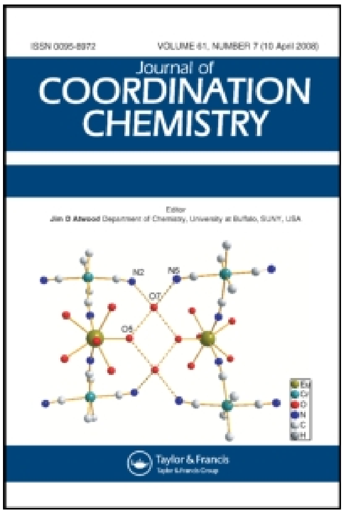

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CHARACTERIZATION OF GALLIUM-NITROGEN ADDUCTS BY X-RAY STRUCTURAL AND NMR SPECTRAL STUDIES. CRYSTAL STRUCTURE OF [(PhMe$_2$CCH$_2$)$_2$GaCI]$_2$ AND OF ITS MONOMERIC *t*-BUTYLAMINE ADDUCT, (PhMe$_2$CCH$_2$)$_2$GaCI[NH$_2$(*t*-Bu)]

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CHARACTERIZATION OF GALLIUM–NITROGEN ADDUCTS BY X-RAY STRUCTURAL AND NMR SPECTRAL STUDIES. CRYSTAL STRUCTURE OF $[(PhMe_2CCH_2)_2GaCl]_2$ AND OF ITS MONOMERIC *t*-BUTYLAMINE ADDUCT, $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$

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The nature of $[(PhMe_2CCH_2)_2GaCl]_2$ and its adducts with $NH_2(t\text{-}Bu)$ and $NH_2(n\text{-}Pr)$ have been investigated. $[(PhMe_2CCH_2)_2GaCl]_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.2495(16)$ Å, $b = 21.4977(32)$ Å, $c = 7.8337(15)$ Å, $\beta = 93.489(14)°$, $V = 1891.0(5)$ Å^3 and D(calcd.) = 1.305 Mg/m^3 for $Z = 2$. The structure was refined to $R(F) = 4.2\%$ for 1672 reflections above $6\sigma(F)$. The molecule has perfect C_i symmetry, a planar $Ga(\mu\text{-}Cl)_2Ga$ core and an expanded $C(\alpha)$–Ga–$C(\alpha)$ angle of 137.9(3)° between the neophyl ligands. $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.4023(10)$ Å, $b = 17.4274(25)$ Å, $c = 22.2389(38)$ Å, $\beta = 94.939(13)°$, $V = 2472.2(7)$ Å^3 and D(calcd.) = 1.225 Mg/m^3 for $Z = 4$. This structure was refined to $R(F) = 3.9\%$ for 1700 reflections above $6\sigma(F)$. The crystal structure is stabilized by intermolecular $Cl \cdots H\text{–}N$ hydrogen bonds and the central Ga(III) atom has a distorted tetrahedral geometry. A benzene solution of $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$ is in equilibrium with $[(PhMe_2CCH_2)_2GaCl]_2[NH_2(t\text{-}Bu)]$ and free amine according to ^{1}H NMR studies. In contrast to this, a solution of $(PhMe_2CCH_2)GaCl_2[NH_2(t\text{-}Bu)]$ is in equilibrium with $[(PhMe_2CCH_2)GaCl_2]_2[NH_2(t\text{-}Bu)]$, free $[(PhMe_2CCH_2)GaCl_2]_2$ and free amine. Solutions of $(PhMe_2CCH_2)_2GaCl[NH_2(n\text{-}Pr)]$ and $(PhMe_2CCH_2)GaCl_2[NH_2(n\text{-}Pr)]$ show no evidence for similar equilibria.

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Keywords: Gallium(III); organogallium; crystal structure; neophyl ligand; hydrogen bonding

INTRODUCTION

Even though organogroup 13 compounds are typically Lewis acids that readily form donor–acceptor complexes, there are surprisingly few reports in the literature that describe X-ray structural studies and NMR spectroscopic studies of both the Lewis acid and its adducts, especially adducts with amines. The propensity for the *t*-butyl group to form crystalline compounds and to simplify ^{1}H NMR spectra has made such derivatives especially attractive for this type of investigation. Thus, the adducts $Me_3Ga[NH_2(t\text{-}Bu)]$,[1] $Me_3In[NH_2(t\text{-}Bu)]$,[1] and $\{Me_2Ga[NH_2(t\text{-}Bu)]_2\}Br$[2] have been fully characterized including X-ray structural studies. The neophyl substituent CH_2CMe_2Ph also has an enhanced tendency to form crystalline compounds.[3] In this paper we report the crystal and molecular structures of $[(PhMe_2CCH_2)_2GaCl]_2$ and $(PhMe_2CCH_2)_2ClGa[NH_2(t\text{-}Bu)]$ as determined by X-ray structural studies and describe the nature of benzene solutions of the adducts $(PhMe_2CCH_2)_2ClGa[NH_2(t\text{-}Bu)]$, $(PhMe_2CCH_2)_2ClGa[NH_2(n\text{-}Pr)]$, $(PhMe_2CCH_2)Cl_2Ga[NH_2(t\text{-}Bu)]$ and $(PhMe_2CCH_2)Cl_2Ga[NH_2(n\text{-}Pr)]$ by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of $[(PhMe_2CCH_2)_2GaCl]_2$ was reported previously.[3]

EXPERIMENTAL SECTION

All compounds described in this investigation were very sensitive to oxygen and water and were manipulated under a purified argon atmosphere in a Vacuum Atmospheres glove box equipped with a Dry Train or by using standard vacuum line techniques. The reagents $[(PhMe_2CCH_2)_2GaCl]_2$ and $[(PhMe_2CCH_2)GaCl_2]_2$ were prepared by using literature procedures.[3] All solvents were purified before use. The ^{1}H NMR Spectra were recorded at 400 MHz using a Varian VXR-400 spectrometer with samples contained in flame-sealed NMR tubes. Chemical shifts are reported in ∂ (ppm) and are referenced to tetramethylsilane (TMS) at $\partial = 0.00$ ppm and benzene at $\partial = 7.15$ ppm. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin Elmer 683 spectrometer. Melting points were observed with a Mel-Temp by using flame sealed capillaries and are uncorrected.

Lewis Acid–Base Studies

The tendencies of $[Ga(CH_2CMe_2Ph)_2Cl]_2$ and $[Ga(CH_2CMe_2Ph)Cl_2]_2$ to react with $NH_2(t\text{-}Bu)$ and $NH_2(n\text{-}Pr)$ to form Lewis acid–base adducts were investigated by vacuum distilling a weighed amount of excess Lewis base onto a weighed amount of the Lewis acid. After the mixture was stirred at room temperature for 1–2 h, the excess base was removed by vacuum distillation. The mole ratio of Lewis acid to Lewis base that reacted and the characterization data of the resulting adduct including melting point, ^1H NMR spectra and IR spectra for each adduct are given below.

$(PhMe_2CCH_2)_2ClGa[NH_2(t\text{-}Bu)]$

Mole ratio: 1.00. m.p.: 86.4–91.9°C (dec.). ^1H NMR (C_6D_6, δ) (see Results and Discussion): 7.31 (d, 7.9 H, *o*-Ar (adduct) + *o*-Ar (intermediate), $^3J_{CCH} = 7.20$ Hz), 7.18 (t, 4.2 H, *m*-Ar (adduct), $^3J_{CCH} = 7.50$ Hz), 7.05 (t, 5.7 H, *p*-Ar (adduct) + *m*-Ar (intermediate), $^3J_{CCH} = 7.64$ Hz), 6.90 (t, 1.8 H, *p*-Ar (intermediate), $^3J_{CCH} = 6.90$ Hz), 1.52 (s, 11.8 H, CMe_2 (adduct), 1.40 (s, 11.1 H, CMe_2 (intermediate)), 1.28 (s, 4.3 H, CH_2 (intermediate) + NH_2 (intermediate)), 1.00 (s, 4.2 H, CH_2 (adduct)), 0.99 (s, 5.3 H, CMe_3 (free)), 0.68 (s, 1.1 H, NH_2 (free)), 0.50 (s, 15.1 H, CMe_3 (adduct) + CMe_3 (intermediate) + NH_2 (adduct)). Composition of the solution: (±5%), 49% adduct, 23% intermediate, 28% free Lewis base; $K = 0.89$. ^1H NMR (C_6D_6, δ) (with excess Lewis base): 7.34 (d, *o*-Ar, $^3J_{CCH} = 7.56$ Hz), 7.08 (t, *m*-Ar, $^3J_{CCH} = 7.50$ Hz), 6.94 (t, *p*-Ar, $^3J_{CCH} = 7.50$ Hz), 1.52 (s, CMe_2 (adduct)), 1.03 (s, CH_2 (adduct)), 0.98 (s, CMe_3 (adduct) + CMe_3 (free)), 0.82 (s, NH_2 (adduct) + NH_2 (free)). ^1H NMR (C_6D_6, δ) (with excess Lewis acid): 7.36, 7.33, 7.28, 7.25, 7.19, 7.17, 7.14, 7.08, 6.96, (br-m, C_6H_5 (adduct + $Ga(CH_2CMe_2Ph)_2Cl$)), 1.52 (s, CMe_2 (adduct)), 1.38 (s, CH_2 ($Ga(CH_2CMe_2Ph)_2Cl$)), 1.32 (s, CMe_2 ($Ga(CH_2CMe_2Ph)_2Cl$)), 1.06 (s, CH_2 (adduct)), 0.62 (s, NH_2 (adduct)), 0.57 (s, CMe_3 (adduct)). IR (Nujol, cm^{-1}: 3270 (vs), 3220 (vs), 3210 (s), 3185 (s), 3155 (s), 3120 (s), 2720 (s), 1960 (m), 1945 (m), 1885 (m), 1870 (m), 1802 (m), 1745 (m), 1672 (m), 1600 (s), 1579 (m), 1565 (vs), 1555 (sh, s), 1442 (vs), 1399 (s), 1331 (m), 1276 (s), 1208 (s), 1195 (sh, m), 1180 (s), 1158 (vs), 1140 (s), 1099 (m), 1080 (m), 1061 (s), 1026 (s), 1015 (sh, m), 997 (m), 945 (m), 929 (sh, m), 925 (m), 905 (m), 900 (m), 892 (m), 860 (m), 840 (w), 770 (vs), 761 (vs), 735 (sh, m), 715 (vs), 700 (vs), 690 (vs), 649 (s), 628 (m), 602 (m), 552 (m), 535 (sh, w), 505 (w), 495 (w), 445 (m), 430 (m), 415 (m), 369 (w), 335 (m), 292 (s). X-ray crystallographic quality crystals were obtained by heating a saturated pentane solution of the preformed

1 : 1 adduct with a 50–60°C water bath and then allowing the solution to slowly cool to ambient temperature over 24 h.

$(PhMe_2CCH_2)_2ClGa[NH_2(n\text{-}Pr)]$

Mole ratio: 1.00. m.p.: 67.1–68.5°C (dec.). ^{1}H NMR (C_6D_6, δ): 7.31 (d, 4 H, *o*-Ar, $^3J_{CCH} = 7.62$ Hz), 7.04 (t, 4 H, *m*-Ar, $^3J_{CCH} = 7.62$ Hz), 6.90 (t, 2 H, *p*-Ar, $^3J_{CCH} = 6.00$ Hz), 1.77 (t, 2 H, NH_2, $^3J_{NCH} = 7.14$ Hz), 1.48 (s, 12 H, CMe_2 (neophyl)), 0.99 (s, 4 H, CH_2 (neophyl)), 0.478 (m, 5 H, CH_3(Pr) and CH_2(Pr)), 0.28 (t, 2 H, NCH_2, $^3J_{CCH} = 7.26$ Hz). IR (Nujol, cm^{-1}): 3280 (s), 3235 (s), 3120 (m), 3080 (s), 3050 (s), 3015 (s), 1950 (m), 1875 (m), 1811 (m), 1750 (m), 1595 (m), 1575 (sh, m), 1569 (vs), 1555 (sh, m), 1490 (s), 1360 (s), 1355 (s), 1279 (m), 1176 (s), 1153 (m), 1103 (m), 1070 (s), 1062 (s), 1025 (m), 957 (m), 901 (m), 880 (w), 850 (m), 762 (vs), 720 (vs), 701 (sh, s), 695 (vs), 685 (sh, s), 630 (m), 618 (m), 602 (m), 555 (m), 535 (w), 440 (vw), 410 (w), 299 (m).

$(PhMe_2CCH_2)Cl_2Ga[NH_2(t\text{-}Bu)]$

Mole ratio: 1.00. m.p.: 78.9–81.3°C (dec.). ^{1}H NMR (C_6D_6, δ): 7.11 (d, 2.6 H, *o*-Ar (adduct) + *o*-Ar (intermediate), $^3J_{CCH} = 7.26$ Hz), 6.99 and 6.93 (m, 0.78 H, C_6H_5 other species), 6.86 (t, 1.8 H, *p*-Ar, $^3J_{CCH} = 7.70$ Hz), 6.72 (t, 2.2 H, *m*-Ar (adduct) + C_6H_5 other species)), 2.02 (s-br, 2.0 H, NH_2 (adduct)), 1.52 (s, 0.43 H, CH_2 $[Ga(CH_2CMe_2Ph)Cl_2]_2$), 1.30 (s, 1.9 H, CMe_2 (intermediate)), 1.27 (s, 6.6 H, CMe_2 (adduct) + CH_2 (intermediate)), 1.24 (s, 1.3 H, CMe_2 $[Ga(CH_2CMe_2Ph)Cl_2]_2$), 1.22 (s, 2.0 H, CH_2 (adduct)), 0.97 (s, 0.32 H, NH_2 (intermediate)), 0.61 (s, 0.05 H, NH_2 (free)), 0.56 (s, 0.22 H, CMe_3 (free)), 0.54 (s, 1.5 H, CMe_3 (intermediate)), 0.51 (s, 9.0 H, CMe_3 (adduct)). Composition of the solution (±5%): 71% adduct, 12% intermediate, 16% free $Ga(CH_2CMe_2Ph)Cl_2$ and 1% free Lewis base. ^{1}H NMR (C_6D_6, δ) (excess Lewis base): 7.35 (d, 2 H, *o*-Ar, $^3J_{CCH} = 7.26$ Hz), 7.09 (t, 2 H, *m*-Ar, $^3J_{CCH} = 7.26$ Hz), 6.95 (t, 1 H, *p*-Ar, $^3J_{CCH} = 7.37$ Hz), 1.53 (s, 6 H, CMe_2), 1.33 (s, 2 H, CH_2), 1.11 (s, 2 H, NH_2), 0.91 (s, CMe_3 (adduct) + CMe_3 (free) + NH_2 (free)). ^{1}H NMR (C_6D_6, δ) (excess Lewis acid): 7.18, 7.00, 6.96, 6.80 (br-m, 13.8 H, C_6H_5 (adduct + intermediate + $Ga(CH_2CMe_2Ph)Cl_2$)), 2.64 (s-br, 2.0 H, NH_2 (adduct)), 1.52 (s, 3.3 H, CH_2 ($Ga(CH_2CMe_2Ph)Cl_2$)), 1.46 (s, 1.8 H, CH_2 (intermediate)), 1.29 (s, 7.8 H, CMe_2 (adduct) + CH_2 (intermediate)), 1.25 (s, 11.9 H, CMe_2 ($Ga(CH_2CMe_2Ph)Cl_2$)), 1.04 (s, 2.0 H, NH_2 (adduct)), 0.80 (s, 0.06 H, NH_2 (free)), 0.64 (s, 0.30 H, CMe_3 (free)), 0.59 (s, 13.0 H, CMe_3 (adduct) + CMe_3 (intermediate)). IR (Nujol, cm^{-1}): 3234 (vs), 3195 (vs), 3109 (s), 3082 (s), 2730 (m), 2665 (m), 2600 (m), 2505 (m), 2469 (m), 2350 (m), 2305 (m), 2235 (m), 1982 (m), 1964 (m), 1905 (m), 1889 (m), 1821 (m), 1765 (w), 1692 (w), 1596 (m), 1475 (sh, m), 1470 (sh, s), 1465 (vs), 1455 (sh, s), 1441 (s), 1400 (s), 1330 (m), 1290 (vs), 1275 (s), 1205 (s), 1190 (s), 1178 (vs), 1159 (s), 1141 (s), 1131 (m), 1104 (m), 1075 (m), 1065 (m), 1029 (s), 1025 (sh, s), 998 (m), 989 (m), 969 (m), 928 (m), 911 (m), 889 (s), 860 (m), 771 (vs), 741 (m), 720 (vs), 705 (s), 699 (vs), 674 (s), 625 (m), 555 (s), 505 (w), 450 (w), 440 (w), 405 (m), 359 (vs), 342 (vs), 324 (s), 262 (m).

$(PhMe_2CCH_2)Cl_2Ga[NH_2(n\text{-}Pr)]$

Mole ratio: 1.00. m.p.: viscous liquid at room temperature. ^1H NMR (C_6D_6, δ): 7.30 (d, 2 H, *o*-Ar, $^3J_{CCH} = 7.23$ Hz), 7.04 (t, 2 H, *m*-Ar, $^3J_{CCH} = 7.67$ Hz), 6.89 (t, 1 H, *p*-Ar, $^3J_{CCH} = 7.23$ Hz), 2.09 (t, 2 H, NCH_2, $^3J_{CCH} = 7.50$ Hz), 1.94 (s-br, 2 H, NH_2), 1.44 (s, 6 H, CMe_2), 1.34 (s, 2 H, CH_2 (neophyl)), 0.81 (m, 2 H, CH_2-Pr), 0.40 (t, 3 H, CH_3-Pr), $^3J_{CCH} = 7.40$ Hz). IR (neat, cm^{-1}): 3270 (vs), 3230 (vs), 3090 (s), 3055 (s), 3030 (s), 2960 (vs), 2930 (vs), 2880 (vs), 2260 (w), 1955 (w), 1880 (w), 1813 (w), 1750 (w), 1680 (vw), 1596 (s), 1575 (sh, vs), 1570 (vs), 1491 (vs), 1465 (vs), 1455 (sh, vs), 1439 (vs), 1399 (sh, m), 1382 (s), 1365 (s), 1319 (m), 1275 (m), 1190 (vs), 1089 (s), 1075 (s), 1065 (s), 1041 (s), 1038 (s), 989 (s), 950 (s), 905 (m), 885 (m), 879 (sh, m), 870 (m), 850 (m), 766 (vs), 721 (vs), 695 (vs), 655 (s), 629 (s), 555 (s), 507 (w), 413 (m), 345 (vs), 261 (w).

Collection of X-ray Diffraction Data, Structural Determination and Refinement for $[(PhMe_2CCH_2)_2GaCl]_2$

A clear, colorless crystal of approximate orthogonal dimensions 0.20 × 0.20 × 0.15 mm was carefully inserted into a glass capillary and sealed under stringently anaerobic and moisture-free conditions. The crystal was mounted on a eucentric goniometer and transferred to a Siemens R3m/V diffractometer. Determination of the crystal's Laue symmetry, crystal class and orientation matrix were carried out as described previously.[4] Details are provided in Table I.

The data were corrected for absorption and for Lorentz and polarization effects. The systematic absences ($h0l = 2n+1$ and $0k0$ for $k = 2n+1$) uniquely define the ubiquitous centrosymmetric monoclinic space group $P2_1/c$. The 3723 reflections were merged to a set of 3351 unique data ($R(\text{int}) = 2.50\%$) of which 1672 (49.9%) had $|F_o| > 6.0\sigma(|F_o|)$.

All crystallographic calculations were carried out on a VAXstation 3100 computer with use of the Siemens SHELXTL PLUS (Release 4.11) VMS

TABLE I Experimental data for the X-ray diffraction studies

	$[(PhMe_2CCH_2)_2GaCl]_2$	$(PhMe_2CCH_2)GaCl[NH_2(t\text{-}Bu)]$
Formula	$C_{40}H_{52}Cl_2Ga_2$	$C_{24}H_{37}ClGaN$
Fw	743.2	444.7
Temperature (K)	298	298
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14, var)
a, Å	11.2495(16)	6.4023(10)
b, Å	21.4977(32)	17.4274(25)
c, Å	7.8337(15)	22.2389(38)
β, deg	93.489(14)	94.939(13)
V, Å^3	1891.0(5)	2472.2(7)
Z	2	4
D(calcd.), mg/m^3	1.305	1.195
μ(Mo Kα), mm^{-1}	1.587	1.225
F(000)	776	944
Diffractometer	Siemens R3m/V	*
Radiation	Mo Kα ($\lambda = 0.71073$ Å)	*
Monochromator	Highly oriented graphite	*
Data collected	$\pm h$, $+k$, $+l$	$+h$, $\pm k$, $\pm l$
Scan type	2θ–θ	2θ–θ
2θ range, deg	5.0–50.0	5.0–45.0
Scan speed (ω), deg/min	2.00	2.00
Scan range (ω)	$0.5 + \Delta(K\alpha_1/K\alpha_2)$	$0.57 + \Delta(K\alpha_1/K\alpha_2)$
Absorption correction	Semi-empirical (ψ)	*
Min/max transmission	0.3107/0.3650	0.2533/0.4237
Reflections collected	3732	7168
Independent reflections with $F_o > 6\sigma$	1672	1700
Number of variables	200	253
Extinction correction (χ)	Not required	0.00016(9)
$R(F)$, R(wF) (obsd. data)	4.19%, 4.42%	3.90%, 4.03%
$R(F)$, R(wF) (all data)	10.33%, 8.13%	9.63%, 7.10%
Goodness-of-fit	0.93	1.05
Largest diff. peak, e/Å^3	0.79	0.67
Largest diff. hole, e/Å^3	−0.62	−0.56

* – Entry same as for previous column.

program package.[5] The scattering factors used were the analytical values for neutral atoms; these were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[6] The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were located and their positional and anisotropic thermal parameters were refined. Hydrogen atoms were included in idealized positions, based upon d(C–H) = 0.96 Å[7] and the appropriate trigonal or staggered-tetrahedral stereochemistry. Refinement was continued until $\Delta/\sigma < 0.01$ for each parameter. A final difference-Fourier synthesis showed no unusual features. The final discrepancy index is $R(F) = 4.19\%$ for those 1672 independent reflections with $|F_o| > 6\sigma(|F_o|)$; the value for all 3351

TABLE II Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^4$) for $[(PhMe_2CCH_2)_2GaCl]_2$

	x	*y*	*z*	*U*(*eq*)
Ga(1)	916(1)	359(1)	1485(1)	41(1)
Cl(1)	1151(1)	−11(1)	−1303(2)	49(1)
C(10)	1619(5)	−225(3)	3137(8)	49(2)
C(11)	2948(5)	−412(3)	3073(8)	48(2)
C(12)	3114(5)	−911(3)	1726(7)	43(2)
C(13)	2525(6)	−1476(3)	1795(9)	58(3)
C(14)	2705(8)	−1957(3)	668(12)	77(3)
C(15)	3497(8)	−1879(4)	−552(11)	74(3)
C(16)	4098(8)	−1334(4)	−684(10)	78(3)
C(17)	3898(6)	−861(3)	451(9)	62(3)
C(18)	3392(7)	−660(4)	4837(9)	74(3)
C(19)	3652(6)	187(3)	2680(11)	71(3)
C(20)	803(6)	1259(3)	1197(8)	50(2)
C(21)	651(5)	1643(3)	2842(7)	43(2)
C(22)	1812(6)	1632(3)	3970(8)	46(2)
C(23)	2806(6)	1934(3)	3455(9)	63(3)
C(24)	3851(7)	1947(4)	4488(12)	77(3)
C(25)	3913(8)	1658(4)	6045(12)	81(4)
C(26)	2949(8)	1343(4)	6567(10)	72(3)
C(27)	1896(6)	1338(3)	5546(8)	55(2)
C(28)	360(7)	2329(3)	2306(9)	66(3)
C(29)	−418(6)	1398(3)	3731(9)	61(3)

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

independent data is substantially higher because of the large number of very weak data. Final atomic coordinates are provided in Table II.

Collection of X-ray Diffraction Data, Structural Determination and Refinement for $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$

A clear, colorless crystal of dimension 0.25 × 0.20 × 0.15 mm was sealed into a glass capillary. The procedure paralleled that for the previous structure; details appear in Table I. Important differences include the following: (1) The systematic absences ($h0l$ for $h+l=2n+1$ and $0k0$ for $k=2n+1$) define the space group $P2_1/n$ (a variant of the standard space group, chosen so that the angle β is not abnormally obtuse). (2) A total of 7168 reflections, representing two equivalent forms, were collected, corrected as before, and merged to a set of 3237 unique data ($R(\text{int}) = 2.69\%$) of which 1700 (52.5%) had $|F_o| > 6.0\sigma(|F_o|)$. (3) The final discrepancy index was $R(F) = 3.90\%$ for those 1700 data with $|F_o| > 6.0\sigma(|F_o|)$ and $R(F) = 9.63\%$ for all 3237 unique data. (4) Final atomic parameters are collected in Table III. (5) It should be noted that we refined the positions of the amine hydrogen atoms, yielding distances of N(1)–H(1A) = 0.92(6) Å and N(1)–H(1B) = 0.79(7) Å.

TABLE III Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^4$) for $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$

	x	*y*	*z*	*U*(*eq*)
Ga(1)	1652(1)	2133(1)	4078(1)	40(1)
Cl(1)	−1653(3)	2195(1)	3633(1)	64(1)
N(1)	3038(11)	1724(3)	3322(3)	47(2)
H(1A)	4347(100)	1940(34)	3385(25)	45(19)
H(1B)	2529(117)	2041(43)	3104(32)	70(29)
C(1)	3122(12)	930(4)	3065(3)	52(3)
C(2)	4419(13)	448(4)	3526(4)	81(3)
C(3)	919(13)	624(5)	2972(4)	88(4)
C(4)	4151(14)	953(5)	2476(3)	83(4)
C(10)	1824(11)	1330(3)	4717(3)	48(2)
C(11)	633(11)	1455(4)	5290(3)	53(2)
C(12)	1430(15)	879(4)	5774(3)	81(4)
C(13)	−1657(12)	1299(5)	5128(4)	77(3)
C(14)	1038(11)	2270(3)	5525(3)	46(2)
C(15)	−467(12)	2831(4)	5494(3)	67(3)
C(16)	−11(16)	3578(5)	5721(4)	87(4)
C(17)	1935(19)	3752(5)	5958(4)	92(4)
C(18)	3453(16)	3207(5)	5994(3)	85(4)
C(19)	2975(13)	2478(4)	5779(3)	61(3)
C(20)	3064(10)	3136(3)	4210(3)	44(2)
C(21)	2493(10)	3856(3)	3830(3)	45(2)
C(22)	4055(12)	4500(4)	4006(3)	67(3)
C(23)	293(11)	4138(4)	3961(3)	62(3)
C(24)	2567(11)	3653(3)	3157(3)	45(2)
C(25)	799(11)	3569(4)	2756(3)	64(3)
C(26)	950(14)	3319(5)	2168(3)	77(3)
C(27)	2865(15)	3150(5)	1972(3)	78(4)
C(28)	4606(13)	3230(5)	2350(4)	70(3)
C(29)	4511(11)	3485(4)	2934(3)	58(3)

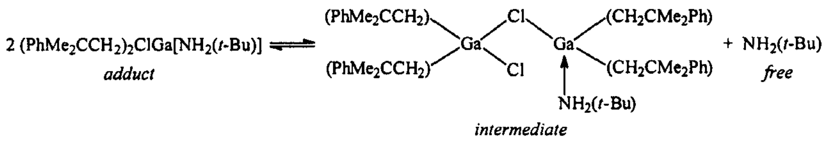
Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

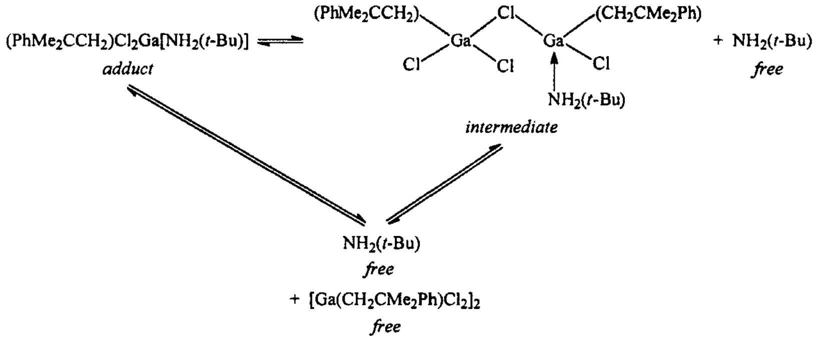
^{1}H NMR Studies

Benzene solutions of the adducts $(PhMe_2CCH_2)_2ClGa[NH_2(t\text{-}Bu)]$, $(PhMe_2CCH_2)_2ClGa[NH_2(n\text{-}Pr)]$, $(PhMe_2CCH_2)Cl_2Ga[NH_2(t\text{-}Bu)]$ and $(PhMe_2CCH_2)Cl_2Ga[NH_2(n\text{-}Pr)]$ were fully characterized by ^{1}H NMR and IR spectroscopy. The adducts $(PhMe_2CCH_2)_2ClGa[NH_2(t\text{-}Bu)]$, $(PhMe_2CCH_2)_2ClGa[NH_2(n\text{-}Pr)]$ and $(PhMe_2CCH_2)Cl_2Ga[NH_2(t\text{-}Bu)]$ were crystalline solids at room temperature whereas $(PhMe_2CCH_2)Cl_2Ga[NH_2(n\text{-}Pr)]$ was a viscous liquid. The ^{1}H NMR spectra of benzene solutions of $(PhMe_2CCH_2)_2ClGa[NH_2(n\text{-}Pr)]$ and of $(PhMe_2CCH_2)Cl_2Ga[NH_2(n\text{-}Pr)]$ at the normal operating temperature of the instrument were consistent with the presence of simple 1 : 1 adducts (Ga/N) and need no further discussion.

In contrast, the spectra of $(PhMe_2CCH_2)_2ClGa[NH_2(t\text{-}Bu)]$ and $(PhMe_2CCH_2)Cl_2Ga[NH_2(t\text{-}Bu)]$ in benzene exhibited many more lines than expected for the protons in the simple adducts. A comparison of the chemical shifts of the lines with other known compounds and an investigation of changes in their intensities after the addition of different reagents confirmed the existence of equilibria which are slow on the NMR time scale. The adduct $(PhMe_2CCH_2)_2ClGa[NH_2(t\text{-}Bu)]$ upon dissolution established an equilibrium between the 1Ga : 1N Lewis acid–base adduct, a 2Ga : 1N adduct and free amine as shown in Scheme 1. This equilibrium was confirmed by adding excess $NH_2(t\text{-}Bu)$ and observing an increase in concentration of the 1Ga : 1N adduct and a corresponding decrease in the concentration of the 2Ga : 1N adduct. When a two-fold excess of base had been added, lines for only the 1Ga : 1N adduct and free amine were observed. When excess $[(PhMe_2CCH_2)_2GaCl]_2$ was added, the spectrum indicated an increase in concentrations of the 2Ga : 1N adduct and the 1Ga : 1N adduct. There was no evidence for formation of the ionic 1Ga : 2N adduct $\{(PhMe_2CCH_2)_2Ga[NH_2(t\text{-}Bu)]_2\}Cl$ as was observed for $\{Me_2Ga[NH_2(t\text{-}Bu)_2]_2\}Br$.[2] The adduct $(PhMe_2CCH_2)Cl_2Ga[NH_2(t\text{-}Bu)]$ is also involved in equilibria (Scheme 2) that may be observed at the normal operating temperature of the instrument. Data for solutions that had a gallium–nitrogen ratio of 1 : 1 suggest equilibria between 1Ga : 1N and



SCHEME 1



SCHEME 2

2Ga : 1N adducts, the free organogallium chloride dimer [$(PhMe_2CCH_2)$-$GaCl_2]_2$ and the free base. The addition of excess amine shifted the equilibrium to reduce the concentration of the 2Ga : 1N adduct and [$(PhMe_2CCH_2)GaCl_2]_2$, whereas excess [$(PhMe_2CCH_2)GaCl_2]_2$ shifted the equilibrium in the opposite direction.

The Structure of [$(PhMe_2CCH_2)_2GaCl]_2$

The molecular geometry of [$(PhMe_2CCH_2)_2GaCl]_2$ in the solid state is illustrated in Figure 1. Interatomic distances and angles are provided in Table IV. The molecule lies on an inversion center (at 0, 0, 0) and has crystallographically-imposed $C_i(\bar{1})$ symmetry. This requires that the dimeric molecule possess a strictly planar Ga_2Cl_2 molecular core. The bridging chloride ligands lie in slightly asymmetric locations, destroying the possible D_{2h} symmetry of this moiety. Thus, the bonds Ga(1)–Cl(1) = Ga(1A)–Cl(1A) = 2.355(2) Å are approximately 0.08 Å shorter than the other two such bonds, Ga(1)–Cl(1A) = Ga(1A)–Cl(1) = 2.440(2) Å. The internal angles at gallium and chlorine are surprisingly close to right angles, with

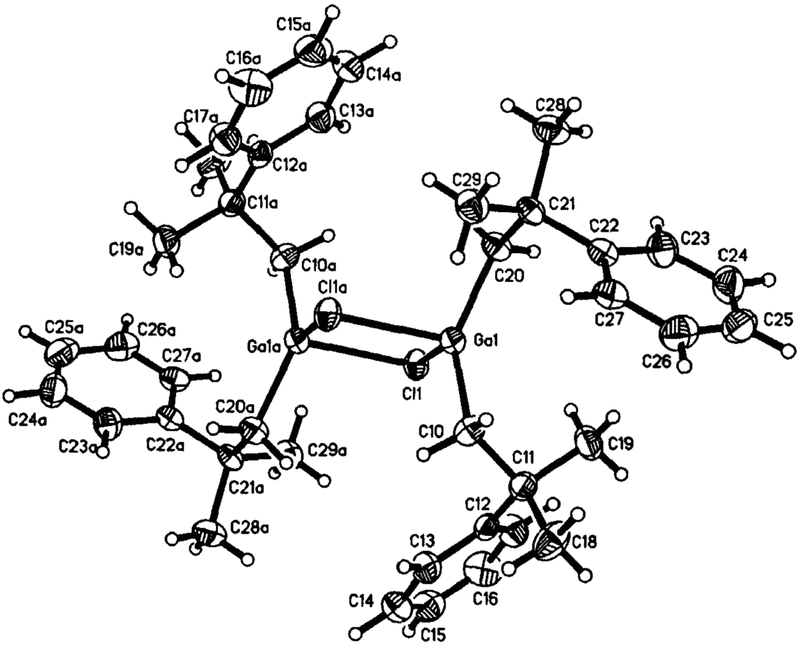


FIGURE 1 Molecular geometry of [$(PhMe_2CCH_2)_2GaCl]_2$. This is an ORTEP2 diagram showing the 30% probability envelopes of the atomic vibration ellipsoids. Hydrogen atoms are reduced for clarity.

TABLE IV Interatomic distances (Å) and angles (°) for $[(PhMe_2CCH_2)_2GaCl]_2$

Bond lengths (Å)			
Ga(1)–Cl(1)	2.355(2)	Ga(1)–C(10)	1.938(6)
Ga(1)–C(20)	1.951(6)	Ga(1)–Cl(1A)	2.440(2)
Cl(1)–Ga(1A)	2.440(2)	C(10)–C(11)	1.551(8)
C(11)–C(12)	1.525(9)	C(11)–C(18)	1.537(9)
C(11)–C(19)	1.551(9)	C(12)–C(13)	1.387(9)
C(12)–C(17)	1.377(9)	C(13)–C(14)	1.382(11)
C(14)–C(15)	1.356(13)	C(15)–C(16)	1.361(12)
C(16)–C(17)	1.379(11)	C(20)–C(21)	1.548(8)
C(21)–C(22)	1.532(8)	C(21)–C(28)	1.562(9)
C(21)–C(29)	1.520(9)	C(22)–C(23)	1.374(10)
C(22)–C(27)	1.386(9)	C(23)–C(24)	1.387(11)
C(24)–C(25)	1.367(13)	C(25)–C(26)	1.362(12)
C(26)–C(27)	1.388(11)		
Bond angles (°)			
Cl(1)–Ga(1)–C(10)	109.6(2)	Cl(1)–Ga(1)–C(20)	103.8(2)
C(10)–Ga(1)–C(20)	137.9(3)	Cl(1)–Ga(1)–Cl(1A)	90.1(1)
C(10)–Ga(1)–Cl(1A)	100.9(2)	C(20)–Ga(1)–Cl(1A)	104.1(2)
Ga(1)–Cl(1)–Ga(1A)	89.9(1)	Ga(1)–C(10)–C(11)	120.0(4)
C(10)–C(11)–C(12)	111.3(5)	C(10)–C(11)–C(18)	108.8(5)
C(12)–C(11)–C(18)	109.3(5)	C(10)–C(11)–C(19)	107.3(5)
C(12)–C(11)–C(19)	111.2(5)	C(18)–C(11)–C(19)	108.9(6)
C(11)–C(12)–C(13)	120.8(6)	C(11)–C(12)–C(17)	123.9(6)
C(13)–C(12)–C(17)	115.2(6)	C(12)–C(13)–C(14)	122.8(7)
C(13)–C(14)–C(15)	119.1(7)	C(14)–C(15)–C(16)	120.7(8)
C(15)–C(16)–C(17)	119.1(8)	C(12)–C(17)–C(16)	123.1(7)
Ga(1)–C(20)–C(21)	116.2(4)	C(20)–C(21)–C(22)	109.8(5)
C(20)–C(21)–C(28)	108.1(5)	C(22)–C(21)–C(28)	109.1(5)
C(20)–C(21)–C(29)	109.1(5)	C(22)–C(21)–C(29)	113.6(5)
C(28)–C(21)–C(29)	106.9(5)	C(21)–C(22)–C(23)	120.2(5)
C(21)–C(22)–C(27)	122.1(6)	C(23)–C(22)–C(27)	117.7(6)
C(22)–C(23)–C(24)	121.0(7)	C(23)–C(24)–C(25)	120.5(8)
C(24)–C(25)–C(26)	119.7(8)	C(25)–C(26)–C(27)	119.9(7)
C(22)–C(27)–C(26)	121.3(7)		

∠Cl(1)–Cl(1A) = 90.1(1)° and ∠Ga(1)–Cl(1)–Ga(1A) = 89.9(1)°. The cross-ring contacts, Ga(1)···Ga(1A) = 3.386 Å and Cl(1)···Cl(1A) = 3.395 Å are, again, very similar and confirm the "oblong" (and almost square) nature of the Ga_2Cl_2 core.

Each gallium(III) atom completes its distorted tetrahedral geometry with σ-bonds to two neophyl ($PhMe_2CCH_2$–) ligands. The two gallium–carbon bond lengths are Ga(1)–C(10) = 1.938(6) Å and Ga(1)–C(20) = 1.951(6) Å, with an average value of Ga–C(av) = 1.945 Å. The C(10)–Ga(1)–C(20) angle of 137.9(3)° is almost 30° larger than the ideal tetrahedral value of 109.5°. This probably arises to compensate for the steric bulk of the neophyl ligands taken in conjunction with the undemanding nature of the bridging chloride ligands. We may compare this enlarged C(α)–Ga–C(α′) angle to those in other symmetrical dimeric species. In order of decreasing C(α)–Ga–C(α′) angle, we have 128.3(1)° in $[(PhMe_2CCH_2)_2Ga(\mu\text{-}NHPr)]_2$[3] 123.5(2)°

and 122.2(2)° for the two independent molecules in $[(PhMe_2CCH_2)_2Ga(\mu\text{-}NHPh)_2{}^8$ and 117.9(1)° in $[(PhMe_2CCH_2)Ga(\mu\text{-}NH(t\text{-}Bu))]_2$.[9] We find that the $C(\alpha)-Ga-C(\alpha')$ angle decreases from 137.9(3)° to 117.9(1)° as the effective steric bulk of the bridging ligands increases in the order: $Cl < NHPr < NHPh < NH(t\text{-}Bu)$.

The two neophyl ligands appear to be slightly twisted relative to the Ga_2Cl_2 core. Thus, the plane C(10)–Ga(1)–C(20) makes an angle of 93.2° (rather than the expected 90°) with the Ga_2Cl_2 plane.

Finally, we note that the angles at the α-carbon atoms of the neophyl ligands show the customary increase from the ideal tetrahedral value of 109.5°, with ∠Ga(1)–C(10)–C(11) = 120.0(4)° and ∠Ga(1)–C(20)–C(21) = 116.2(4)°.

Crystal Structure of $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$

The crystallographic asymmetric unit consists of one monomeric molecule of $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$. The crystal is stabilized by a network of intermolecular Cl···H–N hydrogen bonds, as illustrated in Figure 2. The system of interest is characterized by Cl(1)···H(1A)*–N(1)* (where the asterisks represent a transformation of $x-1, y, z$ from the defined molecule). Distances and angles of interest include Cl(1)···H(1A)* = 2.61 Å,

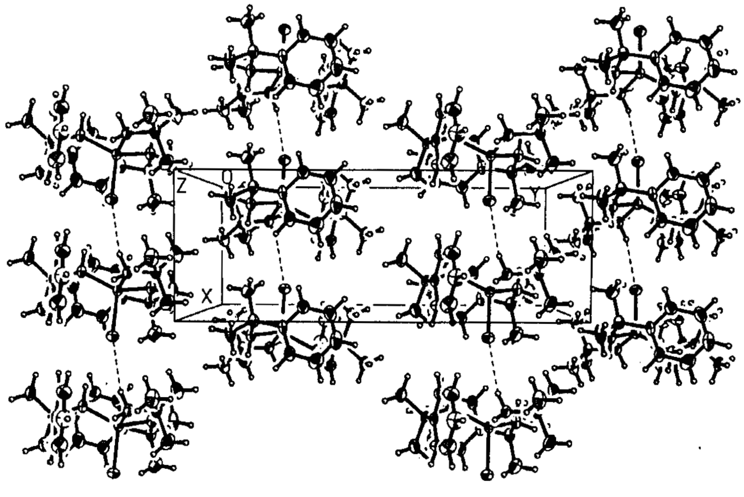


FIGURE 2 Crystal packing diagram for $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$. The *b*-axis is horizontal and the short *a*-axis is vertical. Note the Cl···H–N hydrogen bonding in the *x*-direction.

H(1A)*–N(1)* = 0.92 Å, Cl(1)···N(1)* = 3.51 Å and ∠Cl(1)···H(1A)*–N(1)* = 165°.

The atomic labeling of the monomeric compound is shown in Figure 3. Interatomic distances and angles are provided in Table V. The central gallium(III) atom has a distorted tetrahedral stereochemistry with angles ranging from C(10)–Ga(1)–C(20) = 121.3(2)° (between the two bulky neophyl ligands) down to Cl(1)–Ga(1)–N(1) = 96.3(2)°.

The two neophyl ligands are associated with gallium–carbon distances of Ga(1)–C(10) = 1.991(6) Å and Ga(1)–C(20) = 1.977(6) Å, with an average value of 1.984 Å – some 0.04 Å longer than in the chloro-bridged dimer (*vide supra*). Angles at the α-carbon atoms of the neophyl ligands are Ga(1)–C(10)–C(11) = 119.0(4)° and Ga(1)–C(20)–C(21) = 123.7(4)°.

The terminal gallium–chlorine linkage of 2.261(2) Å is, as expected, significantly shorter than the bridging gallium–chlorine distances (2.355(2)–2.440(2) Å) found in the chloro-bridged dimer.

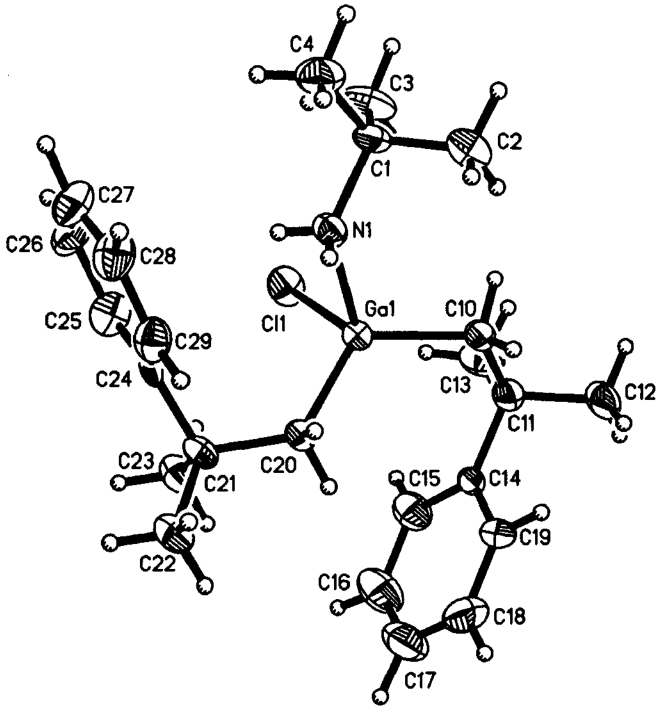


FIGURE 3 Molecular geometry for $(PhMe_2CCH_2)_2GaCl[NH_2(t\text{-}Bu)]$ (30% probability ellipsoids, with hydrogen atoms artificially reduced).

TABLE V Interatomic distances (Å) and angles (°) for $(PhMe_2CCH_2)_2GaCl[NH(t\text{-}Bu)]$

Bond lengths (Å)			
Ga(1)–Cl(1)	2.261(2)	Ga(1)–N(1)	2.093(7)
Ga(1)–C(10)	1.991(6)	Ga(1)–C(20)	1.977(6)
N(1)–H(1A)	0.919(62)	N(1)–H(1B)	0.786(74)
N(1)–C(1)	1.500(9)	C(1)–C(2)	1.517(10)
C(1)–C(3)	1.506(11)	C(1)–C(4)	1.516(11)
C(10)–C(11)	1.555(9)	C(11)–C(12)	1.529(10)
C(11)–C(13)	1.504(11)	C(11)–C(14)	1.528(9)
C(14)–C(15)	1.369(10)	C(14)–C(19)	1.366(10)
C(15)–C(16)	1.419(12)	C(16)–C(17)	1.345(15)
C(17)–C(18)	1.357(14)	C(18)–C(19)	1.382(12)
C(20)–C(21)	1.540(8)	C(21)–C(22)	1.532(9)
C(21)–C(23)	1.544(9)	C(21)–C(24)	1.541(9)
C(24)–C(25)	1.388(9)	C(24)–C(29)	1.409(10)
C(25)–C(26)	1.389(11)	C(26)–C(27)	1.368(13)
C(27)–C(28)	1.344(12)	C(28)–C(29)	1.380(11)
Bond angles (°)			
Cl(1)–Ga(1)–N(1)	96.3(2)	Cl(1)–Ga(1)–C(10)	109.8(2)
N(1)–Ga(1)–C(10)	109.4(2)	Cl(1)–Ga(1)–C(20)	115.0(2)
N(1)–Ga(1)–C(20)	101.5(3)	C(10)–Ga(1)–C(20)	121.3(2)
Ga(1)–N(1)–H(1A)	100.5(37)	Ga(1)–N(1)–H(1B)	94.2(54)
H(1A)–N(1)–H(1B)	97.5(66)	Ga(1)–N(1)–C(1)	130.7(5)
H(1A)–N(1)–C(1)	111.9(39)	H(1B)–N(1)–C(1)	116.1(55)
N(1)–C(1)–C(2)	106.8(5)	N(1)–C(1)–C(3)	108.4(6)
C(2)–C(1)–C(3)	110.4(6)	N(1)–C(1)–C(4)	109.7(6)
C(2)–C(1)–C(4)	110.2(6)	C(3)–C(1)–C(4)	111.2(6)
Ga(1)–C(10)–C(11)	119.0(4)	C(10)–C(11)–C(12)	109.1(6)
C(10)–C(11)–C(13)	108.4(5)	C(12)–C(11)–C(13)	108.0(6)
C(10)–C(11)–C(14)	109.3(5)	C(12)–C(11)–C(14)	109.4(5)
C(13)–C(11)–C(14)	112.5(6)	C(11)–C(14)–C(15)	123.2(6)
C(11)–C(14)–C(19)	120.6(6)	C(15)–C(14)–C(19)	116.2(6)
C(14)–C(15)–C(16)	121.0(7)	C(15)–C(16)–C(17)	120.1(9)
C(16)–C(17)–C(18)	120.0(9)	C(17)–C(18)–C(19)	119.2(9)
C(14)–C(19)–C(18)	123.5(7)	Ga(1)–C(20)–C(21)	123.7(4)
C(20)–C(21)–C(22)	109.7(5)	C(20)–C(21)–C(23)	109.5(5)
C(22)–C(21)–C(23)	107.7(5)	C(20)–C(21)–C(24)	108.7(5)
C(22)–C(21)–C(24)	110.1(5)	C(23)–C(21)–C(24)	111.2(5)
C(21)–C(24)–C(25)	123.8(6)	C(21)–C(24)–C(29)	119.4(6)
C(25)–C(24)–C(29)	116.6(6)	C(24)–C(25)–C(26)	121.3(7)
C(25)–C(26)–C(27)	120.3(7)	C(26)–C(27)–C(28)	119.7(7)
C(27)–C(28)–C(29)	121.4(8)	C(24)–C(29)–C(28)	120.6(6)

The *t*-butylamine ligand is associated with the Ga(1)–N(1) bond length of 2.093(7) Å. The molecule has an approximately (but not exactly) staggered conformation relative to the Ga(1)–N(1) axis (see Figure 4). The nitrogen atom has a distorted tetrahedral geometry, with the largest angle being Ga(1)–N(1)–C(1) = 130.7(5)°; other angles, of lower accuracy because of the large esd's associated with their refined hydrogen atoms are Ga(1)–N(1)–H(1B) = 94(5)°, H(1A)–N(1)–H(1B) = 98(7)°, Ga(1)–N(1)–H(1A) = 101(4)°, C(1)–N(1)–H(1A) = 112(4)° and C(1)–N(1)–H(1B) = 116(5)°.

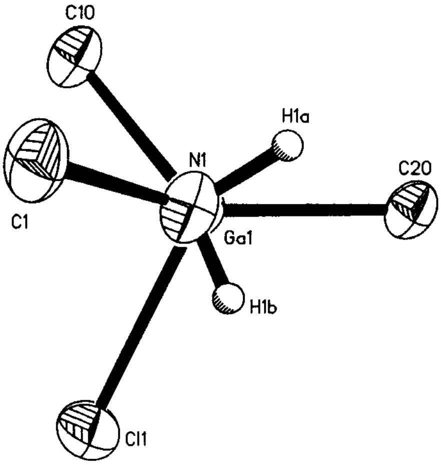


FIGURE 4 Conformation of the (PhMe$_2$CCH$_2$)$_2$GaCl[NH$_2$(*t*-Bu)] molecule about the Ga(1)–N(1) bond. Selected torsional angles[10] are as follows: C(1)–N(1)–Ga(1)–Cl(1) = −80.0°, C(1)–N(1)–Ga(1)–C(10) = 33.6° and C(1)–N(1)–Ga(1)–C(20) = 162.9°. For a Newman projection down N(1)–Ga(1), angles, increasing clockwise, are as follows: (top) H(1a) 0.0°, H(1b) 98.5°, C(1) 228.7°; (bottom) Cl(1) 148.8°, C(10) 262.3°, C(20) 31.6°.

The molecule, taken as a whole, resembles a "paddle-wheel", with Cl(1)–Ga(1) as its axis.

CONCLUSION

The crystal structures of [(PhMe$_2$CCH$_2$)$_2$GaCl]$_2$ and (PhMe$_2$CCH$_2$)$_2$-GaCl[NH$_2$(*t*-Bu)] have been examined and show interesting features including steric effects of the bulky neophyl ligands. The C(α)–Ga–C(α') angle is clearly rather "soft" and can be distorted so as to compensate for the lesser or greater cone-angles required by adjacent ligands.

Supplementary Material

Additional tabular material for the X-ray diffraction studies is available from M.R.C.

Acknowledgments

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References

[1] D.A. Atwood, R.A. Jones, A.H. Cowley, S.G. Bott and J.L. Atwood, *J. Organomet. Chem.*, **434**, 143 (1992).
[2] D.A. Atwood, R.A. Jones, A.H. Cowley, S.G. Bott and J.L. Atwood, *J. Organomet. Chem.*, **425**, C1 (1992).
[3] O.T. Beachley Jr., M.J. Noble, M.R. Churchill and C.H. Lake, *Organometallics*, **11**, 1051 (1992).
[4] M.R. Churchill, R.A. Lashewycz and F.J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).
[5] G.M. Sheldrick, *SHELXTL PLUS*, Release 4.11 (VMS), Siemens Analytical Instrument Corp.; Madison, WI (1989).
[6] *International Tables of X-Ray Crystallography.* (Kynoch Press, Birmingham, England, 1974), Vol. 4, pp. 99–101 and 149–150.
[7] M.R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
[8] O.T. Beachley Jr., M.J. Noble, M.R. Churchill and C.H. Lake, *Organometallics*, **17**, 3311 (1998).
[9] O.T. Beachley Jr., M.J. Noble, M.R. Churchill and C.H. Lake, *Organometallics*, **17**, 5153 (1998).
[10] F.H. Allen and D. Rogers, *Acta Cryst.*, **B25**, 1326 (1969).