Organometallics **1996,** *15,* 3204−3209

Synthesis of Novel Tetrametallic and Trimetallic Compounds from Reactions of MMe$_3$ (M = Al, Ga) with 1,2-(H$_2$E)$_2$C$_6$H$_4$ (E = N, P)

Richard L. Wells,* Hamid Rahbarnoohi, and Paul B. Glaser

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27708

Louise M. Liable-Sands and Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received January 29, 1996[⊗]

The independent 2:1 reactions of MMe$_3$ (M = Al, Ga) with 1,2-(H$_2$P)$_2$C$_6$H$_4$ resulted in the formation of the novel eight-membered tetrametallic ring compounds with the general formula $\{(Me_2M)_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (M = Al (**1**), Ga (**2**)) in a nearly quantitative yield. Combining AlMe$_3$ and 1,2-(H$_2$P)$_2$C$_6$H$_4$ in a 1:1 ratio also afforded **1**. The reaction of AlMe$_3$ with 1,2-(H$_2$N)$_2$C$_6$H$_4$ (2:1) yielded the novel asymmetric compound $[(Me_2Al)_2AlMe(C_6H_4\text{-}(NH)_2)_2]\cdot AlMe_3$ (**3**). Compound **3** is composed of four aluminum centers which are chemically inequivalent. Reaction of GaMe$_3$ with 1,2-(H$_2$N)$_2$C$_6$H$_4$ in a 3:2 ratio gave $\{(Me_2Ga)_3[(\mu\text{-}NH)_2\text{-}(C_6H_4)(\mu\text{-}NH)(C_6H_4NH_2)]\}$ (**4**). The synthesis and characterization of **1**−**4**, including their solid-state structures, are presented.

Introduction

The syntheses and characterization of organometallic compounds which contain both group 13 and group 15 elements have been a subject of interest for many years.[1−5] These compounds have the potential to serve as intermediates to ceramic, semiconductor, or electronic materials.[6−16] Considering this, we were interested in exploring the feasibility of forming large-aggregate or polymeric 13−15 compounds by allowing bidentate ligands of group 15 to react with group 13 alkyl derivatives. To this end, we investigated the reactivity of 1,2-(H$_2$N)$_2$C$_6$H$_4$ and 1,2-(H$_2$P)$_2$C$_6$H$_4$ toward AlMe$_3$ and GaMe$_3$. Chelating ligands such as diethylenetriamine, diazabutadiene, and ethylenediamine have been used successfully to stabilize electrophilic group 13 elements,[12,17−23] and recent work on the chemistry of bidentate ligands of group 15 has produced a number of interesting compounds. For example, Al(PhNCH$_2$CH$_2$NH$_2$)Me$_2$,[24] $[Al(\mu\text{-}PhNCH_2CH_2NH)Me]_3$,[24] $[{}^tBu_2PCH_2CH_2C_5H_4]InCl_2$,[25] $[{}^tBu_2PCH_2CH_2C_5H_4]GaMe_2$,[25] $[\{HN({}^tBu)CH({}^tBu)CH_2N({}^tBu)\}AlH_2]$,[26] $[({}^iPr)_2ATI]AlH_2$,[27] and $[({}^iPr)_2ATI]AlMe_2$[27] (ATI = N-^{i}Pr-2-(^{i}Pr-amino)troponimine) have been prepared and characterized.

As early as 1957, Ulmschneider and Goubeau[28] reported the reaction of BMe$_3$ with 1,2-(H$_2$N)$_2$C$_6$H$_4$, and Norman and co-workers have also used this ligand in the reaction with RPCl$_2$ (R = Me, Ph) to produce $[C_6H_4N_2(PR)_2]_2$.[29] Also, Isseleib and co-workers have investigated the reactivity of 1,2-(H$_2$P)$_2$C$_6$H$_4$ with main group and transition metal compounds.[30] To our knowledge, no structurally authenticated compounds of group 13 elements with the 1,2-(H$_2$E)$_2$C$_6$H$_4$ (E = N, P) ligands have been reported. In this paper, we present the

---

* Author for correspondence.

⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds, Volume 1: The Main Group Elements*; Butler & Tanner Ltd.: London, 1967.

(2) Mole, T.; Jeffrey, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, 1972.

(3) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 1.

(4) Robinson, G. H. *Coordination Chemistry of Aluminum*; VCH: New York, 1993.

(5) Downs, A. J. *Chemistry of Aluminium, Gallium, Indium and Thallium*; Chapman & Hall: London, 1993.

(6) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208.

(7) Interrante, L. V.; Sauls, F. C. *Coord. Chem. Rev.* **1993**, *128*, 193.

(8) Wells, R. L. *Coord. Chem. Rev.* **1992**, *112*, 273−291.

(9) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634.

(10) Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248.

(11) Buhro, W. E. *Polyhedron* **1994**, *13*, 1131−1148.

(12) Jiang, Z.; Interrante, L. V.; Kwon, D.; Tham, F. S.; Kulling, R. *Inorg. Chem.* **1991**, *30*, 995.

(13) Paine, R. T.; Narula, C. N. *Chem. Rev.* **1990**, *90*, 73.

(14) Paine, R. T.; Noth, H. *Chem. Rev.* **1995**, *95*, 343−379.

(15) Aubuchon, S. R.; McPhail, A. T.; Wells, R. L.; Giambra, J. A.; Bowser, J. R. *Chem. Mater.* **1994**, *6*, 82−86.

(16) Wells, R. L.; Aubuchon, S. R.; Kher, S. S.; Lube, M. S.; White, P. S. *Chem. Mater.* **1995**, *7*, 793.

(17) Goebel, D. W., Jr.; Hencher, J. L.; Oliver, J. P. *Organometallics* **1983**, *2*, 746.

(18) Wissing, E.; Jastrzebski, J. T. B. H.; Boersma, J.; Koten, G. V. *J. Organomet. Chem.* **1993**, *459*, 11.

(19) Muller, J.; Englert, U. *Chem. Ber.* **1995**, *128*, 493.

(20) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6862.

(21) Zaworotko, M. J.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 268.

(22) Jiang, Z.; Interrante, L. V.; Kwon, D.; Tham, F. S.; Kullnig, R. *Inorg. Chem.* **1992**, *31*, 4815.

(23) Jones, C.; Koutsantonis, G. A.; Raston, C. L. *Polyhedron* **1993**, *12*, 1829.

(24) Wang, S.; Trepanier, S. J. *J. Chem. Soc., Dalton Trans.* **1995**, 2425.

(25) Cowley, A. H.; King, C. S.; Decken, A. *Organometallics* **1995**, *14*, 20−23.

(26) Raston, C. L.; Lawrence, S. M.; Gardiner, M. G. *Inorg. Chem.* **1995**, *34*, 4652.

(27) Dias, H. V. R.; Jin, W.; Ratcliff, E. R. *Inorg. Chem.* **1995**, *34*, 6100.

(28) Ulmschneider, D.; Goubeau, J. *Chem. Ber.* **1957**, *90*, 2733.

(29) Barendt, J. M.; Bent, E. G.; Young, S. M.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1991**, *30*, 325.

(30) Issleib, K.; Leissring, E.; Schmidt, H. *Phosphorus Sulfur* **1983**, *18*, 15.

S0276-7333(96)00055-6 CCC: $12.00

synthesis and solid-state structural determination of $\{(Me_2M)_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (M = Al (**1**), Ga (**2**)), $[(Me_2Al)_2AlMe(C_6H_4(NH)_2)_2]\cdot AlMe_3$ (**3**), and $\{(Me_2Ga)_3[(\mu\text{-}NH)_2(C_6H_4)(\mu\text{-}NH)(C_6H_4NH_2)]\}$ (**4**).

Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere and by general Schlenk techniques. Toluene and pentane were distilled over Na/K alloy.

1,2-$(H_2P)_2C_6H_4$, $AlMe_3$, and $GaMe_3$ were purchased from Strem and were used as received. 1,2-$(H_2N)_2C_6H_4$ was purchased from Aldrich and was used as received. ^1H and $^{13}C\{^1H\}$NMR spectra were recorded on a QE-300 spectrometer operating at 300 and 75.4 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm, respectively, the upfield pentet of C_7D_8 at δ 2.09 ppm for ^1H NMR spectra and δ 20.4 ppm for $^{13}C\{^1H\}$ spectra, the upfield broad peak of THF-d_8 at δ 1.73 ppm for ^1H NMR spectra, and the upfield pentet at δ 25.3 ppm for $^{13}C\{^1H\}$ spectra. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon. Melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus, and capillaries were flame-sealed under argon. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Mass spectral data were collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. IR spectra were acquired using KBr pellets on a BOMEM Michelson MB-100 FT-IR spectrometer. X-ray crystallographic data were obtained at 25 °C on a Siemens P4 diffractometer utilizing graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation.

Preparation of $\{[Me_2Al]_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (1). Inside the Dri-Lab, a 250 mL Schlenk flask equipped with a magnetic stirbar was charged with 1,2-$(H_2P)_2C_6H_4$ (0.20 g, 1.41 mmol) and ca. 5 mL of toluene. $AlMe_3$ (0.20 g, 2.82 mmol) dissolved in ca. 5 mL of toluene was added to the stirring solution of 1,2-$(H_2P)_2C_6H_4$. The reaction flask was then brought out of the Dri-Lab and left undisturbed at room temperature for 24 h. A slow evolution of gas from the solution was observed. X-ray-quality colorless crystals of **1** were deposited at the bottom of the flask. Yield: 0.32 g, 90% based on Al. Mp: 165 °C (dec). Anal. Calcd (found) for $C_{20}H_{36}Al_4P_4$: C, 47.26 (47.11); H, 7.14 (6.98). ^1H NMR (THF-d_8, δ): 7.54 (4H, m, C_6H_4); 7.21 (4H, m, C_6H_4); 4.33, 3.64 [4H, m, P−H($^1J_{P-H}$ = 207 Hz)]; −0.96 (24H, s, $Al(CH_3)_3$). $^{13}C\{^1H\}$ NMR (THF-d_8, δ): 136.2, 135.4, 129.3 (s, C_6H_4); −9.1 (br, Al−C). Mass spectral data (EI mode): peaks at *m/e* 508, 493, 463, 436, 421, 390, 354, 239, 198, and 183 corresponding to fragments of $C_{20}H_{36}Al_4P_4 = M^+$, $[M - Me]^{\bullet+}$, $[M - 3Me]^{\bullet+}$, $[M - AlMe_3]^{\bullet+}$, $[M - AlMe_4]^{\bullet+}$, $[M - Al_2Me_4]^{\bullet+}$, $[C_6H_4(PH)_2Al_2Me_4]^{\bullet+}$, $[C_6H_4(PH)_2Al_2Me_3]^{\bullet+}$, $[C_6H_4(PH)_2AlMe_2]^{\bullet+}$, and $[C_6H_4(PH)_2AlMe]^{\bullet+}$, respectively. IR (cm^{-1}): 2314 (m), P−H.

Note: Reaction of $AlMe_3$ with 1,2-$(H_2P)_2C_6H_4$ in a 1:1 molar ratio resulted in the formation of **1** but in a lower yield.

Preparation of $\{[Me_2Ga]_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (2). (Compound **2** was synthesized using a procedure similar to that used for **1**). Reactants: 1,2-$(H_2P)_2C_6H_4$ (0.30 g, 2.11 mmol), $GaMe_3$ (0.48 g, 4.2 mmol). Yield: 0.67 g, 94% based on Ga. Mp (dec): 136 °C. Anal. Calcd (found) for $C_{20}H_{36}Ga_4P_4$: C, 35.36 (35.29); H, 5.34 (5.32). ^1H NMR (C_6D_6, δ): 7.54 (4H, m, C_6H_4), 6.90 (4H, m, C_6H_4); 4.18, 3.25 [4H, m, P−H ($^1J_{P-H}$ = 205 Hz)]; −0.73 (24H, pentet, Ga-$(CH_3)_3$, $^3J_{PGaCH}$ = 3.3 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 136.2, 128.8, 127.8 (s, C_6H_4); −5.8 (br, Ga−C). Mass spectral data (EI mode): peaks at *m/e* 678, 663, 565, 550, 339, 324, 240, and 225 corresponding to fragments of $C_{20}H_{36}Ga_4P_4 = M^+$, $[M - Me]^{\bullet+}$, $[M - GaMe_3]^{\bullet+}$, $[M - GaMe_4]^{\bullet+}$, $[C_6H_4(PH)_2Ga_2Me_4]^{\bullet+}$, $[C_6H_4(PH)_2Ga_2Me_3]^{\bullet+}$, and $[C_6H_4(PH)_2GaMe_2]^{\bullet+}$, $[C_6H_4(PH)_2GaMe]^{\bullet+}$, respectively. IR (cm^{-1}): 2314 (m), P−H.

Preparation of $[(Me_2Al)_2AlMe(C_6H_4(NH)_2)_2]\cdot AlMe_3$ (3). Inside the Dri-Lab, a 250 mL Schlenk flask equipped with a magnetic stirbar was charged with 1,2-$(H_2N)_2C_6H_4$ (0.50 g, 4.62 mmol) and ca. 10 mL of toluene. To the resulting suspension was added $AlMe_3$ (0.67 g, 9.24 mmol) in ca. 10 mL of toluene. Stirring the reaction mixture for a few minutes resulted in a clear-pinkish solution with evolution of gas. The reaction flask was brought out of the Dri-Lab, slightly warmed with a heat gun, and covered completely with aluminum foil to allow gradual cooling to room temperature. X-ray-quality crystals of **3** were deposited at the bottom of the flask overnight. Yield: 0.86 g, 85% based on Al. Mp (dec): 120 °C. Anal. Calcd (found) for $C_{20}H_{36}Al_4N_4$: C, 54.54 (54.26); H, 8.24 (8.02); N, 12.72 (12.50). ^1H NMR (C_6D_6, δ): 6.11−7.54 (8H, m, C_6H_4); 2.87, 2.73, 2.10, 1.93 (4H, s, N−H); −0.28 (9H, s, Al−Me_3), −0.33, −0.40 (6H, s, $AlMe_2$), −0.53, −0.96 (6H, s, $AlMe_2$), −1.96 (3H, s, AlMe). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 136.5, 134.3, 126.4, 126.1, 124.3, 121.1(s, C_6H_4); −6.6, −9.2 (br, Al−C). Mass spectral data (EI mode): peaks at *m/e* 368, 352, 337, 296, 281, 205, 165, and 148 corresponding to fragments $[M - AlMe_3]^{\bullet+}$, $[M - AlMe_4]^{\bullet+}$, $[M - AlMe_5]^{\bullet+}$, $[M - Al_2Me_6]^{\bullet+}$, $[M - Al_2Me_7]^{\bullet+}$, $[C_6H_4(NH)_2Al_2Me_3]^{\bullet+}$, $[C_6H_4(NH)_2AlMe_2]^{\bullet+}$, and $[C_6H_4(NH)_2AlMe]^{\bullet+}$, respectively. IR (cm^{-1}): 3245 (s), N−H.

Preparation of $\{(Me_2Ga)_3[(\mu\text{-}NH)_2(C_6H_4)(\mu\text{-}NH)(C_6H_4NH_2)]\}$ (4). (Compound **4** was synthesized using a procedure similar to that used for **3**). Reactants: 1,2-$(H_2N)_2C_6H_4$ (0.37 g, 3.41 mmol), $GaMe_3$ (0.58 g, 5.04 mmol). Yield: 0.77 g, 90% based on Ga. Mp: 125 °C. X-ray-quality crystals were grown by a method similar to that given for **3**. Anal. Calcd (found) for $C_{18}H_{31}Ga_3N_4$: C, 42.17(41.97); H, 6.10 (6.16); N, 10.93 (10.73). ^1H NMR (C_6D_6, δ): 6.40−6.74 (8H, m, C_6H_4); 2.68 (5H, br, N−H, NH_2); −0.38 (18H, m, Ga−Me_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 135.3, 120.2, 116.7 (s, C_6H_4); −7.2 (br, Ga−C). Mass spectral data (EI mode): peaks at *m/e* 496, 382, 291, 206, and 190 corresponding to fragments $[M - Me]^{\bullet+}$, $[M - GaMe_4]^{\bullet+}$, $[C_6H_4(NH)_2Ga_2Me_3]^{\bullet+}$, $[C_6H_4(NH)_2GaMe_2]^{\bullet+}$, and $[C_6H_4(NH)_2GaMe]^{\bullet+}$, respectively. IR (cm^{-1}): 3285, 3427, and 3358 cm^{-1}, N−H stretching mode; 1624 and 1592 cm^{-1}, N−H bending mode.

X-ray Structural Solution and Refinement. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals of **1**−**4** were mounted in thin-walled capillaries and temporarily sealed with silicone grease under an argon atmosphere and then flame-sealed.

The photographic data, unit cell parameters, and occurrences of equivalent reflections and systematic absences in the diffraction data are uniquely consistent with the $P2_1/n$ space group for **1** and **2**, $P2_1/c$ for **3**, and C_2, Cm, or C_2/m for **4**. The *E*-statistic suggested the centrosymmetric option for **4,** and the space group choices were confirmed by chemically reasonable results of refinement. The unit-cell parameters were obtained by least-square refinement of the angular setting of 24 reflections (20° ≤ 2θ ≤ 24°).

Structures of **1**, **3**, and **4** were solved using direct methods, completed by difference Fourier syntheses, and refined by full-matrix least-squares procedures. The atomic coordinates of **1** were used as a trial solution for the isomorphous structure **2**. Semi-empirical absorption corrections were applied for **2** but were not required for **1**, **3**, and **4** because there was less than 10% variation observed in the ψ-scan data. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Structures **1** and **2** have an inversion center. Structure **4** is located on a mirror plane. Hydrogen atoms, bonded to phosphorus atoms in **1** and **2**, were located from the difference map, constrained with an average refined P−H distance, and treated with idealized isotropic parameters. The hydrogen atoms on N(1) and N(2) in **4** are disordered over a mirror plane and were ignored. All other hydrogen atoms were treated as idealized contributions. The largest remaining peak

Table 1. Crystal Data and Structure Refinement for $\{(Me_2M)_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (M = Al (1), Ga (2)), $[(Me_2Al)_2AlMe(C_6H_4(NH)_2)_2]\cdot AlMe_3$ (3), and $\{(Me_2Ga)_3[(\mu\text{-}NH)_2(C_6H_4)(\mu\text{-}NH)(C_6H_4NH_2)]\}$ (4)

	1	2	3	4
empirical formula	$C_{20}H_{36}Al_4P_4$	$C_{20}H_{36}Ga_4P_4$	$C_{20}H_{36}Al_4N_4$	$C_{18}H_{31}Ga_3N_4$
fw	508.29	679.25	440.45	512.63
temp, K	298(2)	298(2)	241(2)	298(2)
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/m$
a, Å	10.479(2)	10.466(2)	15.611(1)	14.184(6)
b, Å	13.975(3)	13.93(1)	9.173(1)	10.454(3)
c, Å	10.498(2)	10.538(2)	18.959(2)	18.926(5)
β, deg	108.43(3)	108.54(1)	104.079(9)	111.37(3)
V, Å^3	1458.5(5)	1456.8(4)	2633.5(4)	2614(2)
D_{calcd}, g cm^{-3}	1.157	1.548	1.111	1.303
Z	2	2	4	4
abs coeff, mm^{-1}	0.385	3.884	0.189	3.077
F(000)	536	680	944	1040
cryst dimens, mm	0.18 × 0.20 × 0.22	0.30 × 0.30 × 0.10	0.40 × 0.35 × 0.28	0.40 × 0.20 × 0.20
cryst habit	colorless plate	colorless plate	colorless block	colorless block
θ range for data collcn, deg	2.39−22.52	2.51−22.50	2.21−30.00	2.48−22.50
no. of rflns collcd	2489	2458	7880	2316
indepdt rflns	1900 (R_{int} = 0.0254)	1886 (R_{int} = 0.0785)	6337 (R_{int} = 0.0469)	1811 (R_{int} = 0.0617)
data/restraints / param	1900/2/135	1886/2/136	6337/0/254	1803/0/130
goodness-of-fit on F^2	1.144	0.717	1.001	1.485
final R indices[a] [$I > 2\sigma(I)$]	$R1 = 0.0389$ $wR2 = 0.0865$	$R1 = 0.0561$ $wR1 = 0.1290$	$R1 = 0.0492$ $wR2 = 0.1051$	$R1 = 0.0818$ $wR2 = 0.2260$
R indices (all data)	$R1 = 0.0600$ $wR2 = 0.0961$	$R1 = 0.0937$ $wR2 = 0.1453$	$R1 = 0.1022$ $wR2 = 0.1142$	$R1 = 0.1109$ $wR2 = 0.2675$
extinction coeff	0.0058(14)	0.0014(11)	0.0059(4)	
$D(r)$ and hole, e/Å^{-3}	0.27 and −0.193	0.910 and −1.128	0.316 and −0.300	1.351 and −1.081

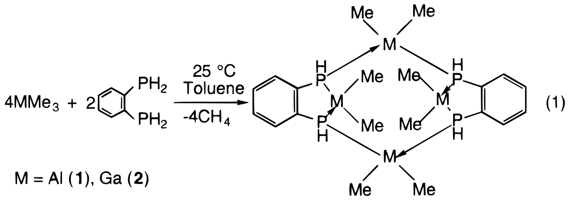
[a] Quantity minimized = $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

in the difference map of **4** (1.35 e Å^{-3}) occurs at a chemically unreasonable position and was considered as noise.

All software and sources of the scattering factors are contained in the SHELXTL (5.3) program libraries.[31]

Results and Discussion

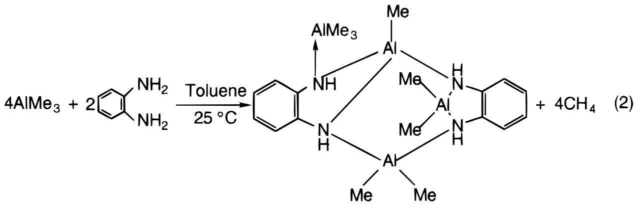
Syntheses. Independent reactions of MMe_3 (M = Al, Ga) with 1,2-$(H_2P)_2C_6H_4$ in a 2:1 ratio resulted in the formation of $\{(Me_2M)_4[(\mu\text{-}P(H))_2(C_6H_4)]_2\}$ (M = Al (**1**), Ga (**2**)) in nearly quantitative yields (eq 1). Slow evolution of gas was apparent after mixing the reagents in toluene at room temperature. The possible reaction pathway could include the formation of the adduct followed by the elimination of methane, to give **1** or **2**; however, under the applied conditions, no intermediate adducts were isolated from these reactions. In contrast to this, in a related study, the reaction of $AlMe_3$ with $H_2PCH_2CH_2PH_2$ in a 2:1 ratio and under similar mild conditions afforded the bis-adduct $Me_3Al\cdot P(H)_2CH_2CH_2(H)_2P\cdot AlMe_3$, which will be discussed elsewhere.[32]



1 or **2**

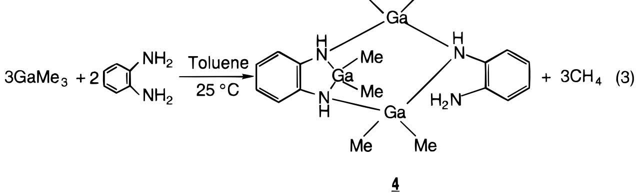
It is interesting to note that compound **1** was isolated even when a 1:1 ratio of $AlMe_3$ and 1,2-$(H_2P)_2C_6H_4$ was used. Compounds **1** and **2** crystallized from toluene but show very little solubility in toluene, once crystallized. Compound **1** was soluble in the donor solvent THF, and the ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained in THF-d_8 solutions to account for the ratio of $AlMe_3$ protons vs the aromatic protons. Compound **2** was insoluble in THF; thus the ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained from a very dilute C_6D_6 solution.

Compounds **3** and **4** were prepared in a manner similar to **1** and **2** but showed better solubility in toluene. Unlike **1** and **2**, compound **3** is an asymmetric molecule *(vide infra)* (eq 2).



3

Compound **4** was prepared according to eq 3. Initially the stoichiometry of 4:2 was used



4

and a white, toluene-insoluble powder was isolated. The partial elemental analysis (C, H, N) of this powder is in accordance with the chemical formula $\{[Me_2Ga]_4[(\mu\text{-}NH)_2(C_6H_4)]_2\}$, analogous to **1** and **2**. However, reaction in a 3:2 molar ratio (eq 3) resulted in quantitative formation of **4**, which is of different aggregation than

---

(31) *SHELXTL PC*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990.

(32) Rahbarnoohi, H.; Wells, R. L.; Heeg, M. J. Unpublished results.

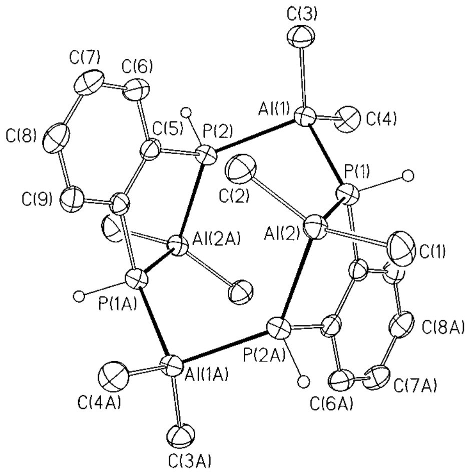


Figure 1. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $\{(Me_2Al)_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (**1**). Hydrogen atoms on the CH_3 and C_6H_4 groups are omitted for clarity.

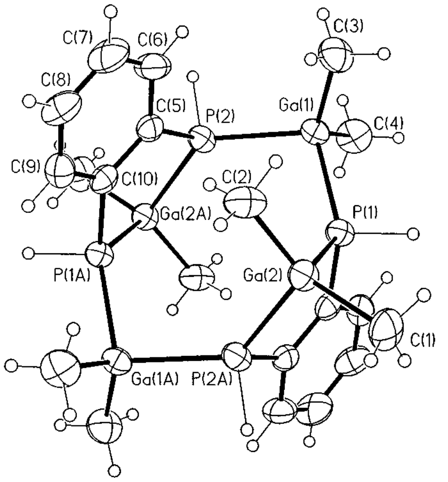


Figure 2. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of $\{(Me_2M)_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (**2**).

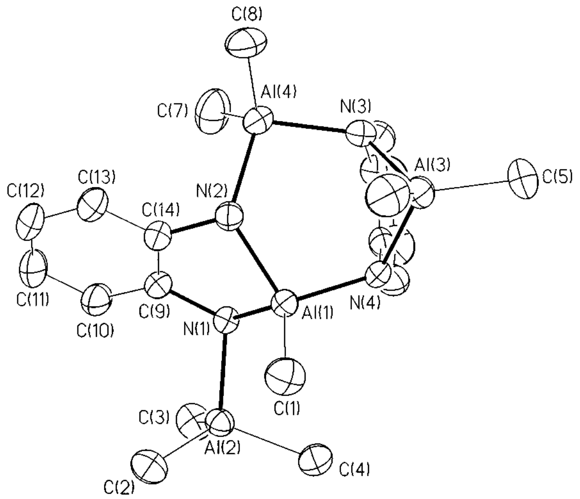


Figure 3. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $[(Me_2Al)_2AlMe(C_6H_4(NH)_2)_2]\cdot AlMe_3$ (**3**). Hydrogen atoms are omitted for clarity.

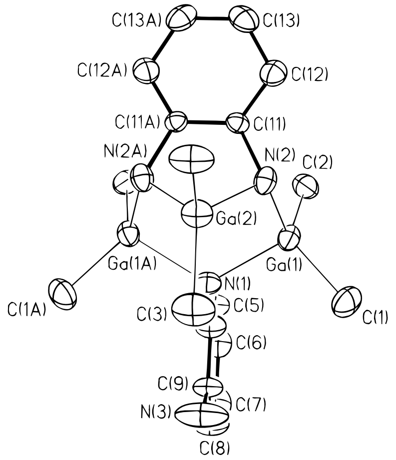


Figure 4. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $\{(Me_2Ga)_3[(\mu\text{-}NH)_2(C_6H_4)(\mu\text{-}NH)(C_6H_4NH_2)]\}$ (**4**). Hydrogen atoms are omitted for clarity.

that for **1**−**3** *(vide infra)*. Compounds **1**−**4** are colorless crystals which decompose slowly when exposed to air and moisture.

Structure and Bonding. Thermal ellipsoid diagrams of **1**−**4** are shown in Figures 1−4. Crystal data and structure refinement for **1**−**4** are given in Table 1. Selected interatomic bond distances and bond angles for **1**−**4** are presented in Tables 2−5, respectively. Compounds **1** and **2** belong to the monoclinic system $P2_1/n$ with two molecules per unit cell and an inversion center for each molecule. The geometry of the $(MP)_4$ core is that of an eight-membered ring in a chair conformation with approximately equal M−P bond lengths. The Al−P bond distances in **1** range from 2.4310(14) to 2.447(2) Å, average 2.44 Å, which can be compared to six-membered ring compounds such as $[(Me_3Si)_2AlP(c\text{-}C_6H_{11})(H)]_3$ (average 2.44 Å),[33] $[Me_2AlPMe_2]_3$ (2.43 Å),[34] and $[Me_2AlCH_2PMe_2]_2$ (2.45 Å).[35] The chair conformation of the eight-membered ring in **1** is shown in Chart 1. The internal angles of Al−P−Al are almost identical (130.07(5) and 130.79(5)°). These values are very close to the Al−P−Al angles reported for $[Me_2AlPMe_2]_3$ (131.7(8)°), which was studied in the gas phase.[34] The P(2A)−Al(2)−P(1) and P(2)−Al(2A)−P(1A) angles in **1** are smaller than the corresponding angles in $[Me_2AlPMe_2]_3$ (83.95(5)° vs 96.4(7)°) and in $[(Me_3Si)_2AlP(c\text{-}C_6H_{11})(H)]_3$ (83.95(5)° vs 99.6(1)°). This could be due to the fact that the five-membered ring fragment (which forms part of the eight-membered ring) $\overline{\mathrm{Al{-}P{-}C{-}C{-}P}}$ imposes a ring strain, since the P···P separation is held rigid by the aromatic ring. The Al−C bond distances in **1** range from 1.944(3) to 1.959(4) Å and are similar to values reported in the literature.[4]

Compound **2** is the gallium analog of **1** and is isomorphous with **1**. Due to the close similarity in the atomic radii of aluminum and gallium atoms, the angles and bond lengths in **1** and **2** were identical and within experimental errors. The Ga−P bond lengths in **2** range from 2.419(3) to 2.433(3) Å with an average of 2.424 (3) Å. This is in order with the trimeric $(GaP)_3$ compounds $[Me_2GaPPh_2]_3$ (2.433(1) Å),[36] $[{}^tBuGaP(\mu\text{-}PH_2)]_3$ (2.439 (3) Å),[37] $[Me_2Ga(\mu\text{-}P\text{-}{}^iPr_2]_3$ (average 2.44 Å),[38] $[Me_2GaP(Me)\text{-}$

---

[33] Janik, J. F.; Duesler, E. N.; McNamara, W. F.; Westerhausen, M.; Paine, R. T. *Organometallics* **1989**, *8*, 506.

[34] Haaland, A.; Hougen, J.; Volden, H. V.; Hanika, G.; Karasch, H. H. *J. Organomet. Chem.* **1987**, *322*, C24.

[35] Karsch, H. H.; Appelt, A.; Kohler, F. H.; Müller, G. *Organometallics* **1985**, *4*, 231.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $\{[Me_2Al]_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (1), with Estimated Standard Deviations in Parentheses[a]

	Bond Lengths		
Al(1)−C(3)	1.956(4)	Al(1)−C(4)	1.959(4)
Al(1)−P(1)	2.4310(14)	Al(1)−P(2)	2.4340(14)
Al(2)−C(2)	1.947(4)	Al(2)−C(1)	1.944(3)
Al(2)−P(2A)	2.4390(14)	Al(2)−P(1)	2.447(2)
P(1)−C(10A)	1.833(3)	P(2)−C(5)	1.836(4)
P(2)−Al(2A)	2.4390(14)	C(5)−C(6)	1.396(5)
C(5)−C(10)	1.398(5)	C(10)−P(1A)	1.833(3)
	Bond Angles		
C(3)−Al(1)−C(4)	119.9(2)	C(3)−Al(1)−P(1)	104.79(12)
C(4)−Al(1)−P(1)	110.69(13)	C(3)−Al(1)−P(2)	110.49(12)
C(4)−Al(1)−P(2)	106.43(13)	P(1)−Al(1)−P(2)	103.44(5)
C(2)−Al(2)−C(1)	123.2(2)	C(2)−Al(2)−P(2A)	114.50(13)
C(1)−Al(2)−P(2A)	108.51(14)	C(2)−Al(2)−P(1)	112.12(13)
C(1)−Al(2)−P(1)	107.55(13)	P(2A)−Al(2)−P(1)	83.95(5)
C(10A)−P(1)−Al(1)	113.59(11)	C(10A)−P(1)−Al(2)	102.60(12)
Al(1)−P(1)−Al(2)	130.07(5)	C(5)−P(2)−Al(1)	111.27(12)
C(5)−P(2)−Al(2A)	102.48(12)	Al(1)−P(2)−Al(2A)	130.79(5)
C(6)−C(5)−P(2)	120.3(3)	C(10)−C(5)−P(2)	120.7(3)
C(5)−C(10)−P(1A)	120.5(3)	C(9)−C(10)−P(1A)	120.4(3)

[a] Symmetry transformation used to generate equivalent atoms: $-x, -y + 1, -z + 2$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $\{[Me_2Ga]_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ (2), with Estimated Standard Deviations in Parentheses[a]

	Bond Lengths		
Ga(1)−C(4)	1.983(10)	Ga(1)−P(1)	2.419(3)
Ga(1)−P(2)	2.422(3)	Ga(2)−C(1)	1.952(10)
Ga(2)−C(2)	1.955(11)	Ga(2)−P(2A)	2.423(3)
Ga(2)−P(1)	2.433(3)	P(1)−C(10A)	1.832(9)
P(2)−C(5)	1.830(10)	P(2)−Ga(2A)	2.423(3)
C(5)−C(10)	1.405(13)	C(9)−C(10)	1.385(14)
C(10)−P(1A)	1.832(9)	Ga(1)−C(3)	1.972(10)
	Bond Angles		
C(3)−Ga(1)−C(4)	120.6(5)	C(3)−Ga(1)−P(1)	105.0(3)
C(4)−Ga(1)−P(1)	110.3(3)	C(3)−Ga(1)−P(2)	109.9(4)
C(4)−Ga(1)−P(2)	106.3(3)	P(1)−Ga(1)−P(2)	103.59(9)
C(1)−Ga(2)−C(2)	123.8(5)	C(1)−Ga(2)−P(2A)	107.8(4)
C(2)−Ga(2)−P(2A)	114.1(3)	C(1)−Ga(2)−P(1)	107.3(3)
C(2)−Ga(2)−P(1)	112.2(3)	P(2A)−Ga(2)−P(1)	84.55(9)
C(10A)−P(1)−Ga(1)	113.8(3)	C(10A)−P(1)−Ga(2)	102.1(3)
Ga(1)−P(1)−Ga(2)	130.09(12)	C(5)−P(2)−Ga(1)	111.6(3)
C(5)−P(2)−Ga(2A)	102.6(3)	Ga(1)−P(2)−Ga(2A)	130.32(13)
C(6)−C(5)−C(10)	119.1(9)	C(6)−C(5)−P(2)	120.4(8)
C(9)−C(10)−P(1A)	120.4(8)	C(5)−C(10)−P(1A)	120.7(7)

[a] Symmetry transformation used to generate equivalent atoms: $-x, -y + 1, -z + 2$.

$Ph)]_3$ (average 2.41 Å),[39] and $[(Me_3CCH_2)ClGaPPh_2]_3$ (average 2.42 Å).[40] The Ga−C bond distances in **2** range from 1.952(10) to 1.983(10) Å and are similar to reported values in the literature.[36−40] The torsion and dihedral angles of compounds **1** or **2** are presented in Chart 1.

Compound **3** crystallizes in the monoclinic system $P2_1/c$ with four molecules in the unit cell. The asymmetric compound **3** has four Al centers which are chemically inequivalent, and all the Al−N bonds are crystallographically independent. To our knowledge, this is the first example of a 13−15 compound in which there are three different M linkages of the type RM, R_2M, and R_3M existing within the same molecule. The Al centers in **3** are all four-coordinate with distorted tetrahedral geometry. Both Al(3) and Al(4) have two methyl groups, while Al(1) possesses only one methyl group. Al(2) has three methyl groups and is bonded in a dative fashion to N(1) with a distance of 2.009(1) Å. This distance is similar to the dative bonds in $[AlEt_2]_2[C_{10}H_{22}N_4][AlEt_3]_2$ (2.073(4) and 2.025(4) Å)[41] and $[AlMe_2]_2[C_{10}H_{20}N_4][AlMe_3]_2$ (2.042(4) Å).[42] The shortest Al−N bond in **3** is 1.905(2) Å for Al(1)−N(4). This bond

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[(Me_2Al)_2AlMe(C_6H_4(NH)_2)_2]\cdot AlMe_3$ (3), with Estimated Standard Deviations in Parentheses

	Bond Lengths		
Al(1)−N(4)	1.905(2)	Al(1)−N(1)	1.925(2)
Al(1)−N(2)	1.927(2)	Al(1)−C(1)	1.931(3)
Al(2)−C(2)	1.982(3)	Al(2)−C(3)	1.983(3)
Al(2)−C(4)	1.983(3)	Al(2)−N(1)	2.009(2)
Al(3)−C(5)	1.950(3)	Al(3)−C(6)	1.951(3)
Al(3)−N(3)	1.960(2)	Al(3)−N(4)	1.990(2)
Al(4)−C(7)	1.951(3)	Al(4)−C(8)	1.955(3)
Al(4)−N(3)	1.960(2)	Al(4)−N(2)	1.986(2)
N(1)−C(9)	1.468(3)	C(15)−C(20)	1.388(4)
	Bond Angles		
N(4)−Al(1)−N(1)	110.20(9)	N(4)−Al(1)−N(2)	108.34(9)
N(1)−Al(1)−N(2)	89.50(8)	N(4)−Al(1)−C(1)	113.54(11)
N(1)−Al(1)−C(1)	119.01(10)	N(2)−Al(1)−C(1)	113.59(11)
C(2)−Al(2)−C(3)	116.43(11)	C(2)−Al(2)−C(4)	112.07(12)
C(3)−Al(2)−C(4)	111.67(12)	C(2)−Al(2)−N(1)	104.05(10)
C(3)−Al(2)−N(1)	107.38(11)	C(4)−Al(2)−N(1)	104.05(10)
C(5)−Al(3)−C(6)	118.96(14)	C(5)−Al(3)−N(3)	110.70(12)
C(6)−Al(3)−N(3)	115.57(11)	C(5)−Al(3)−N(4)	111.43(12)
C(6)−Al(3)−N(4)	111.35(11)	N(3)−Al(3)−N(4)	83.43(9)
C(7)−Al(4)−C(8)	120.63(14)	C(7)−Al(4)−N(3)	108.94(11)
C(8)−Al(4)−N(3)	107.33(11)	C(7)−Al(4)−N(2)	108.82(12)
C(8)−Al(4)−N(2)	107.28(12)	N(3)−Al(4)−N(2)	102.30(9)
C(9)−N(1)−Al(1)	103.3(2)	C(9)−N(1)−Al(2)	116.02(14)
Al(1)−N(1)−Al(2)	113.61(10)	C(14)−N(2)−Al(1)	102.24(14)
C(14)−N(2)−Al(4)	109.1(2)	Al(1)−N(2)−Al(4)	121.57(10)
C(20)−N(3)−Al(4)	112.1(2)	C(20)−N(3)−Al(3)	100.8(2)
Al(4)−N(3)−Al(3)	119.59(11)	C(19)−N(4)−Al(1)	116.56(14)
C(19)−N(4)−Al(3)	100.33(14)	Al(1)−N(4)−Al(3)	112.12(10)
C(14)−C(9)−N(1)	116.9(2)	C(19)−C(20)−C(15)	119.8(3)

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $\{(Me_2Ga)_3[(\mu\text{-}NH)_2(C_6H_4)(\mu\text{-}NH)(C_6H_4NH_2)]\}$ (4), with Estimated Standard Deviations in Parentheses[a]

	Bond Lengths		
Ga(1)−C(2)	1.908(12)	Ga(1)−C(1)	1.985(12)
Ga(1)−N(1)	2.043(6)	Ga(1)−N(2)	2.048(9)
Ga(2)−C(4)	1.99(2)	Ga(2)−N(2A)	2.027(10)
Ga(2)−N(2)	2.027(10)	Ga(2)−C(3)	2.01(2)
N(1)−C(10)	1.45(2)	N(1)−Ga(1A)	2.043(6)
N(2)−C(11)	1.470(14)	N(3)−C(9)	1.46(3)
C(5)−C(10)	1.46(3)	C(11)−C(12)	1.37(2)
	Bond Angles		
C(2)−Ga(1)−C(1)	125.4(6)	C(2)−Ga(1)−N(1)	111.3(5)
C(1)−Ga(1)−N(1)	104.7(5)	C(2)−Ga(1)−N(2)	108.2(5)
C(1)−Ga(1)−N(2)	105.4(5)	N(1)−Ga(1)−N(2)	98.5(4)
C(4)−Ga(2)−N(2A)	109.6(5)	C(4)−Ga(2)−N(2)	109.6(5)
N(2A)−Ga(2)−N(2)	82.6(6)	C(4)−Ga(2)−C(3)	118.0(9)
N(2A)−Ga(2)−C(3)	115.9(6)	N(2)−Ga(2)−C(3)	115.9(6)
C(10)−N(1)−Ga(1A)	111.9(5)	C(10)−N(1)−Ga(1)	111.9(5)
Ga(1A)−N(1)−Ga(1)	119.5(6)	C(11)−N(2)−Ga(2)	101.3(7)
C(11)−N(2)−Ga(1)	111.0(7)	Ga(2)−N(2)−Ga(1)	116.9(5)
N(1)−C(10)−C(5)	121(2)	C(12)−C(11)−N(2)	122.5(11)

[a] Symmetry transformation used to generate equivalent atoms: $x, -y, z$.

---

(36) Robinson, G. H.; Burns, J. A.; Pennington, W. T. *Main Group Chem.* **1995**, *1*, 153.

(37) Cowley, A. H.; Harris, P. R.; Jones, R. A.; Nunn, C. M. *Organometallics* **1991**, *10*, 652.

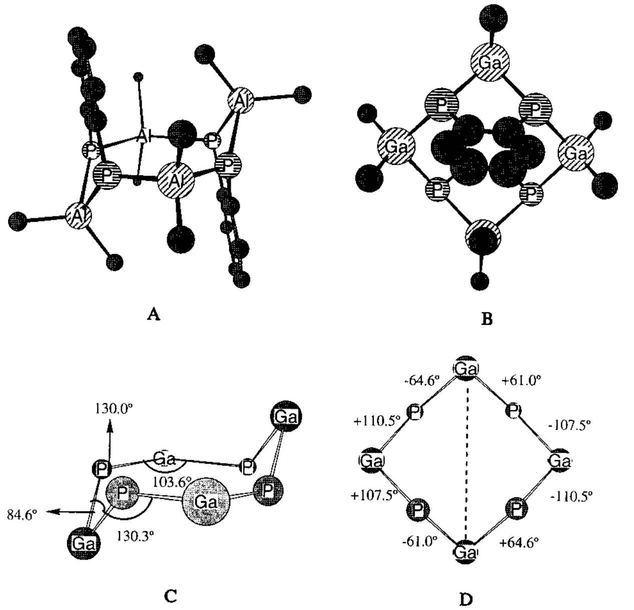
(38) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Nunn, C. M. *Organometallics* **1991**, *10*, 1635.

(39) Beachley, O. T., Jr.; Royster, T. L., Jr.; Arhar, J. R.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1976.

(40) Beachley, O. T., Jr.; Maloney, J. D.; Rogers, R. D. *J. Organomet. Chem.* **1993**, *449*, 69.

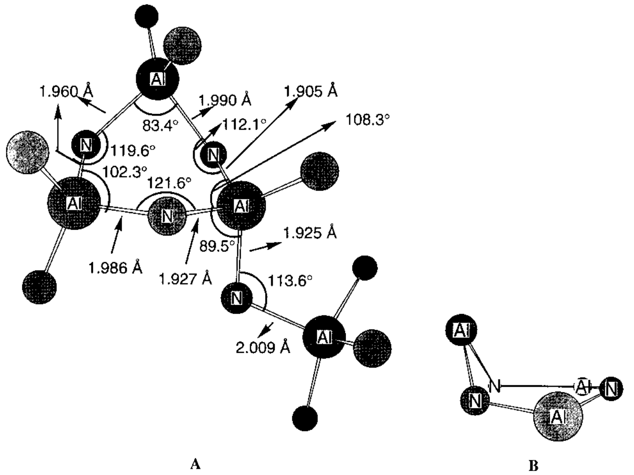
(41) Moise, F.; Pennington, W. T.; Robinson, G. H.; Sangokoya, S. A. *Acta. Crystallogr.* **1990**, *C46*, 1110.

Chart 1[a]



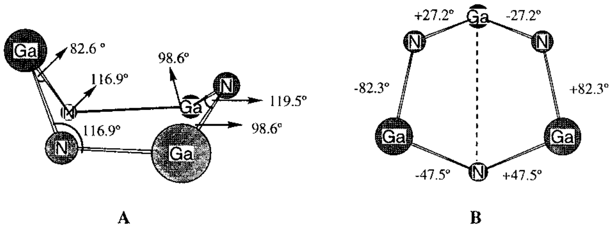
[a] Key: (A) Chair conformation of **1**; (B) view of **2** through the phenyl ring; (C) internal angles in **2**; (D) torsion angles of **2**. (The torsion angle a−b−c−d is defined as positive if, when viewed along the b−c bond, atom a must be rotated clockwise to eclipse atom d.)

Chart 2[a]



[a] Key: (A) Internal angles and Al−N distances given for **3** with C_6H_4 rings and the hydrogen atoms omitted for clarity; (B) trimeric distorted boat conformation of the core in **3**.

Chart 3[a]



[a] Key: (A) Trimeric boat conformation of the core in **4**; (B) torsion angles in **4**. (The torsion angle a−b−c−d is defined as positive if, when viewed along the b−c bond, atom a must be rotated clockwise to eclipse atom d.)

length could be considered a normal covalent bond when compared to the corresponding Al−N bond distances in $[AlEt_2]_2[C_{10}H_{22}N_4][AlEt_3]_2$ (1.906(4) Å),[41] $[AlMe_2]_2[C_{10}H_{20}N_4][AlMe_3]_2$ (1.886(4) Å),[42] and $AlCl_4(\mu\text{-}NMe_2)_2(\mu\text{-}NMe_2)_4$ (1.76 and 1.92 Å).[43] The Al(1)−N(1) and Al(1)−N(2) bond lengths are 1.925(2) and 1.927(2) Å, respectively. These distances are also within normal bonding with very little or no dative character. The remaining Al−N bond lengths in **3**, Al(3)−N(3) (1.960(2) Å) and Al(4)−N(3) (1.960(2) Å), are slightly longer than the Al−N bond lengths discussed above. On the other hand, Al(3)−N(4) (1.990(2) Å) and Al(4)−N(2) (1.986(2) Å) are even longer and may have some dative character. The overall geometry around the nitrogen atoms is pyramidal. The core of **3** is composed of a six-membered $(AlN)_3$ ring which is attached to a five-membered AlN_2C_2 ring through Al(1)−N(2). The six-membered $(AlN)_3$ ring has a distorted boat conformation (Chart 2B). The internal angles and Al−N bond distances are also given in Chart 2A. The Al−C bond distances in **1** range from 1.931(3) to 1.983(3) Å and are similar to values reported in the literature.[4]

Compound **4** crystallizes in the monoclinic system *C*2/*m*. There are four molecules in the unit cell, where each molecule is located on a mirror plane. The Ga−N bond distances range from 2.027(10) to 2.048(9) Å with an average value of 2.04 Å. The Ga−N bonds are slightly shorter than the Ga−N bond distances in $[o\text{-}(Me_2NCH_2)C_6H_4]GaCl_2$ (2.071(2) Å) and $[o\text{-}(Me_2NCH_2)C_6H_4]GaH_2$ (2.087(7) Å).[44] To our knowledge, there are only two trimeric gallium-nitrogen systems which have been structurally characterized in the solid state. One such is the trimer $[(Me_2GaNH_2]_3$, which possesses a twisted chair conformation for the $(GaN)_3$ core and an average Ga−N bond length of 1.98 Å.[45] In the other trimer, $[(CH_2)_2NGaH_2]_3$, the $(GaN)_3$ core has a chair conformation with an average Ga−N bond length of 1.97 Å.[46] These values are slightly shorter than the Ga−N bond length in **4**. The six-membered core $(GaN)_3$ has a boat geometry which is shown in Chart 3A. Torsion angles in **4** are presented in Chart 3B.

Acknowledgment. We are grateful for the financial support of this work provided by the Office of Naval Research. P.B.G. wishes to thank the National Science Foundation REU summer program for support. We also thank Dr. George R. Dubay at Duke University for performing the electron ionization mass spectroscopy of our compounds.

Supporting Information Available: Complete listings of crystal and X-ray data collection parameters, bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms (21 pages). Ordering information is given on any current masthead page.

OM9600553

---

(42) Robinson, G. H.; Rae, A. D.; Campana, C. F.; Byram, S. K. *Organometallics* **1987**, *6*, 1227.

(43) Thewalt, U.; Kawada, I. *Chem. Ber.* **1970**, *103*, 2754.

(44) Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1995**, *14*, 2400.

(45) Almond, M. J.; Drew, M. G. B.; Jenkins, C. E.; Rice, D. A. *J. Chem. Soc., Dalton Trans.* **1992**, 5.

(46) Harrison, W.; Storr, A.; Trotter, J. *J. Am. Chem. Soc., Dalton Trans.* **1972**, 1554.