallium phosphide trimer had different substituents on gallium,[15] $[(Me_3CCH_2)(Cl)GaPPh_2]_3$. In this case, the bulky neopentyl groups occupied the E, A, A positions on a chair conformation of the six-membered ring. The internal ring angles of $[Me_2GaP(Me)(Ph)]_3$ range from 105.0(2)° for P–Ga–P(A) to 118.1(2)° for Ga–P–Ga(A). The Ga_3P_3 ring in $[(Me_3CCH_2)(Cl)GaPPh_2]_3$[15] also had larger Ga–P–Ga angles (113.6(1)–117.5(1)°) than P–Ga–P angles (104.2(1)–109.0(1)°).

The bond lengths in $[Me_2GaP(Me)(Ph)]_3$ are normal. The Ga–P distances range from 2.413(6) for Ga–P to 2.407(4) Å for Ga(A)–P. The distances are comparable to those of 2.414(3)–2.433(4) Å in $[(Me_3CCH_2)(Cl)GaPPh_2]_3$,[15] of 2.439(3) Å in $(t\text{-}Bu_2GaPH_2)_3$,[16] and of 2.419(3)–2.457(3) Å for $[Me_2GaP(i\text{-}Pr)_2]_3$.[17] The Ga–C methyl bond distances of 1.963(16) Å (Ga–C(1)) and 1.998(20) Å (Ga–C(2)) are also normal. The P–C(methyl) distance of 1.906(25) Å was longer than the P–C(phenyl) distances of 1.824(13) Å. The P–C(phenyl) distance in $[(Me_3CCH_2)(Cl)GaPPh_2]_3$[15] ranged from 1.81(1) to 1.84(1) Å.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere in a Vacuum Atmospheres drybox. The starting material $Me_2Ga(C_5H_5)$ was prepared and purified by the literature method.[11] Amines were typically dried over KOH and then distilled prior to use. Phosphines were vacuum distilled prior to use. Solvents were dried by conventional procedures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. The ^1H NMR spectra were recorded at 300 MHz by using a Varian Gemini-300 spectrometer or at 90 MHz by using a JEOL EM-390 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 ppm and C_6H_6 at δ 7.15 ppm. The ^{31}P NMR spectrum was recorded at 161.9 MHz on a Varian VXR-400 spectrometer. Proton-decoupled ^{31}P NMR spectra are referenced to 85% H_3PO_4 at δ 0.00 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries and are uncorrected. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon.[18]

Reaction of $Me_2Ga(C_5H_5)$ with HERR′ (E = N, P). In a typical synthesis, dry, freshly purified amine or phosphine was vacuum distilled or syringed into a tared tube equipped with a Teflon valve and a standard taper joint. Then, a stoichiometric amount of $Me_2Ga(C_5H_5)$ was placed into a two-neck flask equipped with a magnetic stirbar, a Teflon valve adapter, and the tube containing the amine or phosphine. Benzene or pentane, 35 mL, was vacuum distilled onto the $Me_2Ga(C_5H_5)$, and the flask was warmed to ambient temperature. The desired amine or phosphine was added to the solution. After the reaction mixture was stirred overnight, the resulting solution was filtered by using a medium glass frit. With the filtrate cooled to −10 °C, the solvent, cyclopentadiene, and possibly excess starting material were removed by vacuum distillation to leave an off-white product.

The product $(Me_2GaERR')_n$ was then finally purified by vacuum sublimation or recrystallization depending upon the nature of the product. The following give characterization data for all compounds prepared from $Me_2Ga(C_5H_5)$. For known compounds, only the melting point and characterization data not previously reported are given. All gallium-containing products were isolated as colorless, crystalline solids at room temperature. Three amines, dicyclohexylamines $(HN(C_6H_{11})_2)$, 2,4,6-tri-*tert*-butylaniline $[HN(H)(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]$, and 2,2,4,4-tetramethylpiperidine $[HN(2,2,4,4\text{-}Me_4C_5H_6)]$ did not undergo an elimination reaction with $Me_2Ga(C_5H_5)$.

$[Me_2GaNH_2]_3$: product isolated by sublimation at 90 °C in 93% yield; mp 100–101.5 °C; lit.[3] mp 97.2–97.5 °C; ^1H NMR (C_6D_6) δ −0.41 $(Ga\text{–}CH_3)$; IR (Nujol mull, cm^{-1}) 3330 (w) (NH), 3270 (w) (NH), 1640 (m), 1600 (w), 1475 (sh), 1430 (vs), 1395 (m), 1360 (s), 1285 (w), 1265 (w), 1235 (s), 1200 (w), 1190 (w), 1120 (w), 1080 (w), 1015 (w), 930 (w), 915 (w), 880 (m), 820 (w), 800 (w), 770 (w), 640 (w), 620 (w), 510 (w), 460 (w), 380 (w), 340 (w). Anal.

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Calcd: C, 20.74; H, 6.96. Found: C, 21.04; H, 6.99. Cryoscopic molecular weight, formula weight 116 (obsd molality, obsd mol wt, association): 0.0758, 379, 3.27; 0.0625, 370, 3.19; 0.0514, 352, 3.04.

$[Me_2GaN(H)(Me)]_3$:[3,8] product isolated by sublimation at room temperature in 90% yield; mp 117–119 °C; ^1H NMR (C_6D_6) δ –0.45 (s, Ga–CH_3, 0.5H), –0.44 (s, Ga–CH_3, 0.8H), –0.39 (s, Ga–CH_3, 1.5H), –0.37 (s, Ga–CH_3, 2.1H), –0.30 (s, Ga–CH_3, 0.4H), 1.875 (d, J = 7.0 Hz, N–CH_3, 2.4H), 1.955 (d, J = 7.0 Hz, N–CH_3, 0.6H) (see Results and Discussion and ref 8); IR (Nujol mull, cm^{-1}) 3270 (w) (NH), 1515 (sh), 1505 (s), 1472 (m), 1462 (w), 1430 (w, br), 1200 (m), 1195 (m), 1138 (w), 1040 (m), 985 (m), 970 (m), 942 (m), 925 (m), 680 (m, br), 565 (s), 542 (s), 522 (vs), 431 (w), 275 (w).

$[Me_2GaN(H)(t\text{-}Bu)]_2$:[4,10] product isolated by sublimation at 45 °C in 68% yield; mp 73.5–75 °C; lit. mp 80 °C,[4] 72–76 °C dec;[10] ^1H NMR (C_6D_6) δ –0.06 (s, Ga–CH_3, 6H), 0.98 (s, C–CH_3, 9H); ^1H NMR (CH_2Cl_2) δ –0.25 (s, Ga–CH_3, 6H), 1.17 (s, C–CH_3, 9H); IR (Nujol mull, cm^{-1}) 3250 (m) (NH), 1390 (w), 1360 (s), 1355 (m), 1230 (m), 1200 (s), 1187 (s), 1180 (m), 1030 (w), 1020 (w), 935 (s), 910 (s), 892 (s), 875 (m), 750 (s), 682 (m), 590 (s), 565 (s), 530 (s), 468 (w), 390 (w), 380 (sh). Anal. Calcd: C, 41.92; H, 9.38. Found: C, 42.06; H, 9.41. Cryoscopic molecular weight, formula weight 172 (obsd molality, obsd mol wt, association): 0.0660, 369, 2.14; 0.0496, 377, 2.19; 0.0306, 405, 2.36.

$[Me_2GaN(H)(C_6H_{11})]_2$: product isolated by sublimation at 60 °C in 63% yield; mp 98–99.5 °C; ^1H NMR (C_6D_6) δ –0.21 (s, Ga–CH_3, cis, 1.9H), –0.17 (s, Ga–CH_3, trans, 1.8H), –0.14 (s, Ga–CH_3, cis, 1.9H), 1.08 (m, C_6H_{11}, 11.7H); ^1H NMR (CH_2Cl_2) δ –0.45 (s, Ga–CH_3, cis, 1.4H), –0.38 (s, Ga–CH_3, trans, 3.2H), –0.36 (s, Ga–CH_3, cis, 1.4H), 1.45 (m, C_6H_{11}, 11H); IR (Nujol mull, cm^{-1}) 3285 (w) (NH), 2960 (sh), 1465 (sh), 1445 (sh), 1435 (m), 1360 (m), 1345 (w), 1285 (w), 1260 (w), 1200 (m), 1190 (m), 1120 (w), 1060 (m), 1030 (w), 970 (m), 915 (w), 890 (m), 863 (m), 859 (m), 840 (m), 785 (w), 680 (w), 600 (m), 570 (m), 555 (m), 525 (m), 500 (w), 425 (w), 390 (w). Anal. Calcd: C, 48.54; H, 9.17. Found: C, 48.57; H, 9.09.

$[Me_2GaNEt_2]_2$: product isolated by sublimation at room temperature in 81% yield; mp 39–40.5 °C; ^1H NMR (C_6D_6) δ –0.20 (s, Ga–CH_3, 3.1H), 0.73 (t, J = 7.2 Hz, C–CH_3, 3.2H), 2.66 (q, J = 7.2 Hz, CH_2–C, 2H); IR (Nujol mull, cm^{-1}) 2720 (w), 1470 (sh), 1465 (sh), 1435 (sh), 1360 (sh), 1285 (w), 1200 (m), 1170 (w), 1140 (m), 1110 (w), 1040 (w), 1000 (m), 850 (w), 790 (m), 735 (sh), 670 (w), 590 (m), 560 (m), 530 (m). Anal. Calcd: C, 41.92; H, 9.38. Found: C, 42.18; H, 9.55. Cryoscopic molecular weight, formula weight 172 (obsd molality, obsd mol wt, association): 0.0733, 382, 2.22; 0.0582, 387, 2.25; 0.0369, 410, 2.38.

$[Me_2GaN(Me)(C_6H_{11})]_2$: product isolated by sublimation at 90 °C in 89% yield; mp 158–159 °C; ^1H NMR (C_6D_6) δ –0.18 (s, Ga–CH_3, cis, 1.4H), –0.135 (s, Ga–CH_3, trans, 3.1H), –0.10 (s, Ga–CH_3, cis, 1.6H), 1.20 (m, N–C_6H_{11}, 22H), 2.18 (s, N–CH_3, cis, 2.9H), 2.23 (s, N–CH_3, trans, 3.1H); ^1H NMR (CH_2Cl_2) δ –0.33 (s, Ga–CH_3, cis, 3H), –0.30 (s, Ga–CH_3, cis, 3H), 1.52 (m, N–C_6H_{11}, cis, 11H), 2.45 (s, N–CH_3, cis, 3H); IR (Nujol mull, cm^{-1}) 1490 (w), 1360 (s), 1345 (m), 1325 (w), 1300 (w), 1255 (m), 1248 (w), 1200 (vs), 1180 (w), 1140 (m), 1085 (m), 1050 (w), 1025 (w), 988 (w), 918 (vs), 890 (m), 875 (m), 840 (m), 780 (m), 735 (sh), 675 (m), 632 (m), 565 (vs), 528 (m), 435 (w), 390 (vw), 310 (w), 295 (vw), 285 (vw), 260 (w), 238 (m), 230 (w). Anal. Calcd: C, 50.99; H, 9.51. Found: C, 51.08; H, 9.68. Cryoscopic molecular weight, formula weight 212 (obsd molality, obsd mol wt, association): 0.0675, 441, 2.08; 0.0525, 426, 2.01; 0.0462, 422, 1.99.

$[Me_2GaN(Me)(Ph)]_2$: product isolated by sublimation at 120 °C in 77% yield; mp 109–111 °C; lit.[9] mp 112–114 °C.

$[Me_2GaN(Et)(Ph)]_2$: product isolated by sublimation at 110 °C in 88% yield; mp 97–98 °C; ^1H NMR (C_6D_6) δ –0.27 (s, Ga–CH_3, cis, 1.9H), –0.030, (Ga–CH_3, trans, 2.2H), 0.16 (s, Ga–CH_3, cis, 1.9H), 0.68 (t, J = 7 Hz, N–C–CH_3, trans, 1.8H), 0.76 (t, J = 7 Hz, N–C–CH_3, cis, 1.2H), 3.19 (q, N–CH_2–C, trans, 1.2H), 3.23 (q, J = 7 Hz, N–CH_2–C, cis, 0.7H); IR (Nujol mull, cm^{-1}) 1735 (vw), 1595 (m), 1581 (sh,m), 1488 (s), 1259 (w), 1204 (m), 1192 (m), 1152 (w), 1135 (w), 1085 (m), 1075 (sh,w), 1022 (m), 920 (vw), 913 (m), 890 (w), 838 (w), 772 (m), 760 (m), 731 (m), 697 (s), 633 (w), 585 (w), 570 (w), 529 (m). Cryoscopic molecular weight, formula weight of $Me_2GaN(Et)Ph$ 220 (obsd molality, obsd mol wt, association): 0.0821, 482, 2.19; 0.0474, 489, 2.22; 0.0259, 492, 2.24. Anal. Calcd: C, 54.60; H, 7.33. Found: C, 54.41; H, 7.49.

Table III. Crystallographic Data for $[Me_2GaP(Me)(Ph)]_3$

	(a) Crystal Parameters		
formula	$[C_9H_{14}PGa]_3$	Z	3
fw	668.71	cryst dimens, mm	0.20 × 0.20 × 0.50
cryst syst	trigonal	cryst color	colorless
space group	R3	D(calc), g cm^3	1.38
a, Å	16.526(5)	μ(Mo Kα), cm^{-1}	27.74
c, Å	10.242(2)	temp, K	298
V, Å^3	2421(1)	τ(max)/τ(min)	1.19
	(b) Data Collection		
diffractometer	Nicolet R3m	no. of reflns collcd	1181
monochromator	graphite	no. of indpt reflns	1181
radiation	MoKα (λ = 0.71073Å)	no. of indpt obsvd rflns $F_o \geq 4\sigma(F_o)$	835
2θ scan range, deg	4 – 52	std reflns	3 std/197 rflns
data collected (h,k,l)	+21, +21, ±13	var in stds, %	<1
	(c) Refinement		
$R(F)$, %	6.78	$\Delta(\rho)$, e Å^{-3}	1.27
$R_w(F)$, %	7.69	N_o/N_v	9.60
Δ/σ(max)	0.034	GOF	1.751

$[Me_2GaP(C_6H_{11})_2]_2$: product isolated by sublimation at 120 °C in 81% yield; mp 161–163 °C; ^1H NMR (C_6D_6) δ 0.10 (t, $^3J_{P\text{–}Ga\text{–}C}$ = 4.5 Hz, Ga–CH_3, 6.0H), 1.35 (m, C_6H_{11}, 22.6H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ –17.68 (s); IR (Nujol mull, cm^{-1}) 1360 (m), 1348 (vw), 1336 (w), 1290 (vw), 1285 (vw), 1260 (w), 1182 (m), 1168 (m), 1111 (w), 1080 (vw), 1065 (vw), 1040 (vw), 1020 (vw), 995 (m), 908 (vw), 890 (w), 880 (m), 845 (m), 740 (m), 665 (w), 550 (m), 520 (m), 460 (vw), 308 (w). Anal. Calcd: C, 56.60; H, 9.50. Found: C, 56.38; H, 9.50. Cryoscopic molecular weight, formula weight 297 (obsd molality, obsd mol wt, association): 0.0551, 647, 2.18; 0.0449, 632, 2.13; 0.0345, 623, 2.10.

$[Me_2GaP(Me)(Ph)]_3$: product purified by recrystallization from pentane and isolated in 67% yield; mp 124–126 °C; ^1H NMR (C_6D_6) δ –0.08 (multiple lines, Ga–CH_3, 6H), 1.39 (multiple lines, P–CH_3, 3H); $^{31}P\{^1H\}$ (C_6D_6) δ 78.79, 77.70 (relative intensities are 1.00 and 2.05); IR (Nujol mull, cm^{-1}) 1193 (w), 1183 (w), 1165 (vw), 1153 (w), 1090 (vw), 1022 (w), 998 (w), 855 (sh, m), 880 (m), 737 (s), 719 (s), 690 (m), 555 (m), 521 (m), 480 (w). Anal. Calcd: C, 48.64; H, 6.48; P, 13.76. Found: C, 48.49; H, 6.33; P, 13.90. Cryoscopic molecular weight, formula weight 223 (obsd molality, obsd mol wt, association): 0.0506, 772, 3.46; 0.0372, 733, 3.29; 0.0177, 741, 3.32.

$[Me_2GaPPh_2]_2$: product purified by recrystallization from benzene and isolated in 88% yield; mp 214–217 °C; lit.[5] mp 194 °C; ^1H NMR (C_6D_6) δ 0.283, 0.293, 0.303, 0.313 (m, apparently two overlapping triplets, J = 0.30 Hz, Ga–CH_3); ^{31}P (C_6D_6) δ –45.9; IR (Nujol mull, cm^{-1}) 3100 (w), 3070 (w), 3050 (w), 2720 (w), 2670 (w), 1580 (w), 1565 (vw), 1475 (vs), 1362 (vs), 1300 (m), 1258 (w), 1200 (w), 1185 (m), 1165 (w), 1155 (m), 1085 (w), 1065 (w), 1030 (w), 1020 (w), 998 (m), 970 (m), 915 (w), 885 (w), 840 (w), 745 (sh), 735 (vs), 690 (s), 670 (m), 555 (m), 520 (m), 503 (m), 475 (w), 435 (w), 390 (w). Anal. Calcd: C, 59.01; H, 5.66. Found: C, 58.73; H, 6.05.

X-ray Crystallography for $[Me_2GaP(Me)(Ph)]_3$. Crystallographic data are collected in Table III. A colorless crystal of the title compound was mounted on a glass fiber with epoxy cement. Unit-cell parameters were determined through least-squares refinement of the angular settings for 25 reflections (20° ≤ 2θ ≤ 25°). The systematic absences in the diffractometer data and photographic evidence allowed all of the rhombohedral space groups except for $R3c$ and $R\bar{3}c$. The anticipated molecular symmetry suggests the space group $R3$. This was confirmed by the results of the refinement. An absorption correction was applied on the basis of 216 ψ scan data with T_{max}/T_{min} = 1.19.

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	*y*	*z*	U^a
Ga	5130(1)	2005(1)	9189	44(1)
P	6476(3)	1912(3)	8494(5)	46(2)
C(1)	5194(14)	2060(13)	11103(15)	60(9)
C(2)	3940(16)	1027(15)	8375(24)	76(10)
C(3)	6317(19)	811(14)	9327(23)	82(13)
C(4)	5725(8)	839(7)	6230(12)	69(9)
C(5)	5682	681	4887	94(14)
C(6)	6354	1355	4065	79(13)
C(7)	7070	2186	4586	72(12)
C(8)	7114	2343	5929	52(8)
C(9)	6441	1670	6751	50(8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The structure was solved by direct methods (SOLV) which located the Ga atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses and least-squares refinements. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated and fixed to ideal isotropic positions [d_{CH} = 0.96 Å, U = 1.2 Å^2 for attached C(1), C(2), and C(3); d_{CH} = 0.96 Å, U = 0.08 Å^2 for attached C(4)–C(9)]. Both enantiomers of the molecule were tested; the one reported has the lower *R* factor. The phenyl ring was constrained as a rigid group. All software and the sources of the scattering factors are contained in the SHELXTL[19] program library. Positional parameters are collected in Table IV.

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Note Added in Proof: The Editor graciously identified a reference which describes reactions of dialkylaluminum cyclopentadienyl compounds with H_2O, ROH, and R_2NH to displace cyclopentadiene: Kroll, W. R. *Trans. N.Y. Acad. Sci.* **1965**, *27*, 337.

Supplementary Material Available: Complete lists of distances and angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

OM9205861

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(19) Sheldrick, G. M. *SHELXTL*; Nicolet Corp. (Siemens): Madison, WI, 1984; V. 5.1.