Experimental Section

3-Iodo-*o*-carborane (1). $[Me_3NH][C_2B_9H_{12}]$ (5.0 g, 26 mmol) was placed in 50 mL of anhydrous ethyl ether in a 250-mL three-necked flask equipped with a magnetic stirrer, reflux condenser, and gas inlet and outlet. The system was slowly flushed with argon while the reaction was in progress. A solution of 2.5 M butyllithium in hexane (21.5 mL, 52 mmol) was added dropwise to the mixture with stirring at 0 °C. After the addition was completed, the reaction mixture was stirred at room temperature for an additional 2 h and then refluxed for 4 h. After the reaction mixture cooled to room temperature, all solvent was removed at the water pump. Anhydrous hexane (100 mL) was added with a syringe to the remaining solid. A solution of BI_3 in hexane was prepared from $LiBH_4$ (1.25 g, 67 mmol) and iodine (22.5 g, 88 mmol) in 50 mL of hexane by following Renner's procedure[9] and was added dropwise with stirring at 0 °C. The stirring was continued for another 6 h at room temperature after the addition was finished. The reaction mixture was hydrolyzed with 10 mL of water to decompose the excess boron triiodide. The organic layer was separated from the mixture in a separatory funnel, dried over $MgSO_4$, and then concentrated at the water pump. The resulting solid was purified by recrystallization from hexane to give 3-iodo-*o*-carborane (4.78 g, 68% yield). Mp: 82.5–83 °C. ^1H NMR (δ, $CDCl_3$): 3.87 (s, 2 H), 3.60–1.29 (m, 9 H). ^{13}C NMR (δ, $CDCl_3$): 59.66. MS [*m/e* (relative intensity)]: 272 (32), 271 (79), 270 (100), 269 (74), 268 (47), 267 (25), 144 (18). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): −1.44 (d, 2 B), −7.31 (d, 3 B), −11.19 (d, 3 B), −12.65 (d, 3 B), −29.47 (s, 1 B). Precise mass: calc for $C_2B_{10}H_{11}I$, 272.0838; found, 272.0845. Anal. Calc for $C_2B_{10}H_{11}I$: C, 8.89; H, 4.10; B, 40.04; I, 46.96. Found: C, 9.01; H, 4.28; B, 40.20; I, 46.92.

9,12-Diiodo-*o*-carborane (2). A. From 9-Iodo-*o*-carborane. A mixture of 9-iodo-*o*-carborane, produced by the procedure of Andrews[3] (1.08 g, 4 mmol), and I_2 (1.02 g, 4 mmol) in 30 mL of methylene chloride was stirred with a catalytic amount of $AlCl_3$ at 35 °C for 3.5 days. The mixture was poured into distilled water, and the water layer was extracted with 15 mL of ether. The organic layers were washed with 3 × 10 mL of aqueous $Na_2S_2O_3$ to remove the remaining I_2 and dried over $MgSO_4$. The filtered solvent was removed at the water pump. ^1H NMR spectroscopy of the resulting solid showed two components, starting material and **2** in the ratio 1:4.5. The crude product was purified by recrystallization from hexane to give pure **2** (1.27 g, 80.3% yield). Mp: 184.5–185.5 °C (lit.[5] 185–186 °C). ^1H NMR (δ, $CDCl_3$): 3.98 (s, 2 H), 3.90–1.40 (m, 9 H). ^{13}C NMR (δ, $CDCl_3$): 52.50. ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): −5.99 (d, 2 B), −13.24 (d, 4 B), −14.50 (s, 2 B), −14.60 (d, 2 B).

B. From *o*-carborane. A mixture of *o*-carborane (10.35 g, 71 mmol), iodine (18.2 g, 71 mmol), and 0.53 g of $AlCl_3$ in 250 mL of CH_2Cl_2 was gently refluxed for 4 h. Iodine (18.2 g) was added slowly to this mixture. After the addition was completed, the reaction mixture was stirred at 45 °C for an additional 14 h. The reaction mixture was then poured into 20 mL of ice-cold water and the organic layer separated from the mixture. The water layer was extracted once with 50 mL of ether; the organic layers were washed with 5% aqueous Na_2CO_3 and distilled water and were dried over $MgSO_4$. The filtered solvent was removed under vacuum. Recrystallization of the crude product from a 6:1 hexanes: $CHCl_3$ mixture gave 25.8 g (91.8% yield) of **2**.

General Procedure for Cross-Coupling. To a stirred mixture of 10 mmol of 3-iodo-*o*-carborane (or 9,12-diiodo-*o*-carborane) and 0.2 mmol of L_2PdCl_2 in 25 mL of anhydrous THF at 0 °C was added 40 mmol (50 mmol in the case of 9,12-diiodo-*o*-carborane) of the appropriate Grignard reagent in 25 mL of THF. After the addition was completed, the reaction mixture was stirred at 40–45 °C (bath temperature) for 20–40 h. The reaction was checked by gas chromatography and was stopped when starting material was almost gone. The reaction mixture was then cooled to room temperature. An additional 100 mL of ether was added, and the excess Grignard reagent was destroyed by the dropwise addition of water. The water layer was washed with ether (3 × 15 mL). The combined organic layers were washed with 3 × 15 mL of 3% HCl solution and then water and dried over $MgSO_4$. The solvent was removed at the water pump. The crude product could be purified on a silica gel column, using hexane as eluting solvent.

3-Ethyl-*o*-carborane. After 16 h, a colorless liquid was produced in 97% yield. ^1H NMR (δ, $CDCl_3$): 3.41 (s, 2 H), 3.18–1.20 (m, 11 H), this signal including 1.54 (s, 2 H) and 1.07 (s, 3 H). ^{13}C NMR (δ, $CDCl_3$): 56.9, 12.5. MS [*m/e* (relative intensity)]: 174 (6.5), 173 (13), 172 (28), 171 (41), 170 (42), 169 (32), 83 (100). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): −2.35 (d, 3 B), −6.81 (s, 1 B), −8.66 (d, 2 B), −12.47 (d, 3 B), −13.87 (d, 2 B). Precise mass: calc for $C_4B_{10}H_{16}$, 174.2183; found, 174.2181.

3-Allyl-*o*-carborane. After 30 h, a colorless liquid was produced in 94.6% yield. ^1H NMR (δ, $CDCl_3$): 5.77 (m, 1 H), 4.99–4.93 (m, 2 H), 3.42 (s, 2 H), 3.20–1.02 (m, 11 H). ^{13}C NMR (δ, $CDCl_3$): 136.3, 116.4, 56.6, 14.0. MS [*m/e* (relative intensity)]: 186 (36), 185 (86), 184 (100), 183 (79), 182 (60), 169 (32), 156 (26). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): −2.57 (d, 3 B), −6.77 (s, 1 B), −8.72 (d, 2 B), −12.59 (d, 2 B), −13.66 (d, 2 B). Precise mass: calc for $C_5B_{10}H_{16}$, 184.2255; found, 184.2259.

9,12-Diethyl-*o*-carborane. After 24 h, a low-melting crystal (mp 41.5–42.5 °C) was obtained in 99% yield. ^1H NMR (δ, $CDCl_3$): 3.38 (s, 2 H), 3.20–1.05 (m, 9 H), 0.86 (d, 3 H), 0.70 (s, 2 H). ^{13}C NMR (δ, $CDCl_3$): 48.2, 14.0. MS [*m/e* (relative intensity)]: 202 (20), 201 (48), 200 (56), 185 (31), 171 (100), 143 (93). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): 9.28 (s, 2 B), −8.66 (d, 2 B), −14.75 (d, 4 B), −16.74 (d, 2 B). Precise mass: calc for $C_6B_{10}H_{20}$, 202.2568; found, 202.2574.

9,12-Diallyl-*o*-carborane. After 32 h, a slightly yellow liquid was obtained in 96.8% yield. ^1H NMR (δ, $CDCl_3$): 5.79 (m, 1 H), 4.83–4.76 (m, 2 H), 3.41 (s, 2 H), 3.20–1.05 (m, 10 H). ^{13}C NMR (δ, $CDCl_3$): 140.8, 112.4, 48.8. MS [*m/e* (relative intensity)]: 226 (11), 225 (28), 224 (33), 210 (90), 201 (100), 194 (99), 179 (48). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): 7.19 (s, 2 B), −8.91 (d, 2 B), −14.61 (d, 4 B), −16.59 (d, 2 B). Precise mass: calc for $C_8B_{10}H_{20}$, 225.2532; found, 225.2529.

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Oligomeric Gallium Amide/Hydride Complexes, $[H_2Ga_2\{(NPr^iCH_2)_2\}_2]$ and $[H_5Ga_3\{(NMeCH_2)_2\}_2]$, via Hydrometalation and Metalation

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There has been recent interest in the chemistry of gallane.[2-5] This includes the utility of tertiary amine adducts, such as H_3GaNMe_3, as precursors for the formation of gallium nitride using vapor deposition technology with nitrogen as a carrier gas[6] and also for the formation of the simple gallium amide $[\{H_2GaNH_2\}_3]$ from H_3GaNMe_3 and ammonia, which can be converted to gallium nitride.[4] We report the synthesis and characterization (X-ray, NMR) of some new gallium/hydride/amide complexes derived from reactions of H_3GaNMe_3 with a bis(imine) and a bis(secondary amine); 1,4-diisopropyl-1,4-diazabutadiene (= Pr^iDAB) undergoes dihydrogallation yielding a dimeric species,

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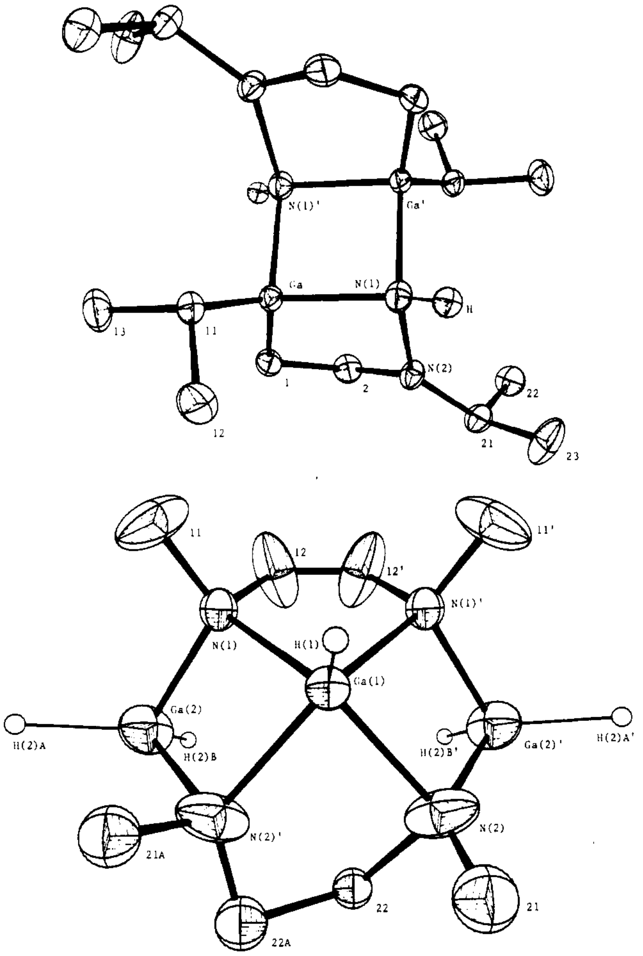
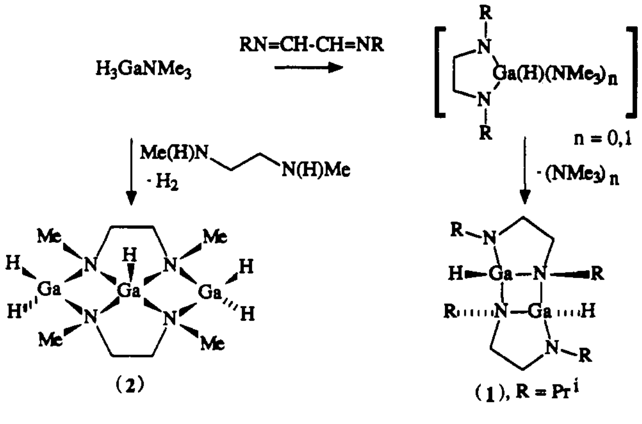


Figure 1. Molecular projections of (top) $[H_2Ga_2\{(NPr^iCH_2)_2\}_2]$ (**1**) and (bottom) $[H_5Ga_3\{(NMeCH_2)_2\}_2$ (**2**), with 20% and 50%, respectively, thermal ellipsoids for non-hydrogen atoms and arbitrary-radius hydrogen atoms shown. Selected bond distances (Å) and angles (deg) are as follows. **1**: Ga–N(1), 2.005 (4); Ga–N(1)', 2.205 (4); Ga–N(2), 1.853 (4); Ga···Ga, 2.970 (5); Ga–H, 1.62; N(1)–Ga–N(2), 89.6 (2); N(1)–Ga–N(1)', 87.5 (5); N(1)'–Ga–N(2), 111.3 (2); Ga–N(1)–Ga', 92.5 (1); N(1)–Ga–H, 123 (2); N(1)'–Ga–H(1), 114 (2); N(2)–Ga–H, 124 (2). **2**: Ga(1)–N(1), 2.082 (8); Ga(1)–N(2), 2.08 (1); Ga(1)–H(1), 1.64; Ga(2)–N(1), 1.962 (8); Ga(2)–N(2)', 1.979 (8); Ga(2)–H(2)A, 1.70; Ga(2)–H(2)B, 1.77; Ga(1)···Ga(2), 2.910 (5); N(1)'–Ga(1)–N(1), 81.7 (4); N(1)–Ga(1)–N(2), 137.3 (4); N(1)–Ga(1)–N(2)', 82.0 (4); N(2)'–Ga(1)–N(2), 83.8 (4); N(1)–Ga(1)–H(1), 114; N(2)–Ga(1)–H(1), 109; N(1)–Ga(2)–N(2)', 87.6 (4); H(2)B–Ga(2)–H(2)A, 127; N(1)–Ga(2)–H(2)A, 110; N(1)–Ga(2)–H(2)B, 103; N(2)'–Ga(2)–H(2)A, 103; N(2)'–Ga(2)–H(2)B, 120; Ga(1)–N(1)–Ga(2), 94.5.

Scheme I



$[H_2Ga_2\{(NPr^iCH_2)_2\}_2]$ (**1**), and *N,N'*-dimethylethylenediamine undergoes dimetalation but the product is a gallane-rich complex, $[H_5Ga_3\{(NMeCH_2)_2\}_2]$ (**2**). It is noteworthy that there have been few structural studies on gallium hydride/amide complexes,[3,4,7,8] in contrast to aluminum hydride/amide complexes.[9]

Table I. Crystal Data for $[H_2Ga_2\{(NPr^iCH_2)_2\}_2]$ (**1**) and $[H_5Ga_3\{(NMeCH_2)_2\}_2]$ (**2**)

	1	2
chem formula	$C_{16}H_{38}Ga_2N_4$	$C_8H_{25}Ga_3N_4$
fw	426.0	386.5
space group	$P2_1/n$	*Pnma*
a, Å	8.6259 (5)	13.9409 (7)
b, Å	11.0895 (9)	15.243 (1)
c, Å	11.427 (2)	7.3722 (4)
β, deg	104.412 (7)	90.0
V, Å^3	1058.7 (4)	1567.6 (2)
Z	2	4
T, K	296	296
λ, Å	1.5418	1.5418
ρ_{calc}, g·cm^{-3}	1.341	1.644
μ(Cu Kα), cm^{-1}	31.13	58.74
transm coeff	0.77–1.22	0.72–0.94
F(000)	448	776
cryst size, mm	0.6 × 0.8 × 0.8	0.11 × 0.18 × 0.04
no. of unique reflns	1426	999
no. of obs reflns ($I > 3\sigma(I)$)	1101	714
$2\theta_{max}$, deg	110	110
R	0.036	0.057
R'	0.042	0.042

Table II. Final Positional Parameters for $[H_2Ga_2\{(NPr^iCH_2)_2\}_2]$ (**1**)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ga	0.11089 (8)	0.59012 (6)	1.06572 (6)
N(1)	0.1294 (5)	0.4336 (4)	0.9823 (4)
N(2)	0.1811 (6)	0.6713 (4)	0.9468 (4)
C(1)	0.1965 (7)	0.4668 (5)	0.8789 (5)
C(2)	0.1529 (7)	0.5963 (5)	0.8410 (5)
C(11)	0.2193 (7)	0.3319 (5)	1.0562 (5)
C(12)	0.3879 (7)	0.3677 (6)	1.1263 (6)
C(13)	0.2268 (8)	0.2205 (5)	0.9808 (6)
C(21)	0.2253 (7)	0.7959 (5)	0.9339 (6)
C(22)	0.0955 (8)	0.8722 (6)	0.8546 (6)
C(23)	0.287 (1)	0.8528 (6)	1.0562 (7)
H	0.183	0.611	1.209

Table III. Final Positional Parameters for $[H_5Ga_3\{(NMeCH_2)_2\}_2]$ (**2**)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ga(1)	0.6835 (1)	0.7500	0.0862 (2)
Ga(2)	0.6070 (1)	0.5909 (1)	−0.0962 (2)
N(1)	0.5718 (6)	0.6606 (5)	0.117 (1)
N(2)	0.7277 (8)	0.8409 (8)	−0.106 (2)
C(11)	0.582 (1)	0.613 (1)	0.289 (2)
C(12)	0.4807 (8)	0.7091 (8)	0.110 (3)
C(21)	0.821 (2)	0.858 (2)	−0.118 (4)
C(21)A	0.808 (2)	0.905 (2)	−0.003 (4)
C(22)	0.722 (1)	0.771 (1)	−0.292 (2)
C(22)A	0.775 (2)	0.821 (2)	−0.256 (3)
H(1)	0.7598	0.7500	0.2559
H(2)A	0.6448	0.4899	−0.0294
H(2)B	0.5142	0.6144	−0.2518

The syntheses of compounds **1** and **2** are shown in Scheme I. The reaction involving Pr^iDAB most likely involves complexation and/or NMe_3 displacement as the primary process, as for many reactions of metal hydrides with unsaturated organic compounds,[10] followed by hydrido migration yielding a mononuclear species (*n* = 0, 1; Scheme I) which then associates. This hydrogallation is chemiselective, consuming 1 equiv of gallane even when it is in

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excess, in contrast to the reaction of the analogous di-*tert*-butyldiazabutadiene with H_3GaNMe_3,[5] where 2 equiv is taken up, affording $[(H_2Ga)_2\{(NBu^tCH_2)_2\}]$[4] in high yield. Here steric hindrance may preclude association, with an intermediate monohydride (R = Bu^t; Scheme I) effectively competing for GaH_3 against complexation of this unit to NMe_3. The reaction of H_3GaNMe_3 with a secondary amine has precedent in the synthesis of trinuclear $[\{H_2Ga(\overline{NCH_2CH_2})\}_3]$.[7]

Both **1** and **2** sublime in vacuo at 110 and 60 °C, respectively, but they slowly decompose at ca. 20 °C over several weeks, yielding gallium metal. NMR data are consistent with the solution structures the same as those in the solid state (see below). In **1** there are four magnetically distinct methyl groups, and in **2** the methylene protons give rise to a poorly resolved AA′XX′ system, although there is no magnetic distinction of the three different types of hydrides, possibly because of the line broadening arising from quadrupolar gallium (^{69}Ga, 60%; ^{71}Ga, 40%; $I = {}^3/_2$).

Results of the X-ray structure determinations of **1** and **2** are presented in Tables I–III and Figure 1. Molecules of **1** are centrosymmetric with two amido centers bridging two Ga centers in a planar four-membered Ga_2N_2 ring system, as in the related compound $[\{H_2GaN(CH_3)_2\}_2]$ (gas phase)[7] but not in $[(H_2Ga)_2\{(NBu^tCH_2)_2\}]$, which has a dihedral angle between each GaN_2 section of 123.7°.[4] The Ga–N ring distances are inequivalent, one at 2.005 (4) Å, which is close to the established range for bridging amides,[3,4,7,10,11] and the other exceptionally long at 2.205 (4) Å. The exocyclic Ga–N distance is much shorter than both of these, 1.853 (4) Å, as expected for a terminal sp^2 N center ($\sum_{angles} = 358.7°$).

Overall, the structure represents a new type for gallium hydride/amide complexes. The same also applies for **2**, which can be considered as a GaH_3 addition compound of the structural type in **1** with all amido centers now bridging two metal centers. Each molecule lies across a mirror plane, with a five-coordinate central metal and associated hydrogen in the plane; the amido ligands are disordered. The two Ga_2N_2 rings are folded, with the angle between adjacent GaN_2 planes associated with Ga(1) being 70.2°. Ga(1) has a square-pyramidal environment with metal–N distances, mean 2.08 Å, marginally longer than those established elsewhere for four-coordinate gallium with bridging N centers;[4,7,8,11] Ga(2)–N distances, mean 1.97 Å, compare with those in $[(H_2Ga)_2\{(NBu^tCH_2)_2\}]$,[4] mean 2.01 Å. Diffraction data were of sufficient accuracy for both complexes to locate the hydrido atoms; the Ga–H distances are comparable with those in $[(H_2Ga)_2\{(NBu^tCH_2)_2\}]$,[4] $[\{H_2GaN(CH_3)_2\}_2]$ (gas phase),[7] $[\{H_3GaNMe_2(CH_2)\}_2]$, and $[H_3Ga\{N(CH_2CH_2)_3CH\}]$[12] and with the terminal Ga–H bond in $[Ga(BH_4)_2H]$ (gas phase).[13]

Experimental Section

Materials and Methods. H_3GaNMe_3[5] and 1,4-diisopropyl-1,4-diazabutadiene[14] were prepared according to the literature. Gallium(III) chloride and *N,N′*-dimethylethylenediamine were purchased from Aldrich. All reactions were carried out under argon using standard Schlenk and glovebox techniques. Hexane and diethyl ether were dried over Na/K and used immediately; benzene-d_6 was dried over sodium. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer in benzene-d_6. C, H, and N analysis was performed by the Canadian Microanalytical Services Ltd.

Synthesis of $[H_2Ga_2\{(NPr^iCH_2)_2\}_2]$ (1). To a stirred solution of H_3GaNMe_3 (0.72 g, 5.45 mmol) in hexane (30 mL) at −80 °C was added sublimed 1,4-diisopropyl-1,4-diazabutadiene (0.73 g, 5.2 mmol) in hexane (10 mL) over 30 min. After 2 h at room temperature, volatiles were removed in vacuo and the product was sublimed, 0.1 mmHg (colorless, 0.65 g, 58% yield): mp 140 °C dec; ^1H NMR (250 MHz, C_6D_6 25 °C, TMS) δ 0.97, 1.00, 1.19, 1.22 (d, $^3J_{HH} = 7$ Hz, 4 × 3 H, Me), 2.64 (m, 4 H, CH_2), 3.08 (m, 4 H, CH_2), 3.24, 3.42 (sept, $^3J_{HH} = 7$ Hz, 2 × 2 H, CHMe), 5.33 (br s, GaH); ^{13}C NMR δ 19.7, 22.1, 25.2, 25.7 (4 × Me), 45.5, 50.2 (2 × CH_2), 48.6, 52.2 (2 × CHMe); IR ν (cm^{-1}) 1895 (br) (Ga–H). An acceptable microanalysis could not be obtained due to some decomposition in transit.

Synthesis of $[H_5Ga_3\{(NMeCH_2)_2\}_2]$ (2). To a stirred solution of H_3GaNMe_3 (0.87 g, 6.59 mmol) in diethyl ether (50 mL) at 0 °C was added *N,N′*-dimethylethylenediamine (0.62 g, 7.0 mmol) in diethyl ether (5 mL) over 30 min. After the resulting mixture had refluxed for 1 h, volatiles were removed in vacuo and the product was sublimed (colorless, 0.51 g, 61% yield): mp 144–146 °C (dec >195 °C); ^1H NMR (250 MHz, C_6D_6, 25 °C, TMS) δ 2.18 (m, 4 H, CH_2), 2.41 (s, 12 H, Me), 2.93 (m, 4 H, CH_2), 4.97 (br s, GaH); ^{13}C NMR δ 43.0 (NMe), 53.1 (NCH_2); IR ν (cm^{-1}) 1864 (br) (Ga–H). Anal. Calcd for $C_8H_{25}Ga_3N_4$: C, 24.85; H, 6.52; N, 14.49. Found: C, 23.93; H, 6.16; N, 13.65.

Crystal Structure Determinations. Diffraction data was collected on an Enraf-Nonius CAD4 diffractometer with crystals mounted in capillaries. The structures were solved by the heavy-atom method and refined by full-matrix least-squares refinement with non-hydrogen atoms anisotropic. Amido ligands in **2** are disordered with one of two 50% occupancy sets for the carbons shown for ligand 2. For nondisordered carbons, hydrogen atoms were calculated (C–H) or located (Ga–H) from difference maps and included as invariants, U_{iso}(hydride) excepted for **1**. Unit weights were used in the refinements, and for **2** the alternative space group $Pna2_1$ was considered but with no improvement in agreement factors.

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Supplementary Material Available: Tables listing atomic positional parameters, thermal parameters, ligand hydrogen parameters, extended metal core geometries, and ligand non-hydrogen geometries (5 pages); tables of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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