chromatographic separation of product mixtures from the oxidations of IV by Br_2 in ethanol and of $Cr_2(CA_r)^{2+}$ by O_2 in water. Isosbestic points observed throughout the latter reaction confirm the absence of significant concentrations of products other than $Cr(H_2O)_6^{3+}$ and $Cr(CA_{ox})^+$. The grossly irreversible cyclic voltammograms of $Cr_2(CA_r)^{2+}$ in 0.1 M NH_4ClO_4 and 0.1 M $HClO_4$, with $i_{pa}/i_{pc} > 1$, suggest that the anodic oxidation rate and aqueous stability of $Cr_2(CA_{ox})^{4+}$ both fall off rapidly with increasing $[H^+]$.

The $Cr_2(CA_{ox})^{4+}$ species evidently is somewhat less susceptible to decay in 99% ethanol, as indicated by quasi-reversible voltammograms with i_{pa}/i_{pc} near 1. Nevertheless, peak-to-peak separations consistently were much larger than the value of 30 mV characteristic of a reversible, two-electron process. The 60 °C kinetic results demonstrate that a 100-fold excess of Cr(III) over H_2CA is needed to fully convert chloranilate into $Cr_2(CA_{ox})^{4+}$, even in 99% ethanol. The oxidizing strength of the quinonoid moity in $Cr_2(CA_{ox})^{4+}$ is strongly enhanced relative to that of free H_2CA in ethanol. Thus, the apparent $Cr_2(CA_{ox})^{4+}/Cr(CA_r)^{2+}$ $E_{1/2}$ of 0.46 V vs. SCE may be compared with that of 0.42 V vs. NHE (EtOH) reported for H_2CA in 95% EtOH-1 M HCl.[12] On this basis, we estimate a $\Delta E_{1/2}(Cr_2(CA_{ox})^{4+}$ vs. $H_2CA)$ of +0.28 V, corresponding to a substantial increase in the thermodynamic driving force (13 kcal/mol in $\Delta G°$).

The capability of $Cr_2(CA_{ox})^{4+}$, but not H_2CA, as an ethanol oxidation catalyst is a likely consequence of this increase in the thermodynamic driving force. Oxidation of primary alcohols typically proceeds through hydride ion transfer to the two-electron acceptor.[1] The first-order C_2H_5OH dependence observed above 16 M is consistent with rate-limiting direct hydride ion transfer from C_2H_5OH to the bridging CA_{ox}^{2-} ligand. A change of order from first to zeroth or simple zeroth-order ethanol dependence would be expected for the rate-determining two-electron transfer from coordinated C_2H_5OH to CA_{ox}^{2-}, mediated by the Cr atom. As was noted in the pioneering study,[8] the zeroth-order limiting [Cr(III)] dependence in 99% ethanol implies that substitution in the first coordination sphere of Cr(III), to form $Cr_2(CA_{ox})^{4+}$ from the separated reactants, is fast on the time scale of the redox process. The much slower rate of Cr(III) ligand substitution documented for predominantly aqueous solutions[45] accounts for the failure of chromic ion to catalyze the C_2H_5OH-H_2CA redox reaction in <90% ethanol.

The isolation of a solid containing the $Cr_2(CA_r)^{2+}$ unit was only partially successful, as II could not be redissolved in ethanol to give I or IV. Nevertheless, the transient visible spectrum in 0.1 M $HClO_4$ and the powder EPR signal are quite similar to those of the other Cr-$CASQ^{3-}$ complexes. Compound II evidently is a complex salt containing sodium and chromium cations to balance perchlorate, hydroxide, and chloranilate semiquinone anions. Charges balance to give a formula in good agreement with elemental analyses if chromium and chloranilate are present exclusively as Cr(III) and $CASQ^{3-}$, respectively, giving a neutral $Cr_5(CASQ)_2(ClO_4)_9$ core. The 13 Na^+ cations present per $Cr_5(CASQ)_2^{9+}$ unit presumably offset the charges of hydroxo ligands. Since II could not be recrystallized, we cannot be certain that the compound is entirely homogeneous, particularly with respect to Na^+, OH^-, and H_2O content. Nevertheless, the Cr, C, and Cl analyses strongly support the proposed 5:2 Cr(III): $CASQ^{3-}$ stoichiometry. The infrared spectrum of II is not particularly informative but does show a decrease in the C=O stretching frequency (1525 cm^{-1}) and band intensity compared with those of $Na_2CA\cdot 2H_2O$ (1560 cm^{-1}), as would be expected for a semiquinone complex. Although the structure of II remains in doubt, a particularly intriguing possibility, currently under investigation, involves the interaction of two parallel, planar $Cr_2(CASQ)^{3+}$ units, as ligands, with a central Cr(III) ion to form a π "sandwich" complex similar to bis(duroquinone)nickel(0).[44]

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Registry No. H_2CA, 87-88-7; Cr, 7440-47-3; ethanol, 64-17-5.

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Synthesis and Characterization of ((Trimethylsilyl)amino)- and (Methyl(trimethylsilyl)amino)gallium Dichloride

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The reaction of $GaCl_3$ with $(Me_3Si)_2NH$ has been found to yield $[Cl_2GaN(H)SiMe_3]_2$, and $[Cl_2GaN(Me)SiMe_3]_2$ was obtained from the reaction of $GaCl_3$ with $(Me_3Si)_2NMe$. The trans isomer of each dimer was identified in the solid state from X-ray crystallographic studies. Crystal data for *trans*-$[Cl_2GaN(H)SiMe_3]_2$: orthorhombic space group *Pbca* (No. 61), a = 9.207 (2) Å, b = 18.331 (5) Å, c = 11.344 (2) Å, V = 1914.6 (8) Å^3, Z = 4, ρ(calcd) = 1.588 g cm^{-1}. Crystal data for *trans*-$[Cl_2GaN(Me)SiMe_3]_2$: monoclinic space group $P2_1/c$ (No. 14), a = 11.594 (5) Å, b = 13.024 (7) Å, c = 13.663 (5) Å, β = 91.38 (4)°, V = 2062 (2) Å^3, Z = 4, ρ(calcd) = 1.564 g cm^{-1}. NMR data indicate the existence of an equilibrium mixture of $[Cl_2GaN(H)SiMe_3]_3$, *trans*-$[Cl_2GaN(H)SiMe_3]_2$, and *cis*-$[Cl_2GaN(H)SiMe_3]_2$ in solutions of ((trimethylsilyl)amino)gallium dichloride and an equilibrium mixture of the cis and trans isomers in solutions of $[Cl_2GaN(Me)SiMe_3]_2$. The temperature and solvent dependences of the equilibria were examined by ^1H NMR spectroscopy. The results of this study and the ^{13}C and ^{29}Si NMR spectra in toluene are reported.

Introduction

Reactions involving the cleavage of a Si-N bond in bis(trimethylsilyl)amine and substituted (trimethylsilyl)amines by gallium trichloride and alkylgallium dichlorides have been found to readily yield (substituted amino)gallium dichlorides and alkyl(amino)gallium chlorides. Substituted (trifluoroacetanilido)gallium dichlorides have been prepared from reactions of gallium trichloride with the corresponding substituted (trimethylsilyl)amines,[2] and ((trimethylsilyl)amino)gallium dichloride has been isolated from the thermal decomposition of (bis(tri-

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(1) (a) Davidson College. (b) University of South Carolina. (c) Emory University.

(2) Meller, A.; Maringgele, W.; Oesterle, R. *Monatsh. Chem.* **1980**, *111*, 1087.

methylsilyl)amino)gallium trichloride.[3] Both $[Me(Cl)GaN(H)SiMe_3]_2$ and $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$ have been obtained from the reactions of bis(trimethylsilyl)amine with $MeGaCl_2$ and $n\text{-}BuGaCl_2$.[4]

As an extension of our studies on the synthesis of substituted ((trimethylsilyl)amino)gallium chlorides,[4] the reactions of $GaCl_3$ with $(Me_3Si)_2NH$ and $(Me_3Si)_2NMe$ in ether were examined. During the investigation, the discovery of a trimer of ((trimethylsilyl)amino)gallium dichloride in solution led to an examination of the factors that affect the trimer–dimer equilibrium as well as the isomerization of dimeric ((trimethylsilyl)amino)gallium dichloride. The results of this study and the crystallographic characterizations of $[Cl_2GaN(H)SiMe_3]_2$ and $[Cl_2GaN(Me)SiMe_3]_2$ are reported.

Experimental Section

Materials and General Procedures. Gallium trichloride was prepared from gallium metal (Alcoa Co.) and chlorine (Air Products and Chemicals).[5] Bis(trimethylsilyl)amine (PCR Research Chemicals) was distilled at atmospheric pressure prior to use and methylbis(trimethylsilyl)amine (Petrarch Systems) was used without further purification. The solvents ether and methylene chloride were refluxed over sodium/benzophenone ketyl and phosphorus pentoxide, respectively, and distilled into storage flasks. All experiments were performed under an oxygen-free, dry-nitrogen or argon atmosphere by using Schlenk and glovebox techniques.[6]

The ^1H (80.07-MHz), ^{13}C (20.13-MHz), and ^{29}Si (15.91-MHz) NMR spectra were obtained from toluene-d_8 or methylene-d_2 chloride solutions with an IBM NR 80B spectrometer. Standard broad-band proton noise-modulated decoupling was used where appropriate (vide infra), and standard variable-temperature accessories were employed with an estimated accuracy of ±0.5 °C. Field frequency stabilization was provided by locking to the deuterium resonance of the deuterated solvent in the 5-mm sample tube (^1H, ^{13}C) or in a 10-mm tube in which the 5-mm sample tube was placed coaxially and the annular space between the two tubes was filled with the same deuterated solvent (^{29}Si). All NMR sample tubes (5 mm) were sealed under vacuum.

The ^1H, ^{13}C, and ^{29}Si chemical shifts are reported in parts per million (ppm) with respect to Me_4Si at 0.0 ppm. A positive chemical shift denotes a resonance to lower shielding (higher frequency). The ^1H chemical shifts were measured from the ^1H resonance of the residual $CHD_2C_6D_5$ (δ 2.09) and $CHDCl_2$ (δ 5.32) solvent impurity, and the chemical shifts in the ^{13}C NMR spectra were determined from the methyl ^{13}C resonance of the $CD_3C_6D_5$ solvent (δ 20.4). The ^{29}Si chemical shifts were measured with respect to 50% Me_4Si in toluene-d_8 by sample replacement. Attempts to measure the ^{29}Si NMR spectra by continuous broad-band ^1H decoupling produced only a null signal, and thus all ^{29}Si chemical shifts were acquired by the refocused INEPT[7] technique ($\tau = 1/4J_{SiH}$, $\Delta_{opt} = 0.108/J_{SiH}$ for nine equivalent ^1H's with an assumed value of $^2J_{SiH} = 6.6$ Hz ($^2J_{SiH}$ for Me_4Si); $90°(^1H) = 27.8$ μs, $180°(^1H) = 56.5$ μs, $90°(^{29}Si) = 12.0$ μs, $180°(^{29}Si) = 25.5$ μs; phase cycling of the $90°y(^1H)$ pulse was employed[8]).

Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer Model 283 spectrophotometer at high-resolution settings. Absorption intensities are reported with the abbreviations vw (very weak), w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder). All elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Table I. Experimental Data from the X-ray Diffraction Study

	$[Cl_2GaN(H)SiMe_3]_2$	$[Cl_2GaN(Me)SiMe_3]_2$
cryst syst	orthorhombic	monoclinic
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
cell dimens[a]		
a, Å	9.207 (2)	11.594 (5)
b, Å	18.331 (5)	13.024 (7)
c, Å	11.344 (2)	13.663 (5)
β, deg		91.38 (4)
V, $Å^3$	1914.6 (8)	2062 (2)
Z	4	4
mol wt	457.7	485.7
ρ(calcd), g cm^{-3}	1.588	1.564
radiation	Mo $K\bar{\alpha}$ ($\lambda = 0.71069$ Å)	
monochromator	graphite	
2θ range, deg	4–50	
scan type	$\theta/2\theta$	
scan speed, deg min^{-1}	2.02–29.3	
scan width, deg	1	
std reflcns	006, 800, 0,10,0	0,0,10, 080, 600
no. of unique data	1692	3659
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	1477	3025
abs coeff (μ), cm^{-1}	36.3	33.7
R	0.0460	0.0603
R_w	0.0424	0.0568
weighting scheme	$w = [\sigma^2(F_o) + 2 \times 10^{-4} \lvert F_o \rvert^2]^{-1}$	

[a] Unit cell parameters were derived from a least-squares refinement of 15 reflections ($9.67 \leqslant \theta \leqslant 14.69$; $9.05 \leqslant \theta \leqslant 13.87$).

Syntheses. ((Trimethylsilyl)amino)gallium Dichloride. To a stirred solution of freshly sublimed $GaCl_3$ (4.48 g, 25.4 mmol) in 20 mL of ether was added $(Me_3Si)_2NH$ (4.65 g, 28.8 mmol). After the solution was allowed to reflux for 12 h, the liquid portion was removed by vacuum distillation, leaving a crystalline solid (5.82 g). Recrystallization of the solid (3.37 g) from CH_2Cl_2 gave $[Cl_2GaN(H)SiMe_3]_2$ (1.45 g): mp 157–158 °C dec, lit.[3] mp 180 °C; ^1H NMR (toluene-d_8, 0.427 mol/L based on the monomeric unit, 25 °C (Figure 3)) δ 0.46 (s, CH_3Si), 0.39 (s, CH_3Si), 0.13 (s, CH_3Si), 0.08 (s, CH_3Si); ^1H NMR (methylene-d_2 chloride, 0.333 mol/L based on the monomeric unit, 25 °C) δ 0.60 (s, CH_3Si), 0.57 (s, CH_3Si), 0.41 (s, CH_3Si); ^{13}C NMR (toluene-d_8) δ 2.96 (s, CH_3Si), 2.88 (s, CH_3Si), 1.20 (s, CH_3Si), 1.14 (s, CH_3Si); ^{29}Si NMR (toluene-d_8) δ 27.95 (s, CH_3Si), 26.07 (s, CH_3Si), 21.60 (s, CH_3Si); IR (cm^{-1}) 3209 (s, $\nu(NH)$), 1277 (m, sh, $\delta_s(CH_3Si)$), 1263 (s, $\delta_s(CH_3Si)$), 1259 (s, $\delta_s(CH_3Si)$), 1210 (w), 1173 (w), 1132 (m, $\delta(NH)$), 1090 (w, sh), 1058 (w), 1022 (w), 975 (w, sh), 919 (s, $\nu(SiN)$), 848 (vs, $\rho_{as}(CH_3Si)$), 765 (m, $\rho_s(CH_3Si)$), 735 (s, $\rho_s(CH_3Si)$), 702 (m, $\nu_{as}(SiC_3)$), 635 (w, $\nu_s(SiC_3)$), 530 (m, $\nu(GaN)$), 502 (m, $\nu(GaN)$), 408 (m, $\nu(GaCl)$), 375 (m, $\nu(GaCl)$), 232 (vw).[9] Anal. Calcd for $C_3H_{10}Cl_2GaNSi$: C, 15.75; H, 4.40; Cl, 30.99; Ga, 30.47; N, 6.12; Si, 12.27. Found: C, 15.88; H, 4.52; Cl, 30.80; Ga, 30.78; N, 6.14; Si, 12.07.

Purification of the solid was also accomplished by fractional sublimation,[10] but partial decomposition of the solid was observed. Sublimation of the solid (0.99 g) at 0.001 torr gave two fractions and a nonvolatile residue (0.17 g). The IR spectra of both fractions (less volatile (0.37 g, mp 160–162 °C dec) and more volatile (0.083 g, mp 160–162 °C dec)) were identical with that of the recrystallized product. In addition, some of the sublimate (0.31 g, mp 160–161 °C dec) was carried to the unheated part of the sublimator by the volatile decomposition product.

(Methyl(trimethylsilyl)amino)gallium Dichloride. To a stirred solution of freshly sublimed $GaCl_3$ (8.09 g, 45.9 mmol) in 40 mL of ether was added $(Me_3Si)_2NMe$ (8.12 g, 46.3 mmol). After the solution was allowed to reflux for 11.5 h, the liquid portion was slowly removed by vacuum distillation. When approximately 4 mL of the solution remained, the crystalline solid (9.00 g, mp 160–167 °C) was filtered and washed with ether. Further purification of the solid was accomplished by fractional sublimation.[10]

In a typical sublimation of the solid (1.22 g) at 0.001 torr, two fractions were collected and a solid (0.080 g, mp 160–167 °C) along with a small amount of liquid was found in the unheated part of the sublimator. The less volatile fraction was a crystalline solid, $[Cl_2GaN(Me)SiMe_3]_2$ (0.734 g): mp 164–171 °C; ^1H NMR (toluene-d_8, 30 °C (Figure 4)) δ 2.62 (s, CH_3N), 2.55 (s, CH_3N), 0.24 (s, CH_3Si), 0.23 (s, CH_3Si); ^1H NMR (methylene-d_2 chloride, 19 °C) δ 2.89 (s, CH_3N), 2.83 (s, CH_3N), 0.464 (s, CH_3Si), 0.459 (s, CH_3Si); ^{13}C NMR (toluene-d_8) δ 37.26 (s, CH_3N), 35.29 (s, CH_3N), –0.48 (s, CH_3Si); ^{29}Si NMR (toluene-d_8) δ 26.52 (s, CH_3Si), 26.09 (s, CH_3,Si); IR (cm^{-1}) 1273 (s, sh), 1262 (vs), 1210 (w), 1170 (m, sh), 1156 (m, sh), 1152 (m), 1062

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Table II. Atom Coordinates ($\times 10^4$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
$[Cl_2GaN(H)SiMe_3]_2$							
Cl(1)	1041 (2)	6 (1)	2648 (1)	Si(1)	1698 (2)	−1403 (1)	41 (1)
Cl(2)	2514 (2)	1138 (1)	409 (2)	C(1)	3613 (8)	−1306 (5)	499 (9)
Ga(1)	964 (1)	310 (1)	819 (1)	C(2)	587 (10)	−1787 (4)	1249 (6)
N(1)	1042 (4)	−503 (2)	−322 (3)	C(3)	1523 (11)	−1945 (4)	−1332 (7)
$[Cl_2GaN(Me)SiMe_3]_2$							
Cl(11)	4596 (2)	2581 (1)	−78 (2)	Cl(21)	−2618 (2)	4321 (2)	5203 (2)
Cl(12)	2476 (2)	4306 (2)	580 (2)	Cl(22)	−681 (2)	4489 (2)	7185 (1)
Ga(1)	4237 (1)	4175 (1)	127 (1)	Ga(2)	−873 (1)	4684 (1)	5627 (1)
N(1)	5431 (4)	4864 (4)	960 (3)	N(2)	−363 (4)	6023 (4)	5100 (3)
C(14)	3553 (7)	5851 (7)	−1128 (6)	C(24)	−1278 (7)	6432 (6)	4384 (5)
Si(1)	4987 (2)	5379 (2)	2129 (1)	Si(2)	44 (2)	7042 (2)	5944 (1)
C(11)	4530 (10)	4254 (8)	2877 (7)	C(21)	−1274 (7)	7407 (7)	6577 (6)
C(12)	3778 (7)	6282 (7)	1968 (6)	C(22)	−1168 (9)	3417 (8)	3128 (7)
C(13)	6261 (8)	6026 (9)	2682 (7)	C(23)	−597 (8)	1881 (7)	4780 (7)

Table III. Intermolecular Distances (Å), Bond Angles (deg), and Selected Dihedral Angles (deg)

	$[Cl_2GaN(H)SiMe_3]_2$	$[Cl_2GaN(Me)SiMe_3]_2$[a]		$[Cl_2GaN(H)SiMe_3]_2$	$[Cl_2GaN(Me)SiMe_3]_2$[a]
Distances					
Ga···Ga′	2.810 (1)	2.810 (2), 2.807 (2)	N···N′	2.759	2.807, 2.810
Ga–Cl(1)	2.150 (2)	2.138 (2), 2.144 (2)	Ga–Cl(2)	2.136 (2)	2.155 (2), 2.150 (2)
Ga–N	1.974 (4)	1.985 (5), 1.983 (5)	Ga–N′	1.964 (4)	1.987 (5), 1.989 (5)
N–C(4)		1.515 (9), 1.523 (9)	N–H(4)	0.838 (47)	
N–Si	1.805 (4)	1.819 (5), 1.813 (5)	Si–C(1)	1.847 (7)	1.871 (11), 1.837 (9)
Si–C(2)	1.850 (8)	1.839 (8), 1.893 (10)	Si–C(3)	1.854 (7)	1.846 (10), 1.841 (9)
Angles					
Ga–N–Ga′	91.0 (1)	90.0 (2), 89.9 (2)	N–Ga–N′	89.0 (1)	90.0 (2), 90.1 (2)
Cl(1)–Ga–Cl(2)	111.9 (1)	107.7 (1), 108.4 (1)	Cl(1)–Ga···Ga′	123.7 (1)	127.0 (1), 126.1 (1)
Cl(2)–Ga···Ga′	124.5 (1)	125.4 (1), 125.4 (1)	Cl(1)–Ga–N	115.8 (1)	112.3 (2), 112.6 (2)
Cl(1)–Ga–N′	110.8 (1)	118.2 (2), 116.7 (2)	Cl(2)–Ga–N	111.7 (1)	116.9 (2), 116.0 (2)
Cl(2)–Ga–N′	116.0 (1)	111.5 (2), 112.4 (2)	C(4)–N–Si		109.3 (4), 108.6 (4)
H(4)–N–Si	109.5		C(4)–N···N′		118.5, 118.4
H(4)–N···N′	108.7		Si–N···N′	141.6	132.2, 133.0
Si–N–Ga	123.6 (2)	117.5 (3), 119.2 (3)	Si–N–Ga′	123.0 (2)	119.3 (3), 118.5 (3)
C(4)–N–Ga		109.8 (4), 109.4 (4)	C(4)–N–Ga′		109.7 (4), 109.9 (4)
H(4)–N–Ga	106.9		H(4)–N–Ga′	99.2	
C(1)–Si–N	107.2 (3)	106.3 (4), 106.4 (3)	C(2)–Si–N	109.4 (3)	111.2 (3), 111.1 (4)
C(3)–Si–N	105.6 (3)	106.7 (3), 107.7 (3)	C(1)–Si–C(2)	110.8 (4)	110.0 (4), 109.5 (4)
C(1)–Si–C(3)	111.8 (4)	111.6 (5), 111.1 (4)	C(2)–Si–C(3)	111.8 (3)	110.9 (4), 110.9 (4)
Dihedral Angles					
Cl(1)–Ga–Ga′–N′	86.1 (2)	94.7 (2), −93.2 (2)	Cl(1)–Ga–Ga′–N	−93.9 (2)	−85.3 (2), 86.8 (2)
Cl(2)–Ga–Ga′–N′	−93.5 (2)	−85.7 (2), 87.1 (2)	Cl(2)–Ga–Ga′–N	86.5 (2)	94.3 (2), −92.9 (2)
Si–N–N′–Ga	90.3	−88.5, 90.7	C(4)–N–N′–Ga		89.9, −89.7
H(4)–N–N′–Ga	−95.5		N′–N–Si–C(1)	−119.6	116.9, −120.2
N′–N–Si–C(2)	0.6	−2.8, −1.2	N′–N–Si–C(3)	121.0	−123.9, 120.5
H(4)–N–Si–C(1)	66.3 (37)		C(4)–N–Si–C(1)		−61.8 (6), 60.1 (5)
H(4)–N–Si–C(2)	−173.5 (37)		C(4)–N–Si–C(2)		178.5 (5), 179.2 (6)
H(4)–N–Si–C(3)	−53.1 (37)		C(4)–N–Si–C(3)		57.4 (6), −59.1 (5)
Ga–N–Si–C(1)	−61.0 (4)	64.0 (5), −66.0 (4)	Ga–N–Si–C(2)	59.2 (3)	−55.7 (4), 53.1 (6)
Ga–N–Si–C(3)	179.6 (4)	−176.8 (4), 174.7 (4)	Cl(1)–Ga–N–Si	−19.1 (3)	−115.9 (2), 117.8 (4)
Cl(1)–Ga–N–H(4)	−147.4 (38)		Cl(1)–Ga–N–C(4)		9.7 (4), −8.0 (4)
Cl(2)–Ga–N–H(4)	−17.8 (38)		Cl(2)–Ga–N–C(4)		134.8 (4), −133.8 (4)
Cl(2)–Ga–N–Si	110.6 (2)	9.2 (3), −8.0 (3)			

[a] Molecule 1, molecule 2.

(w), 955 (vs), 851 (vs), 767 (s), 719 (s, sh), 710 (s), 683 (s), 625 (w), 544 (s), 428 (m), 398 (m), 376 (m), 250 (vw). Anal. Calcd for $C_4H_{12}Cl_2GaNSi$: C, 19.78; H, 4.98; Cl, 29.20; Ga, 28.71; N, 5.77; Si, 11.56. Found: C, 19.93; H, 4.55; Cl, 28.68; Ga, 29.03; N, 5.68; Si 10.27. The more volatile fraction was a crystalline solid (0.104 g, mp 165–169 °C). Examination of the solid under 10× magnification revealed the presence of tiny droplets of liquid, and the crystals appeared to be identical in shape with those in the less volatile fraction.

Collection of Crystallographic Data. Colorless crystals of $[Cl_2GaN(H)SiMe_3]_2$ were grown by slowly cooling a saturated ether solution, and a suitable crystal was mounted in a capillary tube under an argon atmosphere. A suitable crystal of $[Cl_2GaN(Me)SiMe_3]_2$ was selected from the less volatile fraction of the sublimate and mounted in a capillary tube under an argon atmosphere. In each case the determination of the unit cell parameters and the orientation matrix as well as the collection of the intensity data were made on a Syntex P2$_1$ four-circle diffractometer. The diffractometer was equipped with a graphite monochromator (Bragg 2θ angle 12.2°) and used Mo Kα radiation. Unit cell parameters and details of the data collections are given in Table I.

Structure Determination and Refinement. In each case the positions of the gallium atoms were obtained from a Patterson map, and the positions of C, Cl, N, and Si atoms were taken from various Fourier maps. Several cycles of refinement with all non-hydrogen atoms anisotropic were completed by using a block-cascade algorithm as implemented in SHELXTL on the Nova Eclipse Model 140-S (Nicolet, Freemont, CA). The positions of the hydrogen atoms on the C(3) and N atoms in $[Cl_2GaN(H)SiMe_3]_2$ and the C(14), C(21), C(23), and C(24) atoms in $[Cl_2GaN(Me)SiMe_3]_2$ were obtained from a difference Fourier map and allowed to refine independently. The remaining hydrogen atoms were placed at fixed positions (C–H = 0.96 Å; H–C–H = 109.5°) and allowed to refine independently. Additional cycles of refinement led to $R = 0.0460$ and 0.0630 ($R = \sum||F_o| - |F_c||/|F_o|$) and $R_w = 0.0424$ and 0.0568 ($R_w = [\sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}]$). In the final cycle the mean shift/esd was 0.003 and 0.006.

Table IV. Thermodynamic Data for Toluene Solutions

$[Cl_2GaN(H)SiMe_3]_x$[a]			$[Cl_2GaN(Me)SiMe_3]_2$	
T, K	K_T,[b] mol/L	K_D[c]	T, K	K_D[c,d]
313	0.260	0.952	313	0.409, 0.402
324	0.654, 0.746	0.954, 0.945	323	0.423, 0.425
335	1.89, 1.96	0.981, 0.993	339	0.435, 0.439
345	4.38, 4.20	1.01, 1.02	352	0.451, 0.460
355	8.16, 7.30	1.06, 1.05	362	0.455
366	10.88, 10.53	1.07, 1.05		

[a] $x = 2, 3$. [b] $K_T = [\text{dimer}]^3/[\text{trimer}]^2$. [c] $K_D = [\text{cis dimer}]/[\text{trans dimer}]$. [d] Maintained at each temperature for at least 32 h prior to measurement.

Scattering factors for all atoms included real and imaginary anomalous dispersion components. In all refinements, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ and a weighting scheme based on counting statistics ($w = [\sigma^2(F_o) + 2 \times 10^{-4} |F_o|^2]^{-1}$) was employed for calculating R_w. The final positional parameters are found in Table II. The bond lengths, bond angles, and dihedral angles are given in Table III. Tables of observed and calculated structure factors and thermal parameters are available as supplementary material.

Thermodynamic Studies. The equilibrium constants, K_T, for the conversion of $[Cl_2GaN(H)SiMe_3]_3$ to $[Cl_2GaN(H)SiMe_3]_2$ (Table IV) at various temperatures were calculated from ^1H NMR data of a toluene-d_8 solution (0.427 mol/L based on the monomeric unit).[11] The solution was maintained at each temperature until no further change in the spectrum was observed (a minimum of 30 min). The equilibrium concentrations of the dimer were set equal to (0.427 mol/L)/2 times the ratio of the integration of the signals for the cis and trans dimers to the integration of the signals for the cis dimer, trans dimer, and trimer. The equilibrium concentrations of the trimer were calculated in a similar manner.

The equilibrium constants, K_D, for the isomerization of *trans*-$[Cl_2GaN(H)SiMe_3]_2$ to *cis*-$[Cl_2GaN(H)SiMe_3]_2$ at various temperatures (Table IV) were obtained from the ratios of the intensity of the signal for the cis isomer to the intensity of the signal for the trans isomer in the ^1H NMR spectra.[12] The equilibrium constants for the trans to cis isomerization of $[Cl_2GaN(Me)SiMe_3]_2$ at various temperatures (Table IV) were obtained from ^1H NMR data of a toluene-d_8 solution. The intensities of the signals that were assigned to the protons of the trimethylsilyl groups in the trans and cis isomers of $[Cl_2GaN(Me)SiMe_3]_2$ were used to calculate K_D.

Results and Discussion

When $(Me_3Si)_2NH$ or $(Me_3Si)_2NMe$ was allowed to react with $GaCl_3$ in a 1:1 mole ratio, $[Cl_2GaN(R)SiMe_3]_2$ was isolated where R = H or Me (eq 1). Both compounds are colorless crystalline

$$GaCl_3 + (Me_3Si)_2NR \rightarrow {}^1/_2[Cl_2GaN(R)SiMe_3]_2 + Me_3SiCl \tag{1}$$

solids and are stable to elimination of Me_3SiCl at room temperature. However, when $[Cl_2GaN(H)SiMe_3]_2$ was heated just above the melting point for 1.5 h, Me_3SiCl (39% yield) and an unidentified solid were obtained. The solid did not melt below 360 °C. The compound $[Cl_2GaN(H)SiMe_3]_2$ has been prepared previously from the thermal decomposition of $(Me_3Si)_2NH{\cdot}GaCl_3$.[3]

Since two geometrical isomers (cis and trans) of the dimer $[Cl_2GaN(R)SiMe_3]_2$ are possible, isolation of these isomers as well as other oligomers from the solid products was attempted by means of fractional sublimation.[10] The sublimation of each solid product gave two fractions, but the crystalline solids in each fraction appeared to be identical. In the case of $[Cl_2GaN(Me)SiMe_3]_2$, the melting point ranges of the solids and the shape of the crystals in both fractions were very similar. The broad melting point range of the sublimate suggests that both isomers may be present and that the separation of the isomers by sublimation was not affected. However, isomerization during the melting of the pure compound could also account for the broad melting point range.[13] In the case of $[Cl_2GaN(H)SiMe_3]_2$, the IR spectra and melting points of both fractions were identical. These data and the narrow melting point range strongly support the assertion that only one isomer of $[Cl_2GaN(H)SiMe_3]_2$ is present in the isolated solid.

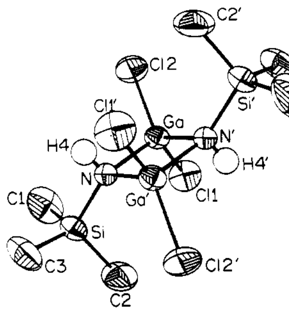

Figure 1. ORTEP diagram of $[Cl_2GaN(H)SiMe_3]_2$.

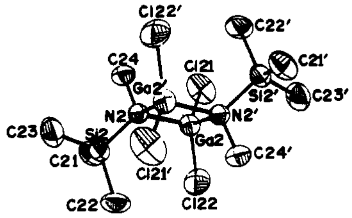

Figure 2. ORTEP diagram of $[Cl_2GaN(Me)SiMe_3]_2$ (molecule 2).

The crystal and molecular structures of the isolated compounds were determined from X-ray crystallographic studies. The ORTEP diagrams of $[Cl_2GaN(H)SiMe_3]_2$ and $[Cl_2GaN(Me)SiMe_3]_2$ are shown in Figures 1 and 2. Each dimer has a crystallographically imposed C_i symmetry. The least-squares plane calculations indicate that the four-membered $(GaN)_2$ ring in each dimer is planar with a root-mean-square displacement from the ring of 0.0000 for each ring atom.[14] The plane that is formed by the Si, N, and N' atoms makes an angle of 90.3 and 91.1° (av) with the $(GaN)_2$ ring in the respective dimers, and the C(2) atoms lie above and below the ring. In $[Cl_2GaN(H)SiMe_3]_2$, the plane of the Cl(1), Ga, and Cl(2) atoms is tilted away from the trimethylsilyl groups and forms an angle of 93.7° (av) with the $(GaN)_2$ ring. The corresponding angle in $[Cl_2GaN(Me)SiMe_3]_2$ is 93.8° (av). The N–H bond length of 0.838 (47) Å compares favorably with the value of 0.85 (5) Å in $(GaN)_6(GaH_2)_2(\mu_3\text{-}O)_2(\mu_3\text{-}NCH_2CH_2NMe_2)_4(\mu\text{-}NHCH_2CH_2NMe_2)_2$.[15]

A comparison of the bond lengths and angles for $[Cl_2GaN(H)SiMe_3]_2$ and $[Cl_2GaN(Me)SiMe_3]_2$ (Table III) reveals some interesting features. Despite the fact that the hydrogen atom on the nitrogen atom in the former dimer has been replaced with a methyl group in the latter dimer, there is no significant change in the Ga–Cl, Ga–N, and Si–N bond lengths. However, the Si–N···N' angle (141.6°) in $[Cl_2GaN(H)SiMe_3]_2$ is substantially larger than the corresponding angle (132.5° (av)) in $[Cl_2GaN(Me)SiMe_3]_2$, and the C(2)–Si–N angle (109.4 (3)°) is smaller when compared wth the C(2)–Si–N angle (111.2° (av)) in the latter compound. The values for the Cl(1)–Ga–Cl(2) angles are 111.9 (1) and 108.0° (av). These differences in the angles of the two dimers are probably a consequence of the larger steric requirements of the methyl groups on the nitrogen atoms in $[Cl_2GaN(Me)SiMe_3]_2$.

When the bond lengths and angles for $[Cl_2GaN(H)SiMe_3]_2$ and $[Me(Cl)GaN(H)SiMe_3]_2$ are compared,[4] the Ga–Cl bond length (2.143 Å (av)) in the former dimer is found to be shorter than the corresponding length (2.212 (3) Å) in the latter dimer. The Cl–Ga···Ga' angle (124.1° (av)) is larger than the corresponding angle (113.6°) and smaller than the C(1)-Ga···Ga' angle (133.7°) in $[Me(Cl)GaN(H)SiMe_3]_2$. Since the van der Waals radii of the chlorine atom and the methyl group (1.70–1.90 and

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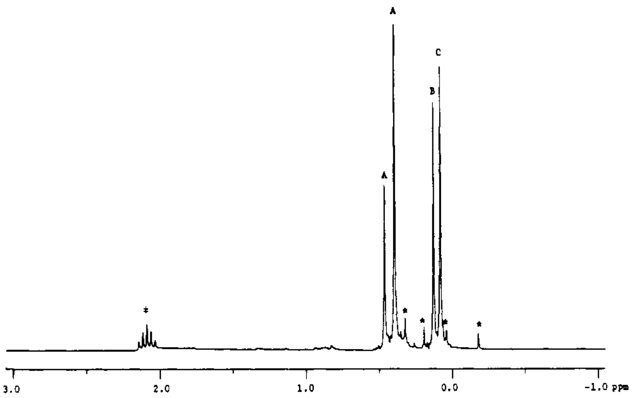

Figure 3. ^1H NMR spectrum of a toluene solution of ((trimethylsilyl)amino)gallium dichloride at 25 °C: A, trimer; B, cis dimer; C, trans dimer; asterisk, decomposition products; dagger, $CHD_2C_6D_5$.

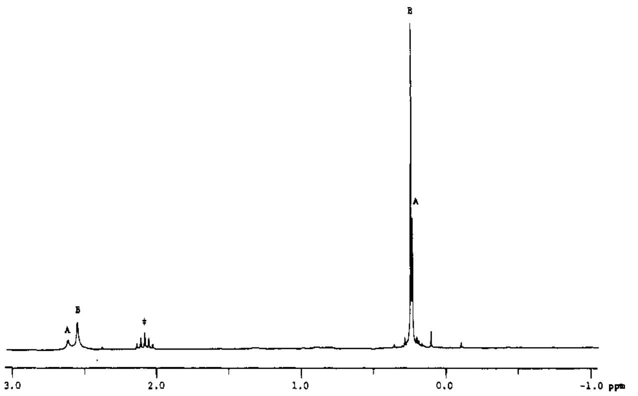

Figure 4. ^1H NMR spectrum of a toluene solution of $[Cl_2GaN(Me)SiMe_3]_2$ at 30 °C: A, cis dimer; B, trans dimer; dagger, $CHD_2C_6D_5$.

2.00 Å)[16] are similar, these differences may be attributed to electronic effects. The minimization of the steric strain between the chlorine atoms and the trimethylsilyl groups in the former compound is probably achieved through a lengthening of the Si–N bond (1.805 (4) Å). In $[Me(Cl)GaN(H)SiMe_3]_2$, the Si–N bond length is shorter (1.744 (8) Å) and the steric strain is probably reduced through the tilting of the plane of the Si, N, and N′ atoms away from the chlorine atoms (93.2° with respect to the $(GaN)_2$ ring) and the rotation (7.2° from the Si–N···N′ plane) of the C(4) atom (corresponds to the C(2) atom in this study) toward the C(1) atom. The large C(1)–Ga···Ga′ angle minimizes the steric interaction between the methyl group on the gallium atom and the trimethylsilyl group.

The ^1H NMR spectrum of ((trimethylsilyl)amino)gallium dichloride in toluene-d_8 (Figure 3) is found to be concentration and temperature dependent. The relative intensities of the signals at 0.13 and 0.08 ppm to the intensities of the signals at 0.46 and 0.39 ppm increase with a decrease in concentration and an increase in temperature. The cryoscopic molecular weight measurement of this compound in benzene indicates a degree of association of 2.33.[3] These data are consistent with the existence of a trimer–dimer equilibrium in solution. The singlets at 0.13 and 0.08 ppm have been assigned to the protons of the trimethylsilyl groups in the cis and trans dimers. These assignments are based on the assumption that the steric strain between the trimethylsilyl groups in the cis isomer will be large and, hence, the trans isomer will be the more thermodynamically stable dimer. The two signals at 0.46 and 0.39 ppm, which are in the ratio of 1:2, are assigned to the protons of the trimethylsilyl groups in the trans isomer of the trimer. The *trans*-$[Cl_2GaN(H)SiMe_3]_3$ probably has a skew-boat conformation, which is similar to the reported structure of *trans*-$[Me_2AlN(H)Me]_3$.[17] The skew-boat conformation has also been proposed for the structure of the *trans*-$[H_2GaN(H)Et]_3$. The ^1H NMR spectrum of this compound contained two triplets for the protons of the β-methyl groups in a 1:2 ratio.[18]

The equilibrium constants (K_T) for the conversion of $[Cl_2GaN(H)SiMe_3]_3$ to $[Cl_2GaN(H)SiMe_3]_2$ (eq 2) in toluene

$$2[Cl_2GaN(H)SiMe_3]_3 \rightleftarrows 3[Cl_2GaN(H)SiMe_3]_2 \qquad (2)$$

at various temperatures are listed in Table IV. A least-squares plot of ln K_T vs. $1/T$ gave ΔH = 68 (3) kJ/mol and ΔS = 206 (9) J/(mol K) with r^2 = 0.98. These values are comparable in magnitude to the values that were reported for the trimer–dimer equilibrium of dimethyl(azetidino)aluminum in benzene (ΔH = 57.8 kJ/mol, ΔS = 162 J/(mol K)).[11] As expected, the entropy change favors the formation of the dimer although the trimer is the more thermodynamically stable species. In methylene chloride, the equilibrium is shifted to the left with K_T = 0.0390 mol/L at 25 °C (0.0871 mol/L (calcd) in toluene at 25 °C).

Steric effects, entropy, and valency angle strain have been found to play a major role in the position of the trimer–dimer equilibrium.[11,17-19] When the steric strain between the substituents and the entropy is large, the equilibrium lies to the right and the dimer is the favored oligomer. For example, in *tert*-butylaminogallane the large steric interactions between the *tert*-butyl groups would be expected to reduce the stability of the trimer and drive the equilibrium to the right. Indeed, only the cis and trans isomers of $[H_2GaN(H)\text{-}t\text{-}Bu]_2$ have been observed in benzene solutions.[18] When the steric strain between the substituents is small such as in $[H_2GaN(H)Me]_3$,[20] the valency angle strain in the dimer becomes the dominant factor and the equilibrium lies to the left. In the ((trimethylsilyl)amino)gallium dichloride system, observable quantities of the trimer and dimers are present at room temperature and, hence, the steric strain between the trimethylsilyl groups in the trimer is less than the valency angle strain in the dimer. Since the valency angle strains should be comparable in $[Cl_2GaN(H)SiMe_3]_2$ and $[H_2GaN(H)\text{-}t\text{-}Bu]_2$, the presence of $[Cl_2GaN(H)SiMe_3]_3$ in solution but not $[H_2GaN(H)\text{-}t\text{-}Bu]_3$ suggests that the steric interactions between the *tert*-butyl groups are significantly larger than the interactions between the trimethylsilyl groups. The smaller steric strain between the trimethylsilyl groups is probably the result of the longer Si–N and Si–C bond lengths in comparison to the C–N and C–C lengths.

The temperature dependence of the equilibrium for the trans to cis isomerization of $[Cl_2GaN(H)SiMe_3]_2$ (eq 3) in toluene was

$$trans\text{-}[Cl_2GaN(H)SiMe_3]_2 \rightleftarrows cis\text{-}[Cl_2GaN(H)SiMe_3]_2 \qquad (3)$$

also examined (Table IV). A least-squares plot of ln K_D vs. $1/T$ gave ΔH = 2.4 (2) kJ/mol and ΔS = 7.1 (6) J/(mol K) with r^2 = 0.93. The algebraic signs of ΔH and ΔS are dependent on the assumption that the trans isomer is the more thermodynamically stable dimer. The cis and trans isomers of $[Me_2GaN(Me)Ph]_2$ were identified unequivocally in the ^1H NMR spectrum, and temperature studies of the trans to cis isomerization in methylene chloride have shown that the trans isomer is the more stable dimer (ΔH = 4.16 kJ/mol, ΔS = 21.8 J/(mol K)).[21] In the ^1H NMR spectrum of ((trimethylsilyl)amino)gallium dichloride in methylene chloride, only the singlet at 0.41 ppm can be assigned to the protons of the trimethylsilyl groups in the dimer. While it would appear that only one isomer of $[Cl_2GaN(H)SiMe_3]_2$ is present in the methylene chloride solution, it is also possible that the chemical shifts of the signals for the cis and trans isomers of the dimer are accidentally coincident and, hence, indistinguishable. The chemical shifts of the signals for the cis and trans isomers of $[Cl_2GaN(Me)SiMe_3]_2$ differ by only 0.005 ppm in methylene chloride. Solutions of ((trimethylsilyl)amino)gallium dichloride have been

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found to decompose within several days in methylene chloride and several months in toluene at room temperature.

The ^1H NMR spectrum of (methyl(trimethylsilyl)amino)gallium dichloride in toluene (Figure 4) is temperature dependent and concentration independent. The intensities of the singlets at 2.62 and 0.23 ppm increase with respect to the intensities of the singlets at 2.55 and 0.24 ppm with an increase in temperature. The assignment of the former singlets to the protons of the methyl and trimethylsilyl groups in *cis*-$[Cl_2GaN(Me)SiMe_3]_2$ and the latter singlets to the corresponding protons in *trans*-$[Cl_2GaN(Me)SiMe_3]_2$ is based on the assumption that the trans isomer is the more thermodynamically stable dimer. The equilibrium constants (K_D = [cis]/[trans]) for the trans to cis isomerization of $[Cl_2GaN(Me)SiMe_3]_2$ in toluene at various temperatures are listed in Table IV. The values of ΔH and ΔS (2.4 (2) kJ/mol, 0.08 (69) J/(mol K)) for the isomerization were obtained from a least-squares plot of ln K_D vs. $1/T$ ($r^2 = 0.94$). In methylene chloride, the equilibrium is shifted to the right with $K_D = 0.479$ at 19 °C (0.383 (calcd) in toluene at 19 °C). This result suggests that the cis isomer is more readily solvated by polar solvents.

In summary, equilibrium mixtures of the trans trimer and the cis and trans dimers have been observed in solutions of ((trimethylsilyl)amino)gallium dichloride. In solutions of (methyl(trimethylsilyl)amino)gallium dichloride, only the cis and trans dimers were identified. The position of the trimer–dimer equilibrium depends primarily on the steric strain of the substituents, entropy, and the valency angle strain in the dimer. Although the entropy favors the formation of the dimer in both systems, the valency angle strain in $[Cl_2GaN(H)SiMe_3]_2$ is greater than the steric strain in $[Cl_2GaN(H)SiMe_3]_3$, and the trimer as well as the cis and trans isomers of the dimer is present in solutions of ((trimethylsilyl)amino)gallium dichloride. With both a methyl and a trimethylsilyl group on the nitrogen atoms, the steric strain in the trimer will be substantially larger than the valency angle strain in the dimer and, hence, only the cis and trans isomers of $[Cl_2GaN(Me)SiMe_3]_2$ are observed in solution. The equilibria do exhibit a solvent dependency, but the effects of the solvent on the positions of the equilibria are small. Although the trimer and the cis and trans isomers of the dimer are present in solutions of ((trimethylsilyl)amino)gallium dichloride, *trans*-$[Cl_2GaN(H)SiMe_3]_2$ appears to be the only species in the solid state. Likewise, the trans isomer is the predominant if not the only isomer that precipitates from solutions of $[Cl_2GaN(Me)SiMe_3]_2$. These results would suggest that the trans isomer of the dimer is the least soluble species in the polar solvents that were used in the syntheses and recrystallizations of these compounds.

Acknowledgment. The partial support of this research by The Camille and Henry Dreyfus Foundation and Davidson College is gratefully acknowledged. J.A.A. and J.D.O. gratefully acknowledge the financial support from the National Science Foundation (Grant CHE-80-13694) and helpful discussions with Dr. Ron Garber.

Registry No. *trans*-$[Cl_2GaN(H)SiMe_3]_2$, 93779-95-4; *cis*-$[Cl_2GaN(H)SiMe_3]_2$, 93779-96-5; *trans*-$[Cl_2GaN(Me)SiMe_3]_2$, 93683-64-8; *cis*-$[Cl_2GaN(Me)SiMe_3]_2$, 93780-86-0; *trans*-$[Cl_2GaN(H)SiMe_3]_3$, 93714-41-1.

Supplementary Material Available: Listings of hydrogen coordinates, anisotropic temperature factors, and observed and calculated structure factors as well as figures showing ^1H NMR spectra of ((trimethylsilyl)amino)gallium dichloride and $[Cl_2GaN(Me)SiMe_3]_2$ in methylene chloride (33 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto per lo Studio della Stereochimica
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Tetrahedral Structure of the High-Spin Cobalt(I) Complex $(np_3)CoBr$. A Symmetry-Forbidden Rearrangement to Five-Coordination

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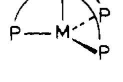
The crystal structure of $(np_3)CoBr$, np_3 = tris(2-(diphenylphosphino)ethyl)amine, has been examined by X-ray methods with the aim of determining whether the triplet ground state of the molecule depends on a particular stereochemistry. Analogous complexes of Co(I), where H and CN replace the bromine anion, are diamagnetic with a trigonal-bipyramidal structure. The application of the 18-electron rule easily rationalizes the latter geometry, where the amine group of np_3 is apically coordinated to the d^8 metal. On the other hand, the tripodal np_3 ligand is known to be flexible enough to coordinate only through its phosphorus atoms, while retaining C_{3v} symmetry. This type of arrangement is found in the title compound, where the cobalt is tetrahedrally coordinated by the phosphorus and bromine atoms. The Co–N distance is 3.34 (1) Å, and the P–Co–Br and P–Co–P angles average 115.2 (20) and 103.2 (3)°, respectively. The space group is monoclinic $P2_1$; the unit cell dimensions are a = 20.578 (9) Å, b = 8.979 (4) Å, c = 10.186 (5) Å, β = 91.15 (6)°, V = 1181.69 Å^3, and Z = 2. Qualitative MO arguments, supported by extended Hückel calculations, indicate that transformation to the trigonal-bipyramidal geometry, attainable by translation of the amine along the threefold axis, may be in some cases symmetry forbidden as a result of a level crossing that switches the nature of HOMO–LUMO levels.

Introduction

The ligand tris(2-(diphenylphosphino)ethyl)amine, np_3, has a very rich coordination chemistry in terms of both unusual stereochemical features and reactivity that it confers to its products. The ligand may use either all of its donor atoms (one N and three P) or only the phosphorus atoms to achieve coordination to the metal; there is no major steric obstacle to adoption of either conformation **1** or **2**.[1] The electronic requirements imposed by the metal and the coligands ultimately determine the coordination mode of np_3.



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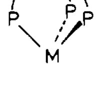

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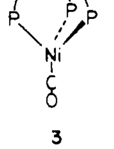

3

Generally the 18-electron rule is suited to predict or rationalize the presence of a trans axial ligand, for example in the case of a CO molecule as shown in **3**.[2] On the other hand, the coordination of nitrogen and the stabilization of the unusual trigonal-pyramidal geometry (TP) is observed in the absence of other coligands (structure **1** is adopted by the complex $(np_3)Ni$).[3] The d^8 configuration predictably favors the trigonal-bipyramidal ge-

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(1) Experimental crystallographic data for a number of complexes containing np_3 variously elongated show that the ligand easily allows the interconversion by simple torsions at the C–C bond of the chains.

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