Group 13 Azatranes: Structure and Reactivity

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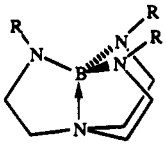
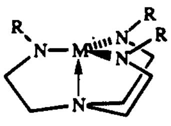
Received January 6, 1994®

The new monomeric azagallatranes $Ga(RNCH_2CH_2)_3N$ (R = $SiMe_3$, **10**; $SiMe_2$-*t*-Bu, **11**) and dimeric azagallatrane $[Ga(MeNCH_2CH_2)_3N]_2$, **14**, were prepared by two synthetic routes: (i) the transamination reaction of $[Ga(NMe_2)_3]_2$, with $(MeNHCH_2CH_2)_3N$, **2**, and (ii) the transmetalation reaction of $[Al(MeNCH_2CH_2)_3N]_2$, **12**, with $Ga(acac)_3$ (acac = penta-2,5-dienoate). Dimeric azaalumatrane **12**, monomeric azaalumatranes $Al(RNCH_2CH_2)_3N$ (R = $SiMe_3$, **8**; $SiMe_2$-*t*-Bu, **9**), and azaboratrane $B(MeNCH_2CH_2)_3N$, **6**, react with a variety of alkoxides giving transition metal or main-group element azatranes. The molecular structures of **12** and **14** were established by X-ray diffraction experiments, and both possess an unusual cis configuration of the substituents on the central four-membered $(M-N)_2$ ring. Crystal data: **12**, a = 37.372(10) Å, b = 14.379(2) Å, c = 8.774(2) Å, V = 4714.9(1) Å^3, Z = 8, orthorhombic space group *Pbca*, R = 5.0%; **14**, a = 9.716(1) Å, b = 11.325(2) Å, c = 11.343(1) Å, α = 110.36(2)°, β = 97.87(1)°, γ = 90.34(1)°, V = 1157.2(3) Å^3, Z = 2, triclinic space group $P\bar{1}$, R = 4.7%.

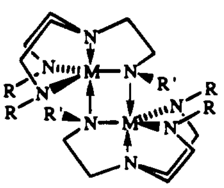
R = H, **1**; Me, **2**; *iso*-Pr, **3**; $SiMe_3$, **4**; $SiMe_2$-*tert*-Bu, **5**



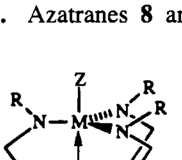
	R
6	Me
7	$SiMe_3$



	M	R
8	Al	$SiMe_3$
9	Al	$SiMe_2$-*tert*-Bu
10	Ga	$SiMe_3$
11	Ga	$SiMe_2$-*tert*-Bu



	M	R	R'
12	Al	Me	Me
13	Al	$SiMe_3$	H
14	Ga	Me	Me



	MZ	R
15	SiMe	Me
16	$V{=}NSiMe_3$	Me
17	V=O	$SiMe_3$
18	V=O	Me
19	TiO-*iso*-Pr	Me

The chemistry of compounds of the group 13 elements bonded to nitrogen is a large and vigorous research area owing to efforts to prepare nitride ceramic materials and semiconductors.[1−6] There is a vast amount of literature on compounds of group 13 elements with multifunctional amine ligands, but comparatively few of them are highly symmetrical ones.[7] We have recently been focusing our attention on the use of symmetrical tripodal tetramine ligands such as **1-5** in the synthesis of azatranes as potential nitride film precursors. For example, we have reported the syntheses and characterization of the group 13 azatranes[8,9] **6-9** which are monomeric and **12** and **13** which are dimeric, depending on the size of the substituents on the equatorial nitrogens and on the nature of the central atom. The monomeric azaalumatrane **8** was shown by X-ray crystallography to possess a rare trigonal monopyramidal (TMP) coordination geometry at the aluminum center while the dimeric molecule **13** contains aluminums in a trigonal bipyramidal (TBP) environment. In addition, the central four-membered $(Al-N)_2$ ring of **13** features an unusual cis configuration of the substituents.[9] By comparing ^{27}Al NMR chemical shifts of the monomeric trigonal planar amides $Al(NR_2)_3$ (R = *i*-Pr, $SiMe_3$) and azaalumatranes **8**, **9**, **12**, and **13** with literature data for hexacoordinate and tetracoordinate species, we demonstrated a trend toward higher shielding of the aluminum nucleus upon increasing its coordination by nitrogens, ($AlN_3 \rightarrow AlN_4 \rightarrow AlN_5 \rightarrow AlN_6$).[9] We also showed that alumaazatrane **12** takes part in an interesting transmetalation reaction with $B(OMe)_3$ to give **6**.[8] Here we report results of our further study of this reaction whose scope is now extended to the transmetalation of **6**, **8**, **9**, and **12** with other main-group and transition metal alkoxides and $Ga(acac)_3$, giving azatranes **11** and **14-19.** Azatranes **8** and **12** were previously shown to transligate cleanly with triethanolamine to give the tetrameric alumatrane $[Al(OCH_2CH_2)_3N]_4$, **20**.[10] Here we describe the analogous reaction for azaboratrane **6** and azasilatrane **15** which provides the boratrane $B(OCH_2CH_2)_3N$, **21**, and the silatrane

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® Abstract published in *Advance ACS Abstracts,* October 1, 1994.

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$MeSi(OCH_2CH_2)_3N$, **22**, respectively. The crystal and molecular structures of dimeric azaalumatrane **12** and azagallatrane **14** determined by single-crystal X-ray diffraction experiments feature in both cases the cis configuration at the central puckered four-membered ring, as was the case for **13**.[9] The two monomeric azagallatranes **10** and **11** are illustrative of the stabilization of monomeric species by bulky substituents.

Experimental Section

All reactions were carried out under argon with the strict exclusion of moisture using Schlenk or drybox techniques.[11] Solvents were dried over and distilled from Na/benzophenone under nitrogen. Deuterated benzene, toluene, and chloroform were dried over and distilled from CaH_2 under an argon atmosphere. The starting materials $(MeHNCH_2CH_2)_3N$, **2**,[12] and $(Me_3SiHNCH_2CH_2)_3N$, **4**,[13] were prepared using our procedures published earlier. $GaCl_3$, $B(NMe_2)_3$, $O{=}V(O\text{-}i\text{-}Pr)_3$, $Ti(O\text{-}i\text{-}Pr)_4$, and $MeSi(OMe)_3$ were purchased from Aldrich and were used as received. $B(OMe)_3$ and $MeC(OMe)_3$ were distilled from Na before use. $Ga(acac)_3$ was purchased from Gelest. $[Al(NMe_2)_3]_2$,[14] $[Ga(NMe_2)_3]_2$,[14] $Me_3SiN{=}V(OSiMe_3)_3$,[15] and $Mo_2(O\text{-}t\text{-}Bu)_6$[16] were prepared according to published procedures.

NMR spectra were recorded at 25 °C, unless otherwise stated, on Varian VXR 300 and Unity 500 spectrometers with deuterated solvents as an internal lock. ^1H (299.949 MHz) and ^{13}C (75.429 MHz) spectra were internally referenced to the corresponding Me_4Si signals. ^{11}B (96.233 MHz) spectra were referenced to $BF_3{\cdot}Et_2O$ in C_6D_6 (50% volume solution) as an external standard; ^{27}Al (78.157 MHz) spectra were measured at 70 °C and were referenced to the external standard 0.2 M $Al(ClO_4)_3$/0.1 M $HClO_4$ in D_2O. The background signal, which was found as a broad peak at ~61 ppm ($\Delta\nu_{1/2}$ = 4100 Hz at 30 °C), did not interfere with our spectra owing to its low intensity.[17] ^{29}Si (59.591 MHz) spectra were referenced to a 30% volume solution of Me_4Si in benzene-d_6 as an external standard. Pulses of 90° and a relaxation delay of 25 s were used for acquisition of the ^{29}Si spectra. ^{71}Ga (91.485 MHz) spectra were recorded at 70 °C and were referenced to the signal of $GaCl_4^-$/5 M HCl in D_2O which was set at 257 ppm so that measured shifts are recorded with respect to $Ga(H_2O)_6^{3+}$.[18] The chemical shifts were corrected for the difference in chemical shift between D_2O and the lock solvent used.

Mass spectra were recorded on a Finnigan 4000 low-resolution (70 eV, EI; NH_3, CI) and a Kratos MS-50 high-resolution instrument. The masses are reported for the most abundant isotope present. IR spectra (4000−400 cm^{-1}) were taken on IBM/Bruker IR-98 and DigiLab FTS-7 FTIR spectrometers using Nujol mulls between KBr disks or as KBr pellets. Spectra were calibrated with a 0.05 mm polystyrene film. Intensities are noted as vs (very strong), s (strong), m (medium), w (weak), vw (very weak), and sh (shoulder). Two specimens for IR experiments were always prepared by recrystallization and sublimation of a particular compound to assure consistency of data. Elemental analyses were carried out by Galbraith Laboratories or Desert Analytics. Melting points (uncorrected) were measured in sealed capillaries.

Trimethylazaboratrane, 6. This compound was prepared for HRMS study according to our previously published procedure[8] with the slight modification that after the reaction all volatiles were removed under vacuum at room temperature and the residue was sublimed at 60−80 °C at 5 × 10^{-3} Torr. A somewhat improved yield of 42% (lit.[8] 37%) of white crystalline solid **6** was obtained. The ^1H NMR shifts of **6** in chloroform-d_1 are given here to demonstrate the aromatic solvent-induced shift effect (see Discussion) by comparing them with values reported for a benzene-d_6 solution:[8] ^1H NMR (chloroform-d_1) δ 2.46 (s, 3 H, NMe), 2.78 (t, 2 H, $N(CH_2)_3$, $^3J_{HH}$ = 5.1 Hz), 2.93 (t, 2 H, $MeNCH_2$, $^3J_{HH}$ = 5.1 Hz).

Trimethylazaalumatrane Dimer, 12. This compound was prepared according to our previously published procedure[8] and further purified by sublimation at 120 °C at 2.5 × 10^{-3} Torr. Single crystals suitable for X-ray diffraction analysis were grown from a THF solution layered with pentane at −20 °C. For the purpose of comparison with azagallatrane **14**, we present here IR data for **12**: IR (KBr pellet, 4000−400 cm^{-1}) ν 2968 s, 2847 vs, 2797 vs, 2765 vs, 2747 s, 2675 m, 1478 sh, 1468 s, 1446 m, 1422 w, 1377 w, 1355 vs, 1342 m, 1307 w, 1272 s, 1262 w, 1238 vw, 1217 vw, 1197 sh, 1190 s, 1164 sh, 1155 vs, 1143 s, 1135 s, 1109 vs, 1082 s, 1061 vs, 1051 vs, 1035 m, 1011 w, 955 m, 944 s, 923 s, 880 vs, 856 m, 845 s, 768 vw, 751 vw, 647 s, 631 vs, 609 vs, 591 s, 575 vw, 563 m, 536 vs, 509 vw, 497 vw, 457 w, 436 s, 413 w.

Reaction of Trimethylazaalumatrane Dimer, 12 with $MeSi(OMe)_3$. Neat $MeSi(OMe)_3$ (0.75 mL, 5.3 mmol) was added dropwise to a stirred solution of **12** (1.11 g, 2.62 mmol) in 150 mL of toluene at room temperature. After the reaction mixture was refluxed for 40 h, a clear solution was decanted from a gel-like precipitate of $[Al(OMe)_3]_n$, and all volatiles were removed under vacuum. A yellow waxy solid was sublimed at 60−75 °C at 5 × 10^{-3} Torr, yielding 0.50 g (42%) of **15**. The product possessed ^1H, ^{13}C, and ^{29}Si NMR spectra which compared well with data published earlier for this compound.[19] Because the ^1H NMR chemical shifts display substantial ASIS effects (see Discussion), the data for benzene-d_6 and chloroform-d_1 solutions of **15** are listed here: ^1H NMR (benzene-d_6) δ 0.43 (s, 3 H, $SiCH_3$, $^1J_{CH}$ = 114.9 Hz, ^{13}C satellites, $^2J_{SiH}$ = 5.7 Hz, ^{29}Si satellites), 2.24 (t, 6 H, $MeNCH_2$, $^3J_{HH}$ = 6.1 Hz), 2.66 (t, 6 H, $N(CH_2)_3$, $^3J_{HH}$ = 6.1 Hz), 2.69 (s, 9 H, NCH_3, $^1J_{CH}$ = 132 Hz, ^{13}C satellites); ^1H NMR (chloroform-d_1) δ 0.11 (s, 3 H, $SiCH_3$), 2.55 (s, 9 H, NCH_3), 2.68 (t, 6 H, $MeNCH_2$, $^3J_{HH}$ = 6.0 Hz), 2.83 (t, 6 H, $N(CH_2)_3$, $^3J_{HH}$ = 6.0 Hz).

Reaction of Trimethylazaalumatrane Dimer, 12 with $Me_3SiN{=}V(OSiMe_3)_3$. Compounds **12** (0.42 g, 0.99 mmol) and $Me_3SiN{=}V(OSiMe_3)_3$ (0.78, 1.9 mmol) were dissolved in 50 mL of toluene. The reaction mixture was refluxed for 1 h during which its color changed to deep red. The solvent was removed under vacuum and the remaining dark brown solid was sublimed at 100−110 °C at 5 × 10^{-3} Torr, giving a red-brown solid whose ^1H, ^{13}C, and ^{27}Al NMR spectra revealed the formation of **16**[20] and the presence of a substantial amount of the byproduct $[Al(OSiMe_3)_3]_2$.[21]

Reaction of Tris(trimethylsilyl)azaalumatrane, 8, with $O{=}V(O\text{-}i\text{-}Pr)_3$. To a solution of **8** (3.11 g, 8.05 mmol) in 70 mL of toluene, $O{=}V(O\text{-}i\text{-}Pr)_3$ (2.01 g, 8.23 mmol) in 10 mL of toluene was added dropwise with stirring. The yellowish color of the solution slowly turned deep red. The reaction mixture was stirred and heated at 70 °C for 3 h. Attempts to separate products by sublimation, vacuum distillation and fractional crystallization from pentane were not successful. However, the presence of **17** in the mixture was indicated by its ^1H NMR spectrum: ^1H NMR (benzene-d_6) δ 0.46 (s, 9 H, $SiCH_3$), 2.32 (t, 2 H, $^3J_{HH}$ = 5.6 Hz, $N(CH_2)_3$), 3.29 (bs, 2 H, $SiNCH_2$).

Reaction of Trimethylazaboratrane, 6, with $O{=}V(O\text{-}i\text{-}Pr)_3$. Neat $O{=}V(O\text{-}i\text{-}Pr)_3$ (0.14 mL, 0.59 mmol) was added dropwise via a microsyringe to a solution of **6** (0.11 g, 0.56 mmol) in benzene-d_6 in an NMR tube. The reaction mixture was mixed thoroughly, after which the color of the solution changed from colorless to deep red. ^1H and ^{13}C NMR spectra of the reaction mixture were recorded and compared with literature data revealing the presence of **18**[22] and $B(O\text{-}i\text{-}Pr)_3$.[23]

Reaction of 6 with $Ti(O\text{-}i\text{-}Pr)_4$. A solution of $Ti(O\text{-}i\text{-}Pr)_4$ (2.5 g, 8.8 mmol) in 60 mL of toluene was added with stirring to a solution of **6** (1.47 g, 7.50 mmol) in 120 mL of toluene, and the mixture was refluxed for 40 h. Only starting materials were observed by ^1H NMR spectroscopy. An aliquot of the reactants was removed and sealed as a benzene-d_6 solution in an NMR tube. ^1H, ^{13}C, and ^{11}B NMR spectra

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taken after 9 months revealed the presence of B(O-*i*-Pr)$_3$,[23] **6**,[8] Ti(O-*i*-Pr)$_4$, and **19**.

19: ^{1}H NMR (benzene-d_6) δ 1.44 (d, 6 H, $^3J_{HH}$ = 6.2 Hz, CH(C*H*$_3$)$_2$), 2.70 (t, 6H, $^3J_{HH}$ = 5.8 Hz, N(CH$_2$)$_3$), 3.16 (t, 6 H, $^3J_{HH}$ = 5.9 Hz, MeNC*H*$_2$), 3.39 (s, 9 H, NCH$_3$), 4.77 (sept, 1 H, $^3J_{HH}$ = 6.1 Hz, C*H*(CH$_3$)$_2$); ^{13}C NMR (benzene-d_6) δ 26.9 (qm, CH(*C*H$_3$)$_2$, $^1J_{CH}$ = 125.4 Hz, $^2J_{CH}$ = $^3J_{CH}$ = 4.5 Hz), 47.7 (qt, NCH$_3$, $^1J_{CH}$ = 131.5 Hz, $^3J_{CH}$ = 2.6 Hz), 52.9 (tm, N(CH$_2$)$_3$, $^1J_{CH}$ = 134.8 Hz), 58.3 (tqt, MeNC*H*$_2$, $^1J_{CH}$ = 131.8 Hz, $^3J_{CH}$ = 6.1 Hz, $^2J_{CH}$ = 2.2 Hz), 74.7 (d sept, *C*HMe$_2$, $^1J_{CH}$ = 141.4 Hz, $^2J_{CH}$ = 4.3 Hz).

Trimethylazagallatrane Dimer, 14. Method A. A solution of tetramine **2** (Me$_3$tren) (2.09 g, 11.1 mmol) in 75 mL of degassed toluene was added dropwise within 15 min to a solution of [Ga(NMe$_2$)$_3$]$_2$ (2.24 g, 11.1 mmol) in 75 mL of toluene with stirring at −40 °C. The reaction solution was left to warm to room temperature and then it was stirred for 24 h. All volatiles were removed under vacuum, giving 2.20 g (78%) of the crude product. Further purification was effected by sublimation at 110 °C at 5×10^{-3} Torr, giving the white solid product **14**: mp 121−128 °C dec; ^{1}H NMR (500 MHz, toluene-d_8) δ 2.10−2.17 (m, 6 H), 2.37 (ddd, 2 H, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH(trans)}$ = 9.7 Hz, $^3J_{HH(gauche)}$ = 5.4 Hz), 2.47−2.55 (m, 4 H), 2.60−2.66 (m, 2 H), 2.68 (s, 6 H, CH$_3$), 2.75 (s, 6 H, CH$_3$), 2.78 (ddd, 2 H, $^2J_{HH}$ = 11.8 Hz, $^3J_{HH(trans)}$ = $^3J_{HH(gauche)}$ = 4.0 Hz), 2.87−2.97 (m, 4 H), 2.93 (s, 6 H, CH$_3$), 3.16 (ddd, 2 H, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH(trans)}$ = 10.0 Hz, $^3J_{HH(gauche)}$ = 4.0 Hz), 3.73 (ddd, 2 H, $^2J_{HH}$ = $^3J_{HH(trans)}$ = 13.2 Hz, $^3J_{HH(gauche)}$ = 5.1 Hz, $^1J_{CH}$ = 139.0 Hz, ^{13}C satellites); ^{13}C NMR (benzene-d_6) δ 40.50 (qdd, CH$_3$, $^1J_{CH}$ = 133.9 Hz, $^3J_{CH}$ = 10.3, 4.3 Hz), 41.85 (qdd, CH$_3$, $^1J_{CH}$ = 129.5 Hz, $^3J_{CH}$ = 6.9, 6.9 Hz), 42.22 (qdd, CH$_3$, $^1J_{CH}$ = 129.5 Hz, $^3J_{CH}$ = 3.0, 3.0 Hz), 54.03, 54.56, 54.83, 54.96, 56.15, 58.86, CH$_2$ groups; ^{71}Ga NMR (benzene-d_6, 70 °C) δ 255 ± 5 ($\Delta\nu_{1/2}$ = 12 kHz); HRMS (EI) calcd for $C_{18}H_{42}N_8{}^{69}Ga^{71}Ga$ (M$^+$) *m/z* 510.203 84, found 510.202 65, calcd for $C_{18}H_{42}N_8{}^{69}Ga_2$ (M$^+$) *m/z* 508.204 64, found 508.204 36, calcd for $C_{15}H_{36}N_7{}^{69}Ga_2$ *m/z* 452.154 62, found 452.154 75, calcd for $C_9H_{21}N_4{}^{69}Ga$ *m/z* 254.102 32, found 254.101 92; LRMS (EI) *m/z* (ions ^{69}Ga$_2$, ^{69}Ga^{71}Ga, ^{71}Ga$_2$, relative intensities) 508, 510, 512 (M$^+$, ~0.04), 452, 454, 456 (M − C$_3$H$_6$N$^+$, 0.16, 0.24, 0.06), 323, 325, 327 (0.5, 0.7, 0.2), 255, 257 (7, 5), 155 (7), 144 (14), 132 (7), 114 (6), 113 (7), 99 (51), 72 (39), 71 (12), 70 (22), 69 (11), 58 (100), 57 (19), 56 (24); CIMS (positive ion detection) *m/z* (ions, relative intensities) 509, 511, 513 (M + H$^+$, 58, 70, 25), 452, 454, 456 (3, 3, 1), 314, 316, 318 (9, 11, 4), 291, 293, 295 (14, 13, 3), 255, 257 (6, 6), 203 (22), 189 (100); IR (KBr pellet, 4000−400 cm^{-1}) ν 2962 s, 2948 s, 2926 s, 2886 s, 2844 vs, 2800 vs, 2760 vs, 2746 s, 2674 m, 1465 m, 1456 m, 1449 m, 1413 vw, 1376 w, 1359 w, 1349 s, 1331 m, 1322 vw, 1304 m, 1279 m, 1263 m, 1240 vw, 1224 vw, 1195 m, 1182 m, 1162 vs, 1112 w, 1092 s, 1080 vs, 1040 vs, 1026 s, 1010 w, 977 s, 948 s, 912 s, 853 vs, 838 s, 803 w, 748 m, 634 vs, 593 m, 563 m, 541 s, 504 vs, 495 sh. Anal. Calcd for $C_{18}H_{42}N_8Ga_2$: C, 42.39; H, 8.30; N, 21.97. Found: C, 43.15; H, 8.78; N, 21.06. Crystals of **14** suitable for X-ray diffraction experiments were grown from a saturated pentane solution at −20 °C.

Method B. A solution of Ga(acac)$_3$ (0.546 g, 1.49 mmol) and **12** (0.320 g, 0.754 mmol) in 70 mL of toluene was stirred at room temperature, and the conversion was monitored by ^{1}H NMR. The reaction was completed after 35 days. The separation of **14** from Al(acac)$_3$ failed owing to their similar volatility and solubility.

Tris(trimethylsilyl)azagallatrane, 10. A solution of tetraamine **4** (5.67 g, 15.6 mmol) in 20 mL of degassed THF was added dropwise to a stirred solution of [Ga(NMe$_2$)$_3$]$_2$ (3.16 g, 15.6 mmol) in 125 mL of THF at room temperature. The reaction mixture was heated to reflux for 24 h. After the removal of all volatiles, 5.91 g (88%) of **10** was obtained as an oily liquid which solidified in a freezer. The crude product was sublimed at 80−90 °C at 5×10^{-3} Torr giving a white solid **10**: mp 43−45 °C; ^{1}H NMR (toluene-d_8) δ 0.21 (s, 9 H, SiMe$_3$, $^1J_{CH}$ = 113.8 Hz, ^{13}C satellites, $^2J_{SiCH}$ = 6.4 Hz, ^{29}Si satellites), 1.97 (t, 2 H, N(CH$_2$)$_3$, $^3J_{HH}$ = 5.3 Hz), 2.83 (t, 2 H, SiNCH$_2$, $^3J_{HH}$= 5.3 Hz); ^{13}C NMR (toluene-d_8) δ −1.6 (SiMe$_3$, $^1J_{SiC}$ = 55.3 Hz, ^{29}Si satellites), 43.6 (SiNCH$_2$), 57.7 (N(CH$_2$)$_3$); ^{29}Si NMR (toluene-d_8) δ 0.34; ^{71}Ga NMR (toluene-d_8) δ 304 ± 10 ($\Delta\nu_{1/2}$ = 40 kHz at 70 °C); HRMS (EI) calcd for $C_{15}H_{39}N_4Si_3{}^{69}Ga$ (M$^+$) *m/z* 428.173 96, found 428.173 01; LRMS (EI) *m/z* (ions ^{71}Ga, ^{69}Ga, relative intensities) 430, 428 (M$^+$, 11, 13), 415,413 (M − CH$_3$$^+$, 14, 18), 328, 326 (M − Me$_3$SiNCH$_2$ − H$^+$, 76, 100), 260 (9), 213 (45), 211 (13), 187 (13), 171 (32), 157 (13), 69 (23). Anal. Calcd for $C_{15}H_{39}N_4Si_3Ga$: C, 41.95; H, 9.15; N, 13.05. Found: C, 41.87; H, 9.53; N, 12.97.

Table 1. Crystallographic Data for **12** and **14**

	12	**14**
formula	$Al_2C_{18}H_{42}N_8$	$Ga_2C_{18}H_{42}N_8$
fw	424.55	510.02
a (Å)	37.372(10)	9.716(1)
b (Å)	14.379(2)	11.325(2)
c (Å)	8.774(2)	11.343(1)
α (deg)	90	110.36(2)
β (deg)	90	97.87(1)
γ (deg)	90	90.34(1)
V (Å^3)	4714.9(1)	1157.2(3)
Z	8	2
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
T (°C)	23 ± 1	−50 ± 1
λ (Å)	0.71069	0.71073
d_{calcd} (g/cm^3)	1.199	1.464
μ (cm^{-1})	1.39	23.5
transmission coeff	0.82/1.00	0.86/0.95
R (F_o, %)	5.0	4.7
R_w (F_o, %)	5.7	5.4

Reaction of Tris(*t*-butyldimethylsilyl)azaalumatrane, 9, with Ga(acac)$_3$. A solution of **9** (0.18 g, 0.35 mmol) and Ga(acac)$_3$ (0.13 g, 0.35 mmol) in 200 mL of toluene was stirred at room temperature, and the reaction was monitored by ^{1}H NMR spectroscopy. After 1 month, 30% of **9** was converted to **11**: ^{1}H NMR (benzene-d_6) δ 0.09 (s, 6 H, SiMe$_2$), 0.99 (s, 9 H, *t*-Bu), 2.33 (t, 2 H, $^3J_{HH}$ = 6.3 Hz, N(CH$_2$)$_3$), 2.80 (t, 2 H, $^3J_{HH}$ = 6.0 Hz, SiNCH$_2$).

Reaction of Trimethylazaboratrane, 6, with Triethanolamine (TEA). An excess of TEA (0.1 mL, 0.8 mmol) was added to a stirred solution of **6** (0.14 g, 0.71 mmol) in 50 mL of toluene at room temperature and further stirred for 2 h until precipitation of a white solid was completed. Filtration followed by washing of the precipitate with 3 × 1 mL portions of Et$_2$O, and drying under vacuum for 45 minutes afforded 0.11 g (99%) of boratrane **21**.[24]

Reaction of Azasilatrane 15 with Triethanolamine (TEA). An excess of TEA (0.15 mL, 1.1 mmol) was added to a solution of **15** (0.179 g, 0.783 mmol) in 0.5 mL of benzene-d_6 in an NMR tube. Products **22** and **2** were characterized by favorable comparisons of their ^{1}H, ^{13}C, and ^{29}Si NMR spectra with published data.[12,25]

Single-Crystal X-ray Diffraction Studies of 12 and 14. Colorless crystals of **12** were mounted in 0.5 mm glass capillaries in a nitrogen-filled glovebox and flame-sealed, while crystals of **14** were covered with paraffin oil, attached to a glass fiber, and quickly transferred into a stream of cold nitrogen on the diffractometer. Pertinent crystal data, experimental conditions for data collection, and solution and structure refinement are listed in Table 1. Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections and a semi-empirical absorption correction based on the azimuthal scans of several reflections were applied to the data. The structures of **12** and **14** were solved by direct methods and refined by a full-matrix least-squares method, using the TEXAN (VAX)[26] and SHELXTL-Plus (MicroVAX)[27] programs, respectively. All non-hydrogen atoms were placed directly from the E-map and refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.[28]

Results and Discussion

Syntheses and Reactions. The metathetical reaction 1 between [Al(NMe$_2$)$_3$]$_2$ and trialkyl borates was reported by Ruff

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(24) (a) Hein, F.; Burkhardt, R. *Zeitschr. Anorg. Allg. Chem.* **1952**, *268*, 159. (b) Fenske, D.; Becher, H. J. *Chem. Ber.* **1972**, *105*, 2085. (c) Lacey, M. J.; Macdonald, C. G. *Aust. J. Chem.* **1976**, *29*, 1119.

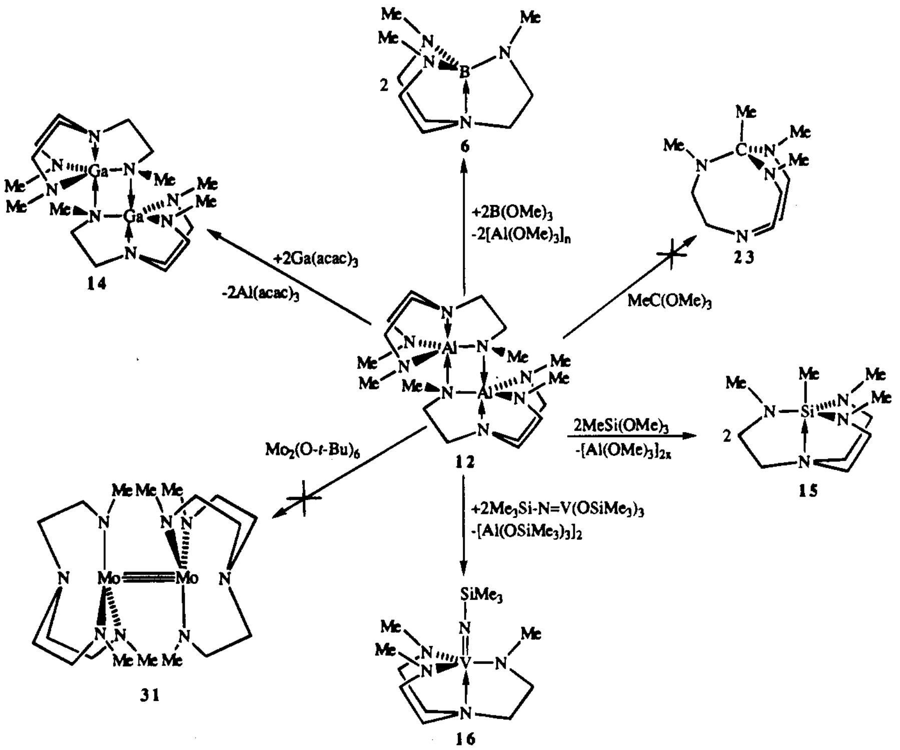
(25) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1.

(26) TEXSAN-TEXRAY Structure Analysis Package; Molecular Structure Corporation: Woodlands, TX, 1985.

(27) SHELXTL PLUS; Siemens Analytical X-ray Instruments, Inc.; Madison, WI.

(28) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U. K., 1974; Vol. IV.

Scheme 1



in the early 1960s.[29] Recently, we used a similar approach to

$$[Al(NMe_2)_3]_2 + B(OR)_3 \rightarrow B(NMe_2)_3 + Al(OR)_3 \quad (1)$$

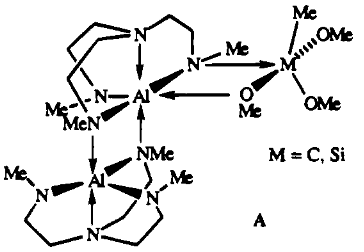
$$R = Me, Et, n\text{-}Bu$$

prepare azaboratrane **6** from azaalumatrane **12** by the transmetalation reaction[8] depicted in Scheme 1. There are two major factors driving these redistribution reactions. The higher strength of Al—O bonds relative to B—O and Al—N bonds is responsible for an enthalpic advantage, while the conversion of dimeric **12** to monomeric **6** is favored entropically. Moreover, the formation of insoluble polymeric $[Al(OMe)_3]_n$, which precipitates from the reaction solution, forces the equilibrium completely toward the products. Another crucial factor in the case of azatrane compounds is the stabilization effect of a transannular bond, as we demonstrated in the case of group 14 elements. Thus while $MeSi(OMe)_3$ reacts easily with dimeric azaalumatrane **12**, as shown in Scheme 1, giving azasilatrane **15** in 42% yield, the analogous reaction of $MeC(OMe)_3$ with **12** failed to produce any pro-azacarbatrane **23** or polymeric $[Al(OMe)_3]_n$ even after several hours of refluxing in toluene. The metathetical reaction 2 of trialkylstannyl amides with carboxylic esters, resulting in the transfer of the OR″ group from carbon to tin and in the formation of a C—N bond, has been reported by Lappert and George.[30] This shows that the formation of

$$R_3SnNMe_2 + R'C(O)OR'' \rightarrow R_3SnOR'' + RC(O)NMe_2 \quad (2)$$

$$R = Me, n\text{-}Bu;\ R' = Me, CH_2{=}C(Me), MeC(O)CH_2;\ R'' = Me, Et$$

pro-azacarbatrane **23** might be feasible on bond energy grounds. However, we can consider two obstacles to this reaction. Assuming the initial step is a nucleophilic attack of the OMe group at aluminum and excluding the breakage of the M—O bond (M = C, Si) with the formation of a cation $MeM(OMe)_2^+$ as a pathway with a prohibitively high activation energy, we can envision structure **A** as a possible reaction intermediate.



A

The formation of **A** requires an increase of the coordination number of M in $MeM(OMe)_3$ from four to five. This is easily accomplished in the case of silicon, but it is much more difficult for carbon, thus kinetically hindering the reaction. Moreover, the lack of stabilization of the desired product by a transannular N→C interaction disfavors **23** with respect to **15** thermodynamically. Azasilatrane **15** was prepared previously in our laboratory by a transamination reaction 3 with a similar yield.[19]

$$MeSi(NMe_2)_3 + \underset{\mathbf{2}}{(MeNHCH_2CH_2)_3N} \rightarrow 3Me_2NH + \underset{\mathbf{15}}{Me\overline{Si(MeNCH_2CH_2)_3N}} \quad (3)$$

Two literature examples of transmetalation reactions involving atranes are worthy of note. The preparation of stibatrane from silatrane in reaction 4[31] makes use of the driving force of strong

$$SbF_3 + R\overline{Si(OCH_2CH_2)_3N} \rightarrow RSiF_3 + Sb(OCH_2CH_2)_3N \quad (4)$$

$$R = Me, vinyl$$

Si—F bonds in the byproduct. On the other hand, no striking

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[29] Ruff, J. K. *J. Org. Chem.* **1962**, *27*, 1020.

[30] George, T. A.; Lappert, M. F. *J. Chem. Soc. A* **1969**, 992.

[31] Müller, R. *Organomet. Chem. Rev.* **1966**, *1*, 359.

energy difference between reactants and products is apparent in transesterification reaction 5 which uses aluminum ethoxide as a catalyst.[32]

$$\overline{B(OCH_2CH_2)_3N} + HSi(OEt)_3 \xrightarrow{Al(OEt)_3} B(OEt)_3 + H\overline{Si(OCH_2CH_2)_3N} \quad (5)$$

In analogy to the transmetalation of monomeric azastannatrane **24**[20,22] (reaction 6), we have shown that dimeric azaalumatrane **12** can serve as a useful starting material for the synthesis of azametalatranes among the transition metals. As summarized in Scheme 1, $Me_3SiN{=}V(OSiMe_3)_3$ reacts with **12**, giving azavanadatrane **16**. This reaction proceeds smoothly upon mixing the reactants as is indicated by the color change from colorless to deep red. The ^1H and ^{13}C NMR spectra showed signals for azavanadatrane **16**[20] and dimeric $[Al(OSiMe_3)_3]_2$.[21] The latter was also identified as the only aluminum-containing species by the ^{27}Al NMR signal at δ 59 ($\Delta\nu_{1/2}$ = 88 Hz at 20 °C). The separation of **16** from $[Al(OSiMe_3)_2]_2$ was precluded by their very similar volatilities and solubilities in hydrocarbon solvents. Recently, Schrock and co-workers[33] reported a series of azavanadatranes **27**–**30** possessing vanadium in oxidation states plus three (**29**) and plus four (**27**, **28**, **30**):

$$\underset{\textbf{24}}{n\text{-}Bu\overline{Sn(MeNCH_2CH_2)_3N}} + ZM(OR)_3 \rightarrow n\text{-}BuSn(OR)_3 + Z\overline{M(MeNCH_2CH_2)_3N} \quad (6)$$

16: $ZM = Me_3SiN{=}V$; $R = SiMe_3$

25: $ZM = t\text{-}BuN{=}V$; $R = SiMe_3$

26: $ZM = N{\equiv}Mo$; $R = t\text{-}Bu$

18: $ZM = O{=}V$; $R = i\text{-}Pr$

$$(LiN(R)CH_2CH_2)_3N + VCl_4{\cdot}DME \rightarrow 3LiCl + ClV(RNCH_2CH_2)_3N \quad (7)$$

27: $R = SiMe_3$

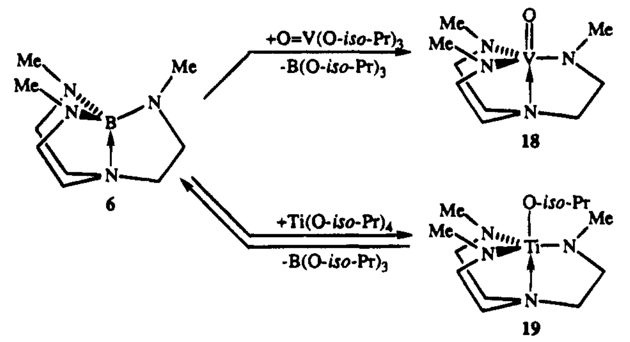
28: $R = SiMe_2\text{-}t\text{-}Bu$

$$\textbf{28} + Na/Hg \rightarrow NaCl + \underset{\textbf{29}}{\overline{V(t\text{-}BuMe_2SiNCH_2CH_2)_3N}} \quad (8)$$

$$\textbf{27} + LiCH_2SPh \rightarrow LiCl + \underset{\textbf{30}}{PhSCH_2V(Me_3SiNCH_2CH_2)_3N} \quad (9)$$

Our reaction of $Ti(O\text{-}i\text{-}Pr)_4$ with **12** afforded an intractable mixture of products. The ^1H NMR spectrum showed the presence of more than seven isopropyl signals in the methine region which probably belong to partially transmetalated intermediates. Despite the complexity of the spectrum, the presence of a monomeric $M(MeNCH_2CH_2)_3N$ unit was clearly indicated by two triplets and a singlet for the CH_2 and CH_3 groups, respectively. An attempt to prepare azatrane **31** in Scheme 1 with the central dimolybdenum unit failed, since the ^1H and ^{13}C NMR spectra of the reaction mixture after 18 h of reflux showed only the presence of unreacted starting materials **12** and $Mo_2(O\text{-}t\text{-}Bu)_6$.[16]

Scheme 2

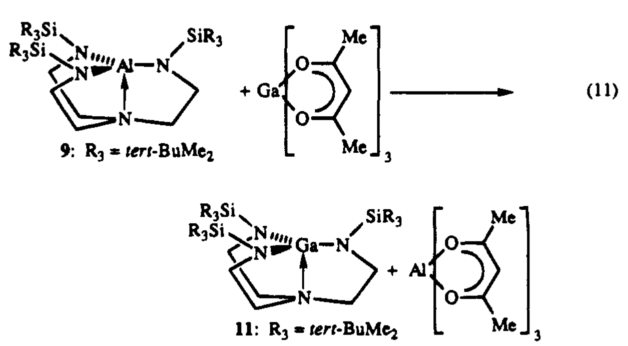


6 **18** **19**

Similarly to dimeric azaalumatrane **12**, monomeric **8**[8] reacts with the same facility with $O{=}V(O\text{-}i\text{-}Pr)_3$ according to reaction 10. The products **17** and $Al(O\text{-}i\text{-}Pr)_3$[21] were identified by ^1H NMR spectroscopy, but attempts to separate them by sublimation or vacuum distillation failed owing to similar volatilities of these products. The fact that azaboratrane **6** is also capable of functioning as a reactant in the transmetalation reaction with transition metal alkoxides was demonstrated in its reactions with $O{=}V(O\text{-}i\text{-}Pr)_3$ and $Ti(O\text{-}i\text{-}Pr)_4$, which are shown in Scheme 2. While the formation of azavanadatrane **18** proceeds to completion at room temperature nearly instantaneously, the reaction of $Ti(O\text{-}i\text{-}Pr)_4$ with **6** reaches equilibrium after it has been left for several months at room temperature. The ratio of reactants to products in the latter reaction was established both by ^1H and ^{11}B NMR spectroscopies to be 30:70. Azatitanatrane **19** was identified by a comparison of the similarity of cage ^1H and ^{13}C NMR chemical shifts to those of the previously reported t-BuO derivative.[34]

$$\underset{\textbf{8}}{3\overline{Al(Me_3SiNCH_2CH_2)_3N}} + 3O{=}V(O\text{-}i\text{-}Pr)_3 \rightarrow [Al(O\text{-}i\text{-}Pr)_3]_3 + \underset{\textbf{17}}{3O{=}\overline{V(Me_3SiNCH_2CH_2)_3N}} \quad (10)$$

Versatility of the transmetalation reaction was demonstrated by extending its scope to acac complexes (penta-2,5-dienoates). Both dimeric **12** (Scheme 1) and monomeric azaalumatrane **9** (reaction 11) react slowly with $Ga(acac)_3$ to replace the central aluminum atom with gallium in a complex multistep reaction. The formation of $[Ga(MeNCH_2CH_2)_3N]_2$, **14**, by transmetalation (Scheme 1) was completed after 35 days at room temperature as concluded from the ^1H, ^{13}C, ^{27}Al, and ^{71}Ga NMR spectra of the reaction mixture. Elevated temperatures did not accelerate



(11)

9: R_3 = tert-BuMe$_2$

11: R_3 = tert-BuMe$_2$

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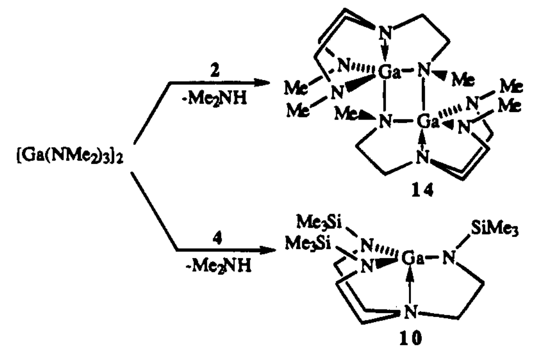
[32] Zelchan, G. I.; Voronkov, M. G. *Khim. Geterotsikl. Soed. (Engl. Transl.)* **1967**, *3*, 371.

[33] (a) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452. (b) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501. (c) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756.

[34] Naiini, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 5009.

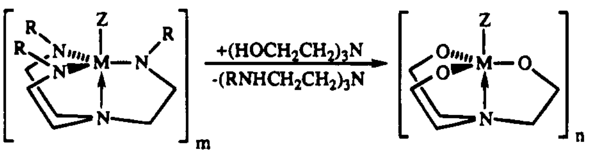
Scheme 3



the reaction but rather caused decomposition of the products. The conversion of only 30% after a month at room temperature was observed by ^1H NMR spectroscopy for reaction 11.

A preparatively more useful route for synthesizing azagallatranes **14** and **10** are the transmetalation reactions in Scheme 3. These facile transformations show that, analogously to the situation for azaalumatranes,[9] the size of the substituents on the equatorial nitrogens governs the degree of oligomerization. The bulky $SiMe_3$ groups in **10** shield the gallium center and prevent dimerization, while smaller methyl groups in **14** allow gallium to expand its coordination number.

A close relationship between azatranes and atranes was recently demonstrated in a facile conversion of azagermatranes **32**–**35**[35] and azaalumatranes **8** and **12**[10] to atranes **36**, **37** and **20**, respectively, by the transligation reaction 12 with triethanolamine. In this metathesis, a triptych framework is retained despite the multiplicity of bonds that must be broken in the reactants and reformed in the products. This result emphasizes a remarkable stability of these multichelated structures. The ligand exchange appears to be driven mainly by the formation of strong oxygen-metal bonds. We have found that azaboratrane **6** and azasilatrane **15** can also be converted to boratrane **21** and silatrane **22**, respectively, as shown in reaction 12. These results extend and generalize the scope of the transligation reaction. Boratrane **21** was isolated in quantitative yield and was characterized by ^1H, ^{11}B, and ^{13}C NMR and MS spectroscopies.[24] Silatrane **22** was characterized by ^1H, ^{13}C, and ^{29}Si NMR spectra in the reaction mixture.[25]

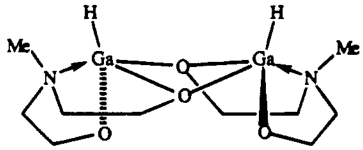


(12)

	m	M	Z	R	n	
32	1	Ge	Me	H	1	**36**
33	1	Ge	Me	Me	1	**36**
34	1	Ge	*tert*-Bu	H	1	**37**
35	1	Ge	*tert*-Bu	Me	1	**37**
12	2	Al	–	Me	4	**20**
8	1	Al	-	$SiMe_3$	4	**20**
6	1	B	–	Me	1	**21**
15	1	Si	Me	Me	1	**22**

Structural Considerations

Recently we found that the molecular structure of dimeric azaalumatrane **13** features an unusual cis configuration of the substituents on the central four-membered ring.[9] Only two other similar examples could be found in the literature, namely, the gallium and titanium derivatives **38**[36] and **39**.[37] Here we present



38

results of our single-crystal X-ray diffraction studies on azaalumatrane **12** and azagallatrane **14**. Their molecular structures are shown in Figures 1 and 2, respectively. Both of these molecules also possess the curious cis configuration of the substituent methyl groups on the central $(M-N)_2$ ring. The structural data for **12** and **14** allow a detailed comparison between the Al and Ga atoms in an identical coordination environment and their influence on the surrounding ligands. The cis diastereomers, similarly to the situation found for **13**,[9] were the only species observed by ^1H and ^{13}C NMR spectroscopies in solutions of **12** and **14**. In fact, no interconversion of the cis isomers to the trans counterparts was observed after heating solutions of **12** and **14** for 60 h at 120 °C in sealed NMR tubes. Moreover, their spectra remain unchanged up to 100 °C in toluene-d_8, thus revealing no fluxionality which could be caused by a racemization process between two enantiomers of the cis species.

Both **12** and **14** contain an $(M-N)_2$ central array in the form of a puckered rectangle. The two planes of the puckered

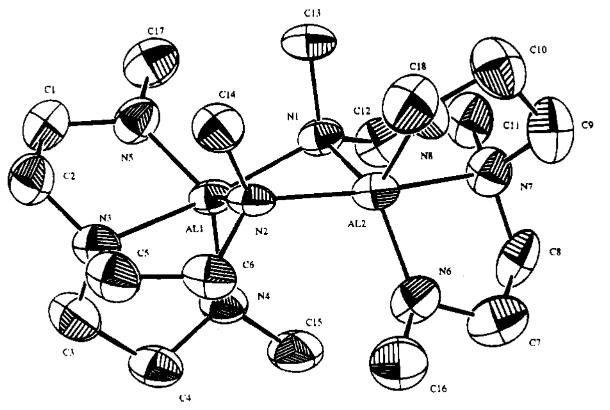


Figure 1. ORTEP drawing of $[Al(MeCH_2CH_2)_3N]_2$, **12**. Ellipsoids are drawn at the 50% probability level.

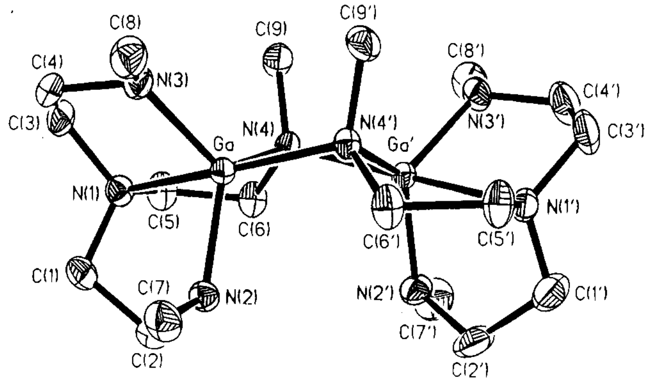


Figure 2. Thermal ellipsoid plot[27] of $[Ga(MeNCH_2CH_2)_3N]_2$, **14**. Ellipsoids are drawn at the 50% probability level.

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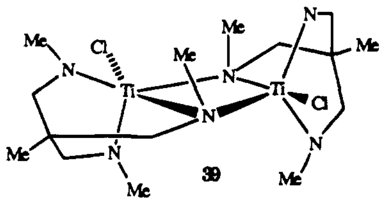

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rectangle are canted with respect to one another by 146° and 148° in **12** and **14**, respectively, which closely corresponds to the value of 149° found in **13**. The central atoms in **12** and **14** are contained in a distorted trigonal bipyramidal coordination sphere, and they are displaced approximately 0.2 and 0.3 Å, respectively, from the plane formed by the equatorial nitrogens toward the bridging nitrogens. The distortion is also reflected in a bending of the TBP axis as shown in Tables 2 and 3. Compounds **12** and **13** are to our knowledge the only structurally verified examples of five-coordinate group 13 atoms surrounded solely by nitrogen ligands, while **14** is only the second example of a GaN$_5$ structure, the first being a square pyramidal azido gallium porphyrin complex.[7d] The covalent radii of aluminum and gallium are very similar owing to the poor screening effect of the filled d-electron shell of gallium. It should be noted, however, that the actual values of the covalent radii vary with the method used for their calculation,[38] thus precluding a firm decision regarding their relative sizes. Moreover, the tabulated values usually do not reflect the influence of different coordination numbers. The bond distances and angles of **12** (Table 2) are comparable to those found in **13**.[9]

Table 2. Selected Bond Distances (Å) and Angles (deg) for **12**

Al(1)—N(3)	2.124(6)	Al(2)—N(7)	2.160(6)
Al(1)—N(4)	1.843(6)	Al(2)—N(6)	1.829(6)
Al(1)—N(5)	1.821(6)	Al(2)—N(8)	1.844(6)
Al(1)—N(1)	1.968(5)	Al(2)—N(1)	2.032(5)
Al(1)—N(2)	2.049(5)	Al(2)—N(2)	2.022(5)
N(1)—Al(1)—N(2)	81.0(2)	N(1)—Al(2)—N(2)	80.1(2)
Al(1)—N(1)—Al(2)	94.9(2)	Al(1)—N(2)—Al(2)	92.7(2)
N(1)—Al(1)—N(3)	161.9(2)	N(2)—Al(2)—N(7)	160.6(2)
N(3)—Al(1)—N(2)	82.6(2)	N(7)—Al(2)—N(1)	80.9(2)
N(3)—Al(1)—N(4)	84.5(2)	N(7)—Al(2)—N(6)	83.4(3)
N(3)—Al(1)—N(5)	82.1(3)	N(7)—Al(2)—N(8)	84.8(3)
N(2)—Al(1)—N(5)	126.3(2)	N(1)—Al(2)—N(6)	126.0(2)
N(2)—Al(1)—N(4)	108.4(2)	N(6)—Al(2)—N(8)	117.2(3)
N(4)—Al(1)—N(5)	120.8(3)	N(1)—Al(2)—N(8)	112.3(3)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **14**

Ga—N(1)	2.284(3)	Ga′—N(1′)	2.297(3)
Ga—N(2)	1.908(3)	Ga′—N(2′)	1.891(3)
Ga—N(3)	1.900(3)	Ga′—N(3′)	1.904(4)
Ga—N(4)	2.037(3)	Ga′—N(4′)	2.043(3)
Ga—N(4′)	2.048(3)	Ga′—N(4)	2.060(3)
N(4)—Ga—N(4′)	82.6(1)	N(4)—Ga′—N(4′)	82.2(1)
Ga—N(4)—Ga′	92.4(1)	Ga—N(4′)—Ga′	92.6(1)
N(1)—Ga—N(4′)	162.7(1)	N(1′)—Ga′—N(4)	161.8(1)
N(1)—Ga—N(2)	84.2(1)	N(1′)—Ga′—N(2′)	83.7(1)
N(1)—Ga—N(3)	82.9(1)	N(1′)—Ga′—N(3′)	83.0(1)
N(1)—Ga—N(4)	80.1(1)	N(1′)—Ga′—N(4′)	79.7(1)
N(2)—Ga—N(3)	118.9(1)	N(2′)—Ga′—N(3′)	120.0(2)
N(3)—Ga—N(4)	120.2(1)	N(3′)—Ga′—N(4′)	115.7(1)
N(2)—Ga—N(4)	115.7(1)	N(2′)—Ga′—N(4′)	118.8(1)

A comparison of the Ga—N bond lengths in **14** (Table 3) with their Al—N counterparts in **12** reveals that for the same coordination environment, the Ga—N bonds are somewhat longer than the Al—N bonds. A similar observation was reported by Power and co-workers for the monomeric tricoordinate pairs of derivatives R$_2$MNR′R″ (M = Al, Ga; R, R′, R″ = 2,4,6-*i*-Pr$_3$C$_6$H$_2$, H, 2,4,6-*i*-Pr$_3$C$_6$H$_2$, respectively; *t*-Bu, SiPh$_3$, adamantyl, respectively) wherein the lengthening was about 0.06–0.07 Å.[39] In **14**, we found that the Ga—N bonds within the central ring are on average only 0.03 Å longer than the corresponding Al—N bonds in **12**. However, the equatorial nonbridging Ga—N distances are on average 0.07 Å longer, and the transannular bonds are as much as 0.3 Å longer in **14** relative to **12**, which is consistent with substantial flexibility of the transannular bond.

Table 4. Comparison of Ga—N Distances (Å) in Compounds with TBP Gallium Coordination

	equatorial	axial	ref
14	1.891(3)–1.908(3)[a] 2.040(3)[c]	2.284(3), 2.297(3)[b] 2.048(3), 2.060(3)[c]	this work
38		2.192(5)	36
40a		2.279(3)	40
40b		2.471(4)	40
40c		2.211(3)	41
40d		2.207(9)	42
41		2.276(3)	43
42a		2.110(9)	44
42b		2.071(2)–2.102(2)	45
42c		2.077(3)–2.098(3)	45
42d		2.088(3), 2.111(3)	45
43a		2.304(6), 2.385(6)	46
43b		2.551(2), 2.399(2)	46
44		2.186(3), 2.214(4), 2.268(4)[d]	47
45	2.119(6)[c]	2.433(6)	48
46		2.355(4)	49
47	2.164(5)[c]		50
48	1.945(3),[c] 1.996(3)[c]	2.779(3)	51

[a] Nonbridging. The coordination number of a nitrogen is three. [b] Transannular. [c] Bridging. The coordination number of a nitrogen is four. [d] Three independent molecules.

The Ga—N bond lengths in **14** are comparable to the values found in other compounds possessing TBP coordinated gallium atoms such as **38**,[36] **40a–d**,[40–42] **41**,[43] **42a–d**,[44,45] **43a,b**,[46] **44**,[47] **45**,[48] **46**,[49] **47**,[50] and the polycyclic cage compound (GaH)$_6$(GaH$_2$)$_2$(μ_3-O)$_2$(μ_3-NCH$_2$CH$_2$NMe$_2$)$_4$(μ-NHCH$_2$CH$_2$NMe$_2$)$_2$, **48**,[51] as shown in Table 4.

A major structural difference between azatranes **12** and **14** lies in the degree of pyramidality of the equatorial nonbridging

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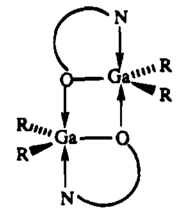
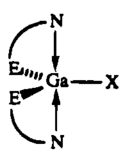
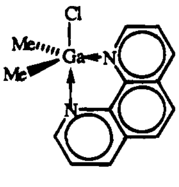


	R	$\widehat{\mathrm{O\ N}}$
40a	H	$OCH_2CH_2NMe_2$
40b	Me	$OCH_2CH_2NMe_2$
40c	Me	8-quinolinol
40d	$(CH_2)_4CH$	8-quinolinol
41	Me	$OCH_2(C_5H_4N)$



	X	$\widehat{\mathrm{E\ N}}$
42a	Cl	2-Me-8-quinolinol
42b	$NCCH_2CO_2$	2-Me-8-quinolinol
42c	CH_3CO_2	2-Me-8-quinolinol
42d	$1/2(CH_2CO_2)_2$	2-Me-8-quinolinol
43a	Cl	$C_6H_4CH_2NMe_2$
43b	$C_6H_4CH_2NMe_2$	$C_6H_4CH_2NMe_2$
44	Cl	$C(SiMe_3)_2(C_5H_4N)$



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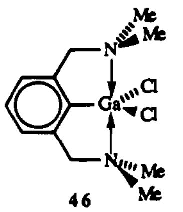

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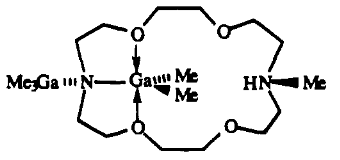

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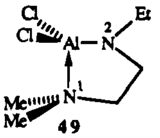
nitrogens. In **12**, N(4), N(5), N(6), and N(8) are in a nearly planar environment. The sum of angles around these atoms range from 354.7(7)° to 358.3(6)°, which is in the range of values found in **13**, implying near sp^2 hybridization. It would appear that while in **13** Si—N π-bonding could be largely responsible for the flattening of these nitrogen geometries, there is no Si atom present in **12**, and we suggest that π—interactions between the nitrogens and the central aluminum atoms may contribute to nitrogen planarity. A short Al—N(2) distance and the planarity of N(2) in **49** was rationalized by the π-donation of the nitrogen N(2) lone pair to aluminum 3d empty orbitals.[52] Perhaps assisting N(2) planarity in **49**, however, are Et$\cdots$Cl steric interactions occasioned by the tetrahedrality of the aluminum. Similar steric assistance is absent in **12** and **13**. In accord with our observations is the greater distortion from planarity of the terminal NMe_2 groups in $[Ga(NMe_2)_3]_2$ compared with those in $[Al(NMe_2)_3]_2$.[14b]



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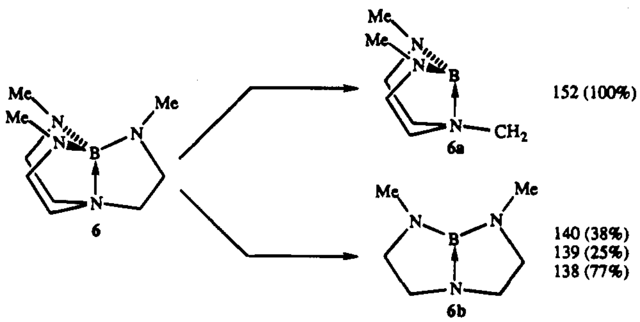
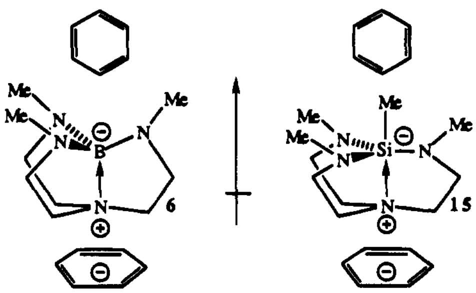
In contrast to **12** and **13**, azagallatrane **14** possesses strongly pyramidal nonbridging equatorial nitrogens N(2), N(3), N(2′), and N(3′) with a range of the sum of angles around them of 336.4(3)° to 344.9(4)°. The difference in the hybridization of the nonbridging equatorial nitrogens in **12** and **14**, in which these atoms possess nearly identical environments, strongly suggests a dissimilar tendency of Al and Ga to accept lone pair electron density from N, especially in view of the similar sizes of the metal atoms.

Scheme 4



Scheme 5



Mass Spectroscopy. Because all the group 13 azatranes known so far are volatile solids, they may prove to be interesting precursors for the preparation of nitrides by CVD techniques. We examined the decomposition of **6** by high-resolution mass spectroscopy, and the results are listed in the supplementary material. Two major fragmentation pathways are shown in Scheme 4.

NMR Spectroscopy. ^1H NMR spectra of **6** and **15** measured in both benzene-d_6 and chloroform-d_1 revealed substantial aromatic solvent-induced shift (ASIS) behavior. For **6**, the change of the solvent from chloroform-d_1 to benzene-d_6 caused a shift of 0.21 ppm to lower field for the NMe signal and upfield shifts of 0.35 and 0.65 ppm for the $MeNCH_2$ and $N(CH_2)_3$ signals, respectively. Similarly, the CH_3—Si and CH_3—N protons of **15** are shifted downfield by 0.32 and 0.14 ppm, respectively, on going from chloroform-d_1 to benzene-d_6. Conversely, upfield shifts of 0.44 and 0.17 ppm were observed for the $N(CH_2)_3$ and $MeNCH_2$ signals, respectively. This phenomenon can be explained by the formation of collision complexes of **6** and **15** with benzene molecules as shown in Scheme 5.[53] The vector of the dipole moment is directed along the N$\rightarrow$M (M = B, Si) transannular dative bond in accord with their respective formal positive and negative charges. In a simplistic but useful view, the electron-rich π-cloud of a benzene molecule is attracted to the positive end of the azatrane cage so that the methylene protons are influenced by the shielding cone of the "ring current". Owing to their proximity to the plane of the benzene molecule, the $N(CH_2)_3$ protons display a larger ASIS effect than the more distant $MeNCH_2$ protons. The negative end of the atrane molecule attracts relatively electron-deficient hydrogens on the periphery of the benzene molecules, thus exposing the $SiCH_3$ and NCH_3 groups to the deshielding torus of the "ring current". A larger downfield shift was observed in **15** for the $SiCH_3$ protons relative to the NCH_3 protons as expected from a closer approach of the former to the benzene molecules.

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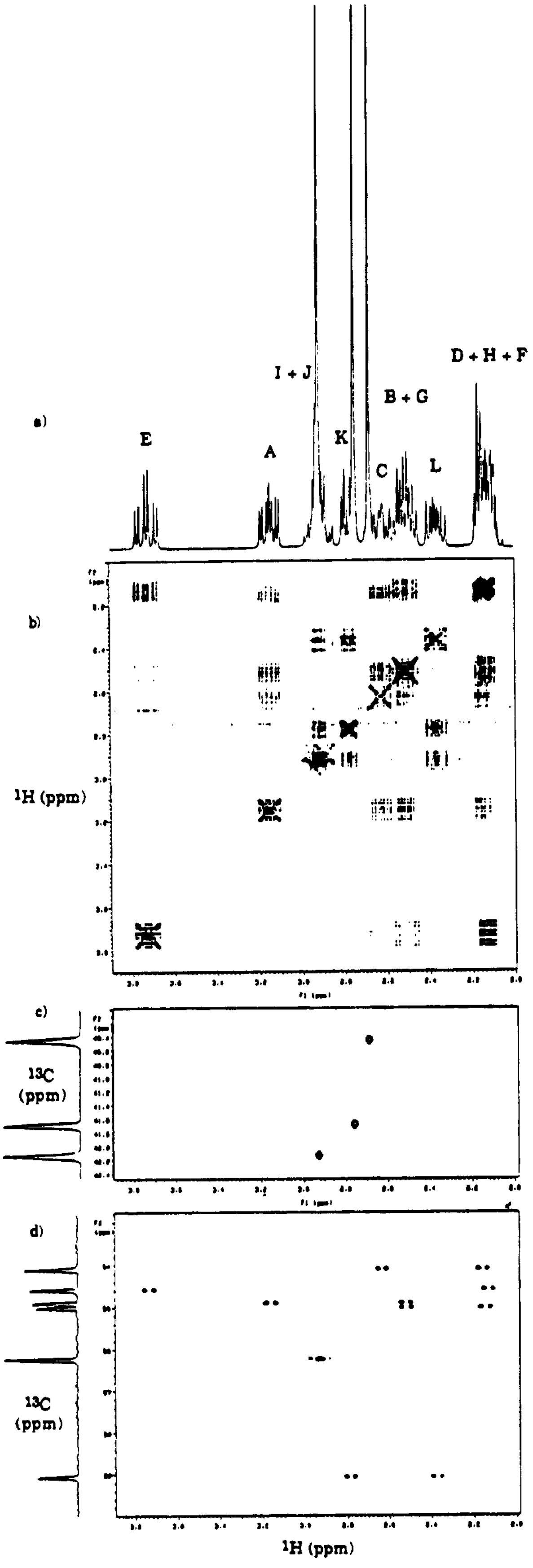

Figure 3. ^{1}H NMR spectrum, (a); ^{1}H, ^{1}H DQF COSY, (b); and methyl (c) and methylene (d) region of ^{1}H, ^{13}C heterocorrelated NMR spectrum of **14**.

Both the ^{1}H and ^{13}C NMR spectra of **14** reflect its dimeric nature, and they are depicted together with its ^{1}H, ^{1}H DQF COSY and ^{1}H, ^{13}C heterocorrelated NMR spectra in Figure 3.

Table 5. Results of ^{1}H$-^1$H and ^{1}H$-^{13}$C NMR Correlation Experiments on **14**

δ^{13}C (ppm)	δ^1H (ppm), assignment[a]
	methyl groups
40.50	2.68 Me (9, 9′)
41.85	2.75 } Me (7, 7′) + Me (8, 8′)
42.22	2.93 } Me (7, 7′) + Me (8, 8′)
	methylene groups
54.03	2.60–2.66, C; 2.10–2.19, D
54.83	3.16 A; 2.47–2.55, B
54.56	3.73 E; 2.10–2.19, F
54.96	2.47–2.55, G; 2.10–2.19 H
56.15	2.87–2.97, I + J
58.86	2.78, K; 2.37, L

[a] For numbering scheme, see Figure 2.

Table 6. ^{71}Ga NMR Chemical Shifts for Selected Gallium Compounds

compound	CN[a]	δ^{71}Ga (ppm)	$\Delta\nu_{1/2}$ (kHz)	ref
Ga(acac)$_3$	6	-2^b	2.8 at 25 °C	this work
50	6	2.8^c	0.06 at 25 °C	this work
14	5	255 ± 5^b	12 at 70 °C	this work
[Ga(NMe$_2$)$_3$]$_2$	4	276^b	8.4	14b
10	4	304 ± 10^d	40 at 70 °C	this work

[a] Coordination number. [b] Benzene-d_6 solution. [c] THF-d_8 solution. [d] Toluene-d_8 solution.

The presence of a 2-fold axis in **14** as the only symmetry element renders inequivalent all the methylene protons as well as the three methyl groups (C(7), C(8), and C(9) in Figure 2) and the three ethylene bridges (C(1), C(2); C(3), C(4); C(5), C(6)). This is manifested by the presence of three methyl singlets and 12 partially overlapped methylene multiplets in the ^{1}H NMR spectrum. Furthermore, the ^{13}C NMR spectrum displays six methylene and three methyl signals. The assignment of the bridging NMe group C(9,9′) was facilitated by the observation of a larger $^1J_{CH}$ coupling constant in the ^{13}C proton-coupled NMR spectrum of **14** relative to smaller and identical values for nonbridging NMe groups C(7,7′) and C(8,8′).[8] Information obtained from an analysis of ^{1}H, ^{1}H DQF COSY and ^{1}H, ^{13}C heterocorrelated NMR spectra (Figure 3) allowed us to break the signals into three groups which belong to three inequivalent ethylene bridges. The assignments are summarized in Table 5.

There are relatively few reports in the literature on ^{71}Ga NMR studies of Ga–N compounds.[54] This is due to the substantially greater line widths of ^{71}Ga signals that can be broadened beyond the detection limits by quadrupolar relaxation. ^{71}Ga chemical shifts are expected to follow the same trends as the ^{27}Al shifts in corresponding aluminum geometries.[55] The paucity of data makes a comparison of our results difficult, but from Table 6 it can be concluded that similarly to our results obtained for AlN compounds,[8,9] the shielding of the Ga nucleus increases with increasing coordination number. A very broad signal for **10**, presumably possessing a trigonal monopyramidal Ga center,[9] was observed in the low-field region (~304 ppm). Tetrahedrally coordinated gallium in [Ga(NMe$_2$)$_3$]$_2$[14b] was reported at a higher field relative to **10** (276 ppm). Azagallatrane **14**, with a coordination number of five, displays its chemical shift even further upfield (255 ppm) as expected. For comparison, the

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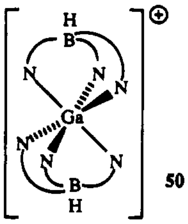
shift for **50**[56] is listed, which shows a gallium signal at 2.8 ppm in the appropriate region for hexacoordinate Ga, similar to that of the $Ga(acac)_3$ signal which we found at −2 ppm. This observation contrasts that in a recent report in which this resonance was stated to be unobservable due to severe broadening.[57]



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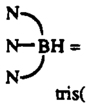

tris(3,5-dimethyl-1-pyrazolyl)hydridoborate

Conclusions

Azaalumatrane **12** and azagallatrane **14** are both dimeric species possessing an unusual cis configuration of the substituents on the central four-membered ring. Both aluminum and gallium are coordinated exclusively by nitrogens in a distorted trigonal bipyramidal geometry. Azaalumatrane **12** was shown to be a versatile reagent in transmetalation reactions by which azatranes of main-group elements and transition metals can be prepared. In order to utilize this preparatively useful system, a methoxide or an ethoxide should be used as a transmetalating agent, since it is converted to the nonvolatile insoluble $[Al(OMe)_3]_n$, which is easily separable from the reaction mixture.

The structural comparison of **12** and **14** indicates that despite the similar sizes of Al and Ga, the degree of $M \leftarrow N$ π-bonding for M = Ga seems to be less than for $Al \leftarrow N$ as is suggested by greater pyramidalization of the nonbridging equatorial nitrogens in **14**. This observation also accords with the slightly longer Ga—N than Al—N bonds.

Acknowledgment. The authors are grateful to the National Science Foundation and the Iowa State Center for Advanced Technology Development for grants in support of this work. We thank Dr. Victor Young of Instrument Services at ISU for the structural determinations of **12** and **14**.

Supplementary Material Available: Tables of positional and thermal parameters and bond lengths and angles (15 pages). Ordering information is given on any current masthead page.

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