Organometallics **1996,** *15,* 3653−3658

Room Temperature Cyclopentadiene Elimination Reaction for the Synthesis of Diethylgallium−Amides, −Phosphides, and −Thiolates. Crystal and Molecular Structures of $[Et_2GaP(t\text{-}Bu)_2]_2$ and $[Et_2GaS(SiPh_3)]_2$

O. T. Beachley, Jr.,* Daniel B. Rosenblum, Melvyn Rowen Churchill,*
Charles H. Lake, and Laurence M. Toomey

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

Received April 11, 1996[⊗]

The compounds $[Et_2GaNEt_2]_2$, $[Et_2GaN(H)(Me)]_2$, $[Et_2GaN(H)(t\text{-}Bu)]_2$, $[Et_2GaP(i\text{-}Pr)_2]_2$, $[Et_2GaP(t\text{-}Bu)_2]_2$, and $[Et_2GaS(SiPh_3)]_2$ have been prepared in high yields at room temperature by the elimination of cyclopentadiene from $Et_2Ga(C_5H_5)$ and the corresponding amine, phosphine, or thiol. The three diethylgallium amides and $[Et_2GaP(i\text{-}Pr)_2]_2$ are liquids, whereas the other phosphide and the thiolate are crystalline solids at room temperature. All compounds were fully characterized by elemental analyses, ^1H and ^{31}P NMR spectroscopy, and cryoscopic molecular weight studies in benzene, as appropriate, and are dimeric in solution. The crystalline compounds $[Et_2GaP(t\text{-}Bu)_2]_2$, and $[Et_2GaS(SiPh_3)]_2$ were characterized by X-ray structural studies. Even though $[Et_2GaN(H)(t\text{-}Bu)]_2$ and $[Et_2GaS(SiPh_3)]_2$ were prepared at room temperature and isolated in high yield, ^1H NMR studies revealed that neither compound was formed in high yield in solution. Removal of the cyclopentadiene by either dimerization or distillation and/or dimerization of the gallium product are necessary to prevent the back-reaction to re-form the reactants.

The preparation of electronic materials typically requires precursors which have an ultrahigh level of purity. The obvious impurities are those imported with the reagents used to prepare the precursors and those which are formed during the synthetic reactions. The simplest and most direct route to single source precursors $R_2GaER'_2$ (E = N, P) from readily available, high purity, but simple, reagents which do not involve atoms from potentially electronically damaging elements is the hydrocarbon elimination reaction (eq 1). After the

$$GaMe_3 + HER_2 \rightarrow (1/n)[Me_2GaER_2]_n + CH_4 \quad (1)$$

impurities associated with the reagents have been minimized, the second source of impurities originates with the high temperatures typically needed for the hydrocarbon elimination reaction. The preparation of gallium−nitrogen precursors uses temperatures of 100−150 °C,[1,2] whereas gallium−phosphorus derivatives typically use higher temperatures of 150−250 °C.[3] A goal of our research has been to discover and study hydrocarbon elimination reactions which occur at or below room temperature.

One novel reaction which satisfied these criteria is the cyclopentadiene elimination reaction[4] which occurs between $Me_2Ga(C_5H_5)$ and primary and secondary amines and phosphines (eq 2). Even though a series of

$$Me_2Ga(C_5H_5) + HERR' \rightleftharpoons (1/n)[Me_2GaERR']_n + C_5H_6 \quad (2)$$

dimethylgallium amides and phosphides were prepared at room temperature, amines with very bulky substituents such as 2,4,6-tri-*tert*-butylphenylamine, $NH_2[(t\text{-}Bu_3)C_6H_2]$, did not give the desired products. The reactants were recovered. The explanation for this observation[4] was that the elimination reaction actually occurred but the resulting monomeric gallium−nitrogen product reacted readily with the cyclopentadiene to re-form the reactants instead of associating to form gallium−nitrogen dimers or trimers. Association of the monomer would tie up the lone pair on the group 15 element and, in turn, prevent the back-reaction of cyclopentadiene as a weak acid.

In this paper we describe the results of our investigations of the reactions of $Et_2Ga(C_5H_5)$[5] with some primary and secondary amines, several secondary phosphines, and a thiol. This study enabled us to learn more about the nature of the reaction, including the relative ease of the forward and reverse reactions, the effects of the multiple gallium reactants which are present in solution due to the occurrence of the redistribution equilibrium[5] (eq 3), and the effects of the ethyl verses the methyl groups on the nature of this reaction.

$$2Et_2Ga(C_5H_5) \rightleftharpoons EtGa(C_5H_5)_2 + GaEt_3 \quad (3)$$

Furthermore, this study provided us with a series of diethylgallium−group 15 and 16 compounds for which very few other examples are known. The other examples of which we are aware are Et_2GaPEt_2,[6] $Et_2GaAs(t\text{-}Bu)_2$,[7] Et_2GaN_3,[8] Et_2GaNH_2,[9] $Et_2GaN(C_5H_{10})$,[10]

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.

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S0276-7333(96)00284-1 CCC: $12.00

$Et_2GaN(C_2H_4)$,[11] $Et_2GaN(i\text{-}Bu)_2$,[12] $Et_2GaN(Cy)_2$,[12] $Et_2GaN{=}C(H)(Ph)$,[13] and $Et_2GaN{=}C(H)(t\text{-}Bu)$.[13]

The reactions of $Et_2Ga(C_5H_5)$ with $HNEt_2$, HN(H)Me, HN(H)(t-Bu), $HP(i\text{-}Pr)_2$, $HP(t\text{-}Bu)_2$, and $HS(SiPh_3)$ in benzene or pentane provide convenient room temperature routes to the preparation of $[Et_2GaNEt_2]_2$, $[Et_2GaN(H)(Me)]_2$, $[Et_2GaN(H)(t\text{-}Bu)]_2$, $[Et_2GaP(i\text{-}Pr)_2]_2$, $[Et_2GaP(t\text{-}Bu)_2]_2$, and $[Et_2GaS(SiPh_3)]_2$ in high yields (70−90%). The insolubility of $HS(SiPh_3)$ in pentane made benzene the preferred solvent for the synthesis of $[Et_2GaS(SiPh_3)]_2$. The only direct comparison between the temperature required for the synthesis of these compounds by the elimination of cyclopentadiene by using $Et_2Ga(C_5H_5)$ with the temperature necessary for the elimination of ethane by using $GaEt_3$ has been provided by this study. When $GaEt_3$ was reacted with the thiol, a temperature of 70 °C was necessary to eliminate ethane and form $[Et_2GaS(SiPh_3)]_2$. Only two other diethylgallium compounds, Et_2GaPEt_2 and $Et_2GaN(C_2H_4)$, have been prepared by hydrocarbon elimination reactions, and both preparative reactions required temperatures in the range of 100−150 °C.[6,11] However, elimination reactions have been used for the preparation of several of the dimethylgallium derivatives of the amines and phosphines used in this study. For example, $GaMe_3$ and HN(H)Me required 125 °C;[1] HN(H)(t-Bu) needed 110 °C,[2] but $HP(t\text{-}Bu)_2$ was heated at 220 °C for 10 days for the elimination of methane to form $[Me_2GaP(t\text{-}Bu)_2]_2$.[14]

All products prepared during this investigation were fully characterized by partial elemental analyses (C and H), cryoscopic molecular weight studies in benzene solution, and ^1H and ^{31}P NMR spectroscopy, as appropriate. All group 13−15 products except $[Et_2GaP(t\text{-}Bu)_2]_2$ were liquids at room temperature and were isolated by vacuum distillation. The solids $[Et_2GaP(t\text{-}Bu)_2]_2$ and $[Et_2GaS(SiPh_3)]_2$ were purified by recrystallization and were characterized additionally by their melting points and by X-ray structural studies.

The characterization data for benzene solutions of all compounds prepared in this study, cryoscopic molecular weight and NMR spectral data, confirm the presence of only dimers. The molecular weight data exhibited no concentration dependence, and the ^{31}P NMR spectra of the phosphorus compounds had only single lines. Thus, it is unlikely that multiple species with different degrees of association are present in solution. When the diethylgallium derivatives are compared with the corresponding dimethyl species, differences in degrees of association are noted. For example, $Me_2GaN(H)(Me)$ is a trimer[15] in benzene solution, and $Me_2GaP(i\text{-}Pr)_2$ has been observed as an equilibrium mixture of dimers and trimers[16] by NMR spectroscopy, but $Me_2GaN(H)(t\text{-}Bu)$,[2,17] Me_2GaNEt_2,[4] and $Me_2GaP(t\text{-}Bu)_2$ [14,18] are dimers. It is also noteworthy that when direct comparisons are made between the physical properties of the methyl- and ethylgallium derivatives, the ethyl compounds have lower melting points and are typically liquids at room temperature, whereas the methyl compounds are solids.

Proton NMR spectroscopy clearly shows that $[Et_2GaN(H)(t\text{-}Bu)]_2$ and $[Et_2GaN(H)(Me)]_2$ exist as mixtures of cis and trans isomers in benzene solution. The cis isomer has two magnetically different ethyl groups on gallium. As a result, two triplets and two quartets of equal intensity are observed. In contrast, the ethyl groups in the trans isomer are equivalent but magnetically different from the ethyl protons in the cis isomer. The methylene protons of the gallium ethyl groups in the trans isomer are also magnetically nonequivalent, and therefore their resonance appears as a doublet of quartets. The methylene protons for both compounds exhibited the same geminal coupling constant, 13.6 Hz. The integrations of the two lines for the *tert*-butyl groups on nitrogen due to the two isomers suggest approximately 77% trans and 23% cis isomer. In contrast, a sample of $[Me_2GaN(H)(t\text{-}Bu)]_2$ prepared by either the analogous cyclopentadiene elimination reaction[4] or a metathesis reaction at −78 °C [17] had resonances for only the trans isomer (benzene solution), whereas when the compound was prepared by the elimination of methane from $GaMe_3$ and HN(H)(t-Bu) at 110 °C,[2] the ^1H NMR spectrum of a toluene solution demonstrated the presence of both isomers (67% trans and 33% cis). A benzene solution of $[Et_2GaN(H)(Me)]_2$ had equal quantities of the cis and trans isomers according to the intensities of the N−Me resonances. Since the corresponding methylgallium compound[4] is a trimer $[Me_2GaN(H)(Me)]_3$, comparisons are inappropriate.

The ^1H and ^{31}P NMR spectra of the two phosphides prepared in this investigation, $[Et_2GaP(i\text{-}Pr)_2]_2$ and $[Et_2GaP(t\text{-}Bu)_2]_2$, are consistent with the presence of only dimers. The ^{31}P NMR spectrum of each compound shows a single resonance. The chemical shifts of the lines are comparable with those observed for the corresponding dimeric dimethylgallium derivatives. The compound $[Et_2GaP(i\text{-}Pr)_2]_2$ has its line at −5.72 ppm, whereas $[Me_2GaP(i\text{-}Pr)_2]_2$ is at −11.0 ppm.[16] Similary, the chemical shift for $[Et_2GaP(t\text{-}Bu)_2]_2$ is 35.22 ppm, whereas $[Me_2GaP(t\text{-}Bu)_2]_2$ is 28.41 ppm.[14,18] The ^1H NMR spectra of both diethylgallium phosphides exhibit virtual coupling between the protons of the substituents on phosphorus and the two ring phosphorus atoms. Thus, the *tert*-butyl resonance for $[Et_2GaP(t\text{-}Bu)_2]_2$ is split into an apparent triplet ($J_{P-H} = 7.0$ Hz), whereas the C−H proton for the methine hydrogen of the isopropyl group in $[Et_2GaP(i\text{-}Pr)_2]_2$ appears as a septet of triplets ($^3J_{P-H} = 7.2$ Hz). It is also noteworthy that the methylene protons for the ethyl groups bound to gallium in $[Et_2GaP(i\text{-}Pr)_2]_2$ also exhibit virtual coupling as a quartet of triplets ($J_{P-H} = 2.4$ Hz) is observed.

The ^1H NMR spectrum of $[Et_2GaS(SiPh_3)]_2$ in benzene has only one set of lines for the protons of the ethyl groups. Thus, either the molecule exists only as the trans isomer or both isomers are present but a rapid isomerization process with breaking of a gallium−sulfur

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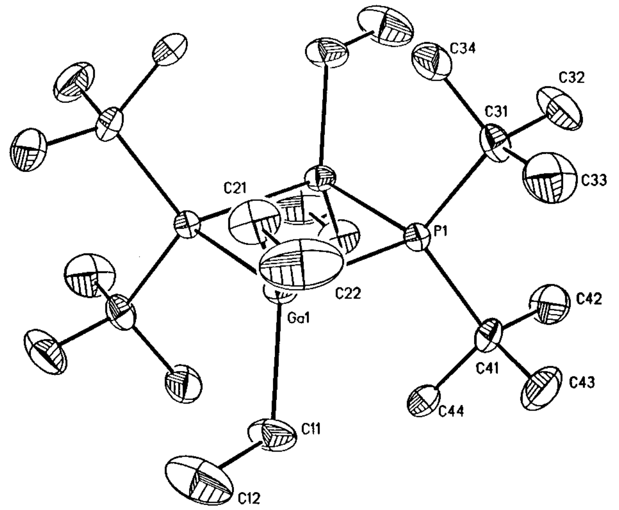

Figure 1. Molecular geometry of $[Et_2GaP(t\text{-}Bu)_2]_2$. ORTEP2 diagram, 30% probability ellipsoids for non-hydrogen atoms with hydrogen atoms omitted for clarity.

Table 1. Important Interatomic Distances (Å) and Angles (deg) for $[Et_2GaP(t\text{-}Bu)_2]_2$

(A) Bond Lengths (Å)			
Ga(1)–P(1)	2.482(2)	Ga(1)–C(11)	1.999(6)
Ga(1)–C(21)	1.998(6)	Ga(1)–P(1A)	2.483(2)
P(1)–C(31)	1.904(6)	P(1)–C(41)	1.900(6)
P(1)–Ga(1A)	2.483(2)	C(11)–C(12)	1.380(12)
C(21)–C(22)	1.418(13)		
(B) Bond Angles (deg)			
P(1)–Ga(1)–C(11)	114.8(2)	P(1)–Ga(1)–C(21)	117.3(2)
C(11)–Ga(1)–C(21)	107.1(3)	P(1)–Ga(1)–P(1A)	86.9(1)
C(11)–Ga(1)–P(1A)	117.1(2)	C(21)–Ga(1)–P(1A)	113.1(2)
Ga(1)–P(1)–C(31)	114.2(2)	Ga(1)–P(1)–C(41)	113.2(2)
C(31)–P(1)–C(41)	110.2(3)	Ga(1)–P(1)–Ga(1A)	93.1(1)
C(31)–P(1)–Ga(1A)	113.2(2)	C(41)–P(1)–Ga(1A)	112.1(2)
Ga(1)–C(11)–C(12)	119.9(6)	Ga(1)–C(21)–C(22)	118.0(6)

ring bond is occurring. Similar observations were recently reviewed by Oliver.[19]

The crystal and molecular structure of $[Et_2GaP(t\text{-}Bu)_2]_2$ is consistent with the observations for solutions. The molecular geometry for $[Et_2GaP(t\text{-}Bu)_2]_2$ is shown in Figure 1. Interatomic distances and angles are collected in Table 1. The molecule has precise C_i symmetry and a planar Ga_2P_2 core in which Ga(1)–P(1) = Ga(1A)–P(1A) = 2.482(2) Å and Ga(1)–P(1A) = Ga(1A)–P(1) = 2.483(2) Å. The P–Ga–P angles are 86.9(1)°, while the Ga–P–Ga angles are 93.1(1)°. Each gallium(III) atom is linked to two ethyl groups with Ga(1)–C(11) = 1.999(6) Å and Ga(1)–C(21) = 1.998(6) Å and an interligand angle of C(11)–Ga(1)–(C21) = 107.1(3)°. The angles at the α-carbon atoms of the ethyl groups are larger than the normal tetrahedral value of 109.5°, with Ga(1)–C(11)–C(12) = 119.9(6)° and Ga(1)–C(21)–C(22) = 118.0(6)°. The carbon–carbon distances within the ethyl groups are anomalously short as a result of artificial librational contraction, with C(11)–C(12) = 1.380(12) Å and C(21)–C(22) = 1.418(13) Å. Note that there are large anisotropic displacement coefficients for these atoms (*viz.*, U_{22} for C(11) is 0.125(7) $Å^2$, while U_{22} for C(12) is 0.228(12) $Å^2$; U_{22} for C(21) is 0.113(6) $Å^2$, while U_{22} for C(22) is 0.285(15) $Å^2$). The bridging di-*tert*-butylphosphide ligands are associated with bond lengths of P(1)–C(31) = 1.904(6) Å and P(1)–C(41) = 1.900(6) Å and an interligand angle of C(31)–P(1)–C(41) = 110.2(3)°; the distances of the $C-CH_3$ linkages are in the expected range with C(31)–Me = 1.490(11) → 1.517(11) Å and C(41)–Me = 1.493(11) → 1.521(9) Å.

A comparison of the major structural features of $[Et_2GaP(t\text{-}Bu)_2]_2$ with other closely related molecules of the type $(R_2GaPR'_2)_2$ suggests some differences but also many similarities. The other molecules $[(n\text{-}Bu)_2GaP(t\text{-}Bu)_2]_2$,[18] $[Me_2GaP(SiMe_3)_2]_2$,[20] and $[(t\text{-}Bu)_2GaP(H)(C_5H_9)]_2$ [21] have planar Ga_2P_2 cores, whereas $[(Me_3CCH_2)_2GaPPh_2]_2$ [22] has a puckered core. Although the halide derivatives $[Cl_2GaP(SiMe_3)_2]_2$ [23] and $[Br_2GaP(SiMe_3)_2]_2$ [24] contain a planar Ga_2P_2 core with equal Ga–P bond lengths, it is noteworthy that $[Et_2GaP(t\text{-}Bu)_2]_2$ is the only molecule containing two organic groups bonded to gallium that has both a planar Ga_2P_2 core and all four gallium–phosphorus distances equal within experimental error. The angle between the organic groups bound to gallium is similar to that in the other structurally characterized di-*tert*-butylphosphide derivative $[(n\text{-}Bu)_2GaP(t\text{-}Bu)_2]_2$,[18] but it is smaller than those observed for $[Me_2GaP(SiMe_3)_2]_2$ [20] (114.5(3)°), $[(Me_3CCH_2)_2GaPPh_2]_2$ [22] (124.35(50) and 121.98(49)°), and $[(t\text{-}Bu)_2GaP(H)(C_5H_9)]_2$ [21] (121.0(2)°).

The compound $[Et_2GaS(SiPh_3)]_2$ has also been subjected to an X-ray structural study and is shown in Figure 2. Interatomic distances and angles are provided in Table 2. This molecule has precise C_i symmetry (crystallography required) with a planar Ga_2S_2 core. Most other structurally characterized molecules of this type, including $[(t\text{-}Bu)_2GaS(H)]_2$,[25] $[Ph_2GaSEt]_2$,[26] and $\{Ph_2GaS[Sn(c\text{-}C_6H_{11})_3]\}_2$,[27] are also planar, but $[Me_2GaS(C_6F_5)]_2$ [28] and $[I_2GaS(i\text{-}Pr)]_2$ [29] are puckered. Bond lengths within the planar Ga_2S_2 core of $[Et_2GaS(SiPh_3)]_2$ alternate in length, Ga(1)–S(1) = Ga(1a)–S(1a) = 2.450(2) Å and Ga(1)–S(1a) = Ga(1a)–S(1) = 2.396(2) Å. Angles within this system are S(1)–Ga(1)–S(1a) = 88.1(1)° and Ga(1)–S(1)–Ga(1a) = 91.9(1)°. The ethyl ligands are associated with bond lengths of Ga(1)–C(1) = 1.934(14) Å and Ga(1)–C(3) = 1.971(11) Å and a large interligand angle C(1)–Ga(1)–C(3) = 125.1(4)°. Similar large interligand angles have been observed for the other thiolate derivatives. The angles at the α-carbon atoms for $[Et_2GaS(SiPh_3)]_2$ are Ga(1)–C(1)–C(2) = 119.6(8)° and Ga(1)–C(3)–C(4) = 114.4(8)°, while the C(α)–C(*β*) bond lengths are C(1)–C(2) = 1.437(14) Å and C(3)–C(4) = 1.446(11) Å. Libration is not as large a problem as in the previous structure. The largest relevant U_{ii} values are U_{33} = 0.143(10) $Å^2$ for C(1) versus U_{33} = 0.186(13) $Å^2$ for C(2), and U_{22} = 0.140(10) $Å^2$ for C(3) versus U_{22} = 0.115(9) $Å^2$ for C(4).

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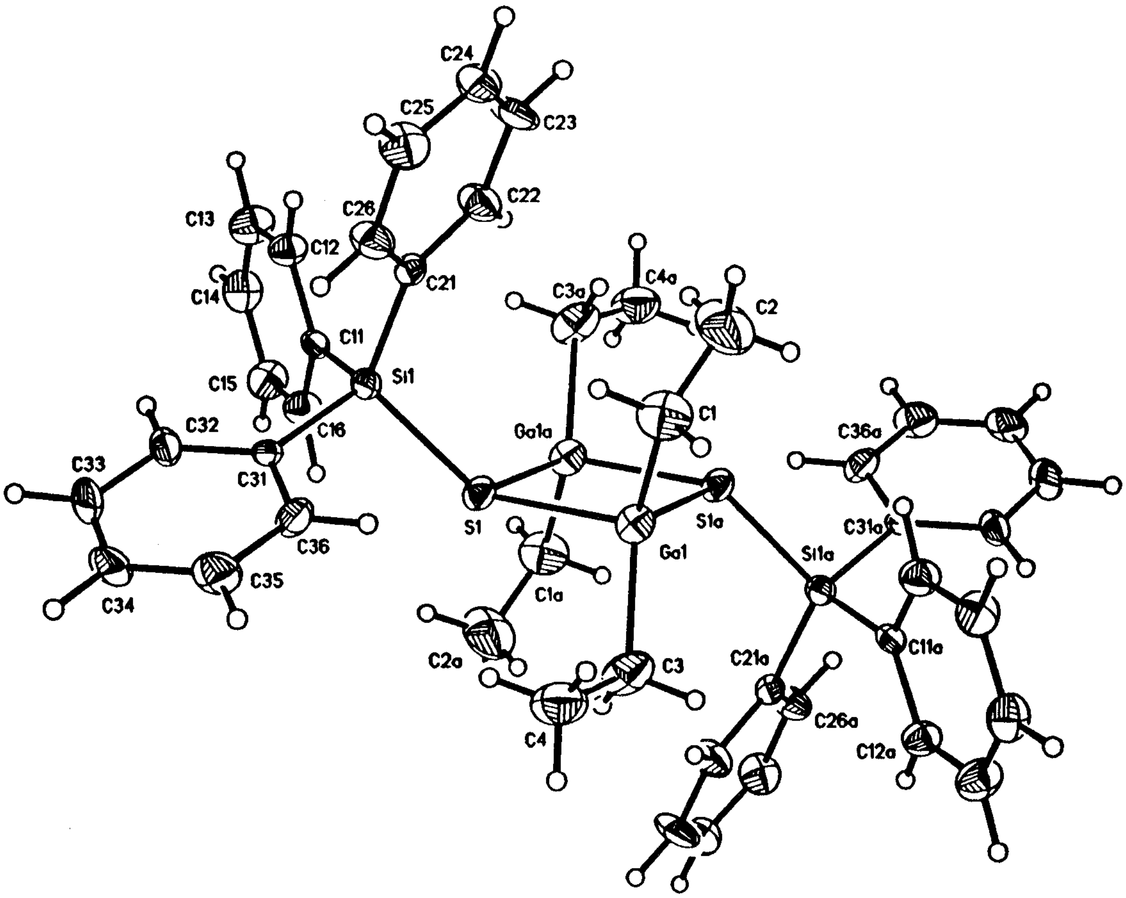

Figure 2. Molecular geometry of $[Et_2GaS(SiPh_3)]_2$. ORTEP2 diagram, 30% probability ellipsoids for non-hydrogen atoms with hydrogen atoms artificially reduced.

Table 2. Important Interatomic Distances (Å) and Angles (deg) for $[Et_2GaS(SiPh_3)]_2$

(A) Bond Lengths (Å)			
Ga(1)−S(1)	2.450(2)	Ga(1)−C(1)	1.934(14)
Ga(1)−C(3)	1.971(11)	Ga(1)−S(1A)	2.396(2)
S(1)−Si(1)	2.148(3)	S(1)−Ga(1A)	2.396(2)
Si(1)−C(11)	1.861(9)	Si(1)−C(21)	1.864(11)
Si(1)−C(31)	1.864(6)	C(1)−C(2)	1.437(14)
C(3)−C(4)	1.446(11)		
(B) Bond Angles (deg)			
S(1)−Ga(1)−C(1)	112.3(3)	S(1)−Ga(1)−C(3)	102.1(3)
C(1)−Ga(1)−C(3)	125.1(4)	S(1)−Ga(1)−S(1A)	88.1(1)
C(1)−Ga(1)−S(1A)	108.8(2)	C(3)−Ga(1)−S(1A)	113.8(3)
Ga(1)−S(1)−Si(1)	124.0(1)	Ga(1)−S(1)−Ga(1A)	91.9(1)
Si(1)−S(1)−Ga(1A)	114.8(1)	S(1)−Si(1)−C(11)	107.1(3)
S(1)−Si(1)−C(21)	115.3(2)	C(11)−Si(1)−C(21)	109.8(4)
S(1)−Si(1)−C(31)	105.2(3)	C(11)−Si(1)−C(31)	110.9(3)
C(21)−Si(1)−C(31)	108.5(4)	Ga(1)−C(1)−C(2)	119.6(8)
Ga(1)−C(3)−C(4)	114.4(8)	Si(1)−C(11)−C(12)	122.7(8)
Si(1)−C(11)−C(16)	122.0(7)	C(12)−C(11)−C(16)	115.2(8)
Si(1)−C(21)−C(22)	121.6(8)	Si(1)−C(21)−C(26)	122.9(6)
C(22)−C(21)−C(26)	115.4(10)	Si(1)−C(31)−C(32)	122.9(6)
Si(1)−C(31)−C(36)	120.4(5)	C(32)−C(31)−C(36)	116.7(6)

The two $SiPh_3$ substituents in $[Et_2GaS(SiPh_3)]_2$ take up the same mutually trans configuration as has been observed for other gallium−thiolate derivatives.[19] Each $S(SiPh_3)$ ligand is associated with a S(1)−Si(1) bond length of 2.148(3) Å and Si−Ph distances of Si(1)−C(11) = 1.861(9) Å, Si(1)−C(21) = 1.864(11) Å, and Si(1)−C(31) = 1.864(11) Å. Angles about silicon range from 105.2(3)° to 115.3(2)°. The S−Si−Ph angles are rather irregular (S(1)−Si(1)−C(31) = 105.2(3)°, S(1)−Si(1)−C(11) = 107.1(3)°, and S(1)−Si(1)−C(21) = 115.3(2)°), while the Ph−Si−Ph angles are closer in value (C(21)−Si(1)−C(31) = 108.5(4)°, C(11)−Si(1)−C(21) = 109.8(4)°, and C(11)−Si(1)−C(31) = 110.9(3)°). The phenyl groups are well-behaved with all 18 C−C bonds in the range 1.353(16)−1.392(13) Å. One point worthy of note is a consistent reduction from the ideal trigonal value for the internal angles at the ipso carbon atoms (viz., C(12)−C(11)−C(16) = 115.2(8)°, C(22)−C(21)−C(26) = 115.4(10)°, and C(32)−C(31)−C(36) = 116.7(6)°).

The reagents $Et_2Ga(C_5H_5)$ and HN(H)(t-Bu) or $HSSiPh_3$ have been used to synthesize $[Et_2GaN(H)(t\text{-}Bu)]_2$ and $[Et_2GaSSiPh_3]_2$ in high yields of the isolated products at room temperature. In order to learn more about the nature of these reactions, ^1H NMR spectroscopy was used to probe the relative rates of the cyclopentadiene elimination reaction and to measure the extent of the overall reaction in solution with time. Stoichiometric quantities of the reagents were combined in sufficient C_6D_6 to form solutions with concentrations which were comparable to those used in the synthetic reactions. When the ^1H NMR spectrum of the reagents upon mixing was observed, the only observed lines were those of the adducts of $Et_2Ga(C_5H_5)$, $EtGa(C_5H_5)_2$, and $GaEt_3$ with either the amine or the thiol. The spectrum was qualitatively similar to that observed when pure $Et_2Ga(C_5H_5)$ was dissolved in benzene,[5] but the chemical shifts were different due to the formation of adducts. Lines for products were not observed. These observations confirm the occurrence of the ligand redistribution reaction[5] (eq 3) and the presence of multiple gallium species when solutions of $Et_2Ga(C_5H_5)$ are in the presence of Lewis bases with acidic protons but also demonstrate that the elimination reaction with this base is either suprisingly slow or the equilibrium constant for the reaction is very small. In the case of the reaction with HN(H)(t-Bu), evidence of product formation was noted only after $3^{1}/_{2}$ h at room temperature by the occurrence of lines for the t-Bu groups of the cis and trans isomers of $[Et_2GaN(H)(t\text{-}Bu)]_2$, 1.02 and 1.00 ppm, respectively. The lines for the gallium−nitrogen products continued to grow such that the reaction was approximately 37% complete after 2 days at room temperature, 43% complete after 3 days, and 49% complete after 4 days. Then, heating of the NMR tube at 65 °C was initiated. After approximately 15 h of heating, the spectrum was consistent with the presence of only two gallium species, the cis and trans isomers of the dimeric product. The chemical shifts of all lines were identical with those observed for the product isolated from the synthetic experiment. All lines for the three initial gallium species had disappeared. In the case of the thiol with the bulky $SiPh_3$ group, the Lewis base with the more acidic proton, the spectrum did not change from that initially observed, even after heating at 45 °C for 2 weeks. Proton NMR lines for the product were not observed. Thus, since $[Et_2GaN(H)(t\text{-}Bu)]_2$ and $[Et_2GaS(SiPh_3)]_2$ can be isolated in high yield after cyclopentadiene elimination reactions at room temperature, removal of the cyclopentadiene monomer by either dimerization or distillation and/or dimerization of the gallium product to prevent the back-reaction of the cyclopentadiene must be necessary to produce the observed high yields of products.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. The starting compound $Et_2Ga(C_5H_5)$ was prepared and purified by the literature method.[5] Amines were dried over KOH and distilled prior to use. Phosphines were vacuum distilled prior to use. The compound $HS(SiPh_3)$ was purchased from Aldrich Chemical Co. and used as received. Solvents were dried by conventional procedures. Elemental analyses were performed by E+R Microanalytical Laboratories, Inc., Corona, NY. The ^1H NMR spectra were recorded at 400 MHz by using a Varian VXR-400 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 and C_6H_6 at δ 7.15. The ^{31}P NMR spectra were recorded at 161.9 MHz by using a Varian VXR-400 spectrometer and are referenced to 85% H_3PO_4 at δ 0.00. The following abbreviations are used to report the multiplicities of lines: s (singlet), d (doublet), t (triplet), q (quartet), br (broad), st (septet of triplets), dq (doublet of quartets), qt (quartet of triplets). All samples for NMR spectra were contained in sealed NMR tubes. Infrared spectra were recorded for either neat liquids, Nujol solutions of liquids, or as Nujol mulls for solids by using CsI plates and a Perkin-Elmer Model 683 spectrometer. Absorption intensities are reported with abbreviations w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder). The spectroscopic data are available with the Supporting Information. 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.[30] Mass spectra were obtained by Electron Impact with a VG Model 70-SE high-resolution mass spectrometer.

Reaction of $Et_2Ga(C_5H_5)$ with HERR′ and HE′R (E = N, P; E′ = S). In a typical experiment, a quantity (1−8 mmol) of the appropriate amine or phosphine was vacuum distilled into a tared tube equipped with a Teflon valve and standard taper joint. Next, a stoichiometric quantity of $Et_2Ga(C_5H_5)$ was placed in a Schlenk flask equipped with a magnetic stir bar. Then, approximately 50 mL of pentane was distilled onto the $Et_2Ga(C_5H_5)$ at −196 °C. The amine or phosphine was then vacuum distilled onto the $Et_2Ga(C_5H_5)$−solvent mixture. Finally, the flask was warmed from −196 °C to ambient temperature and stirred overnight. The reactions of $Et_2Ga(C_5H_5)$ with $HS(SiPh_3)$, $HP(i\text{-}Pr)_2$, and $HP(t\text{-}Bu)_2$ were carried out in benzene rather then pentane for reaction times of 2 h, 2 weeks, and 2 days, respectively. Liquid products were quantitatively transferred to small flasks with stir bars by washing with pentane, and then the flask was attached to a short-path still connected to a preweighed receiving flask. The pentane was removed by vacuum distillation at room temperature, and then heat was applied by means of an oil bath to distill the product.

$[Et_2GaN(H)(t\text{-}Bu)]_2$. Product purified by vacuum distillation, oil bath at 90 °C; bp, 70 °C ($<10^{-3}$ mmHg); yield 95%; mp, 17−20.5 °C. ^1H NMR (C_6D_6): δ 1.36 (t, CH_2CH_3, cis), 1.30 (t, CH_2CH_3, trans), 1.27 (t, CH_2CH_3, cis), 1.02 (s, $C(CH_3)_3$, cis, 2.0H), 1.00 (s, $C(CH_3)_3$, trans, 6.4H), 0.68 (dq, J = 12Hz, CH_2CH_3, trans), 0.43 (dq, J = 12 Hz, CH_2CH_3, trans), 0.66 (q, CH_2CH_3, cis), 0.41 (q, CH_2CH_3, cis). Anal. Calcd for $C_8H_{20}GaN$: C, 48.05%; H, 10.08%. Found: C, 48.11%; H, 10.11%. Cryoscopic molecular weight, benzene solution, fw 200 (obsd molality, obsd mol wt, association): 0.090, 384, 1.93; 0.068, 377, 1.88, 0.041, 344, 1.73.

$[Et_2GaN(H)(Me)]_2$. Product purified by vacuum distillation, oil bath at 125 °C; bp, 45 °C ($<10^{-3}$ mmHg); yield, 85%. ^1H NMR (C_6D_6): δ 2.12 (d, NCH_3, cis), 2.10 (d, NCH_3, trans), 1.28 (t, CH_2CH_3, cis), 1.23 (t, CH_2CH_3, trans), 1.19 (t, CH_2CH_3, cis), 0.38 (dq, J = 12 Hz, CH_2CH_3, trans), 0.55 (q, CH_2CH_3, cis), 0.52 (dq, J = 12 Hz, CH_2CH_3, trans), 0.35 (q, CH_2CH_3, cis). Approximate equal molar quantities of cis and trans isomers were observed. Anal. Calcd for $C_5H_{14}GaN$: C, 38.04%; H, 8.94%. Found: C, 38.56%; H, 8.62%. Cryoscopic molecular weight, benzene solution, fw 158 (obsd molality, obsd mol wt, association): 0.126, 327, 2.08; 0.098, 310, 1.97, 0.072, 316, 2.00; 0.063, 312, 1.98; 0.047, 314, 1.99.

$[Et_2GaNEt_2]_2$. Product purified by vacuum distillation, oil bath at 100 °C; bp, 70 °C ($<10^{-3}$ mmHg); yield, 90%. ^1H NMR (C_6D_6): δ 2.72 (q, NCH_2CH_3, 2H), 1.31 (t, $GaCH_2CH_3$, 3H), 0.78 (t, NCH_2CH_3, 3H), 0.55 (q, $GaCH_2CH_3$, 2H). Mass spectrum (*m*/*e*, relative intensity): 371 (dimer - Et^+), 91; 198 (monomer - H^+), 43; 170 (monomer - Et^+), 91; 127 (Et_2Ga^+), 93; 100 ($EtGa^+$), 66; 69 (Ga^+), 100. Anal. Calcd for $C_4H_{20}GaN$: C, 48.05%; H, 10.08%; N, 7.00%. Found: C, 48.52%; H, 9.76%; N, 7.39%. Cryoscopic molecular weight, benzene solution, fw 200 (obsd molality, obsd mol wt, association): 0.086, 424, 2.12; 0.053, 414, 2.07, 0.034, 422, 2.11.

$[Et_2GaP(i\text{-}Pr)_2]_2$. Viscous product purified by first washing with pentane at −78 °C and then vacuum distillation, oil bath at 72 °C; bp, 70 °C ($<10^{-3}$ mmHg); yield, 72%. ^1H NMR (C_6D_6): δ 2.18 (st, J_{P-H} = 2Hz, J_{H-H} = 7.2Hz, $PC(CH_3)_2H$, 1H), 1.40 (t, $GaCH_2CH_3$, 3H), 1.16 (q, J = 7.2 Hz, $PC(CH_3)_2H$, 6H), 0.84 (qt, $^3J_{P-H}$ = 2.4 Hz, J_{H-H} = 8.4 Hz, $GaCH_2CH_3$, 2H). $^{31}P\{^1H\}$; NMR: δ −5.72 (s); Mass Spectrum (*m*/*e*, relative intensity): 461 (dimer - Et^+), 11; 373 (dimer - $P(i\text{-}Pr)_2{}^+$), 14; 303 (dimer - $GaP(i\text{-}Pr)_2{}^+$), 6; 215 ($EtGaP(i\text{-}Pr)_2{}^+$), 35; 127 (Et_2Ga^+), 70; 118 ($P(i\text{-}Pr)_2{}^+$), 21; 99 (GaP^+), 10; 69 (Ga^+), 93. Anal. Calcd for $C_{10}H_{24}GaP$: C, 49.03%; H, 9.87%. Found: C, 48.97%; H, 9.83%. Cryoscopic molecular weight, benzene solution, fw 245 (obsd molality, obsd mol wt, association): 0.076, 505, 2.06; 0.061, 497, 2.03, 0.040, 497, 2.03.

$[Et_2GaP(t\text{-}Bu)_2]_2$. Product purified by recrystallization from pentane at −40 °C; 64% yield; mp 160.8−162 °C (dec.). ^1H NMR (C_6D_6): δ 1.43 (t, $GaCH_2CH_3$, 3H), 1.33 (t, J = 7.0 Hz, $PC(CH_3)_3$, 9H), 1.00 (q, $GaCH_2CH_3$, 2H). $^{31}P\{^1H\}$ NMR: δ 35.22 (s). Anal. Calcd for $C_{12}H_{28}GaP$: C, 52.79%; H, 10.34%. Found: C, 52.84%; H, 10.41%. Insufficient solubility in benzene for cryoscopic molecular weight studies.

$[Et_2GaS(SiPh_3)]_2$. Product purified by recrystallization from methylcyclohexane at −40 °C; 81% yield; mp 157.8−158.1 °C. ^1H NMR (C_6D_6): δ 7.75−7.78 (m, *o*-Ph-*H*, 6H), 7.10−7.12 (m, *m*,*p*-Ph-*H*, 9H), 1.07 (t, CH_2CH_3, 6H), 0.68 (q, CH_2CH_3,

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(30) Shriver, D. F. *The Manipulations of Air-Sensitive Compounds*; McGraw-Hill: New York, 1968; p 38.

4H). Anal. Calcd for $C_{22}H_{25}GaSSi$: C, 63.02%; H, 6.01%. Found: C, 62.98%; H, 6.11%. Cryoscopic molecular weight, benzene solution, fw 419 (obsd molality, obsd mol wt, association): 0.049, 811, 1.93; 0.038, 812, 1.94, 0.026, 833, 1.99.

Reaction of $GaEt_3$ and $HS(SiPh_3)$ in a 1:1 Mole Ratio. A break-seal tube, which was charged with 0.23 g (0.78 mmol) of $HS(SiPh_3)$ and 0.12 g (0.78 mmol) of $GaEt_3$, was sealed by fusion and then warmed from −196 °C to room temperature. The tube which initially contained a light yellow solid was gradually heated to 70 °C over the period of 2 h. The resulting colorless solid and condensible gas, presumed to be ethane by its physical properties (0.025 g, 0.83 mmol, 100% yield) and ^1H NMR spectrum (^1H NMR (C_6D_6): δ 0.80 (s)) were separated by vacuum distillation. The crude solid was identified as $[Et_2GaS(SiPh_3)]_2$ (0.28 g, 0.67 mmol, 87% yield) by comparison of its properties with those for the compound prepared by the other route; mp 155.2−155.7 °C. ^1H NMR (C_6D_6): δ 7.77−7.79 (m, *o*-Ph-*H*, 6H), 7.12−7.14 (m, *m*,*p*-Ph-*H*, 9H), 1.09 (t, CH_2CH_3, 6H), 0.70 (q, CH_2CH_3, 4H).

Studies of Relative Rates of Reaction by NMR Spectroscopy. (a) $Et_2Ga(C_5H_5)$ and $HS(SiPh_3)$. An NMR tube was charged with 0.024 g (0.08 mmol) of $HSSiPh_3$, 0.016 g (0.08 mmol) of $Et_2Ga(C_5H_5)$, and approximately 1 mL of C_6D_6 at −196 °C and then sealed by fusion. The tube was used for an ^1H NMR study as described in the Results and Discussion.

(b) $Et_2Ga(C_5H_5)$ and HN(H)(t-Bu). An NMR tube was charged with 0.049 g (0.26 mmol) of $Et_2Ga(C_5H_5)$, 0.037 g (0.26 mmol) of HN(H)(t-Bu), and approximately 1 mL of C_6D_6 in order to investigate the relative rate of formation of $[Et_2GaN(H)(t\text{-}Bu)]_2$ (see Results and Discussion).

Collection of X-ray Diffraction Data. In each case crystals were sealed into thin-walled glass capillaries in an argon atmosphere inside a drybox kept under strictly anaerobic and moisture-free conditions. The crystals were inspected under a binocular polarizing microscope to ensure that they were single; they were then centered accurately on a Siemens R3m/V automated four-circle diffractometer. The unit cell parameters and Laue symmetry were determined as described previously.[31] Intensity data (Mo Kα, $\bar{\lambda}$ = 0.710 730 Å) were collected at ambient temperatures (23−25 °C) with graphite-monochromatized radiation. Data were corrected for absorption and for Lorentz and polarization factors. Details are provided in Table 3.

(a) $[Et_2GaP(t\text{-}Bu)_2]_2$. The crystal was of dimensions 0.35 × 0.30 × 0.30 mm. The crystal belonged to the monoclinic system (2/*m* diffraction symmetry); the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely define the centrosymmetric monoclinic space group $P2_1/n$ (No. 14 var.). One hemisphere of data, (i.e., two equivalent forms, $\bar{h}k\bar{l} = \bar{h}\bar{k}\bar{l}$ and $hk\bar{l} = h\bar{k}\bar{l}$) was collected. The 4075 reflections thus collected were merged to 1960 independent, space-group allowed data with R_{int} = 2.45%.

(b) $[Et_2GaS(SiPh_3)]_2$. The crystal was rather small but equidimensional (0.2 × 0.2 × 0.2 mm). It was found to belong to the triclinic system ($\bar{1}$ diffraction symmetry). Possible space groups are the noncentrosymmetric space group $P1$ (No. 1) and the centrosymmetric space group $P\bar{1}$ (No. 2). The centrosymmetric possibility is far more probable,[32] particularly for synthetic materials; the space group $P\bar{1}$ was thus assumed and was confirmed by the successful solution of the structure.

Determination of the Crystal Structures. All crystallographic calculations were carried out on a VAXstation 3100 computer with use of the Siemens SHELXTL PLUS (Release 4.11 (VMS)) program package.[33] The scattering factors used were the analytical values for neutral atoms; these were corrected for both components ($\Delta f'$ and $i\Delta f''$) of anomalous dispersion.[34] The structures were solved by direct methods and difference-Fourier syntheses. All non-hydrogen atoms were located, and their positional and anisotropic thermal parameters were refined. Hydrogen atoms were included in calculated positions based upon d(C−H) = 0.96 Å and the appropriate idealized trigonal or tetrahedral geometry.[35] Refinement was continued until $\Delta/\sigma < 0.003$ for each parameter. The correctness of each structure was confirmed by means of a final difference-Fourier synthesis.

Table 3. Data for X-ray Structural Studies of $[Et_2GaP(t\text{-}Bu)_2]_2$ and $[Et_2GaS(SiPh_3)]_2$

	$[Et_2GaP(t\text{-}Bu)_2]_2$	$[Et_2GaS(SiPh_3)]_2$
mol formula	$C_{24}H_{56}Ga_2P_2$	$C_{44}H_{50}Ga_2S_2Si_2$
cryst syst.	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	8.8379(11)	9.2715(15)
b, Å	11.5032(19)	9.5413(13)
c, Å	14.6460(28)	14.1872(22)
α, deg	90.000	71.135(11)
β, deg	91.010(10)	89.409(13)
γ, deg	90.000	65.247(10)
V, $Å^3$	1488.2(4)	1067.0(3)
Z	2	1
mol wt	546.1	838.6
D(calc), g cm^{-3}	1.219	1.305
μ(Mo Kα), mm^{-1}	1.918	1.435
transm coeff., min/max	0.3808/0.5013	0.8527/0.9445
2θ range, deg	5.0−45.0	5.0−45.0
index ranges		
h	−9 to +9	0 to +9
k	−12 to +12	−10 to +10
l	−15 to +0	−15 to +15
no. of reflns collecd	4075	3002
no. of unique reflns	1960 (R_{int} = 2.45%)	2793 (R_{int} = 1.70%)
no. of reflns > 6σ	1170	1261
R indices (6σ data)		
R, %	4.33	4.36
R_w, %	4.96	3.29
R indices (all data)		
R, %	7.16	11.56
R_w, %	7.66	4.27
largest diff peak, e/$Å^3$	0.80	0.35
deepest diff peak, e/$Å^3$	−0.48	−0.30

(a) $[Et_2GaP(t\text{-}Bu)_2]_2$. The molecule is centered on the inversion center at 0, 0, ½. The Ga_2P_2 ring is therefore required to be planar. Final discrepancy indices are R = 4.33% for those 1170 data with $F_o > 6\sigma(F_o)$ and R = 7.16% for all 1960 reflections. (Note that only 59.7% of the data are above $6\sigma(F_o)$.)

(b) $[Et_2GaS(SiPh_3)]_2$. The molecule lies about the inversion center at 0, 0, ½. The Ga_2S_2 ring is required, by symmetry, to be strictly planar. The final discrepancy indices are R = 4.36% for those 1261 reflections with $F_o > 6\sigma(F)$ and R = 11.56% for all 2793 reflections. (The unattractively high R-value for all data simply reflects the problem of a very weak data set—only 45.1% of the data are above $6\sigma(F_o)$.)

Acknowledgment. This work was supported in part by the Office of Naval Research (O.T.B.). The upgrading of the X-ray diffractometer was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

Supporting Information Available: Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms, and infrared absorptions for each compound (15 pages). For ordering information see any current masthead page.

OM960284P

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