by the column. In view of the high, >70%, combined yield of the isolated compounds **3** and **4**, this side reaction, if it occurred, took place only to a limited extent.

The analytical data obtained for (Me₃Si)₂NB(NH₂)₂ and [(Me₃Si)₂NBNH₂]₂NH are in agreement with the assigned structures. Both compounds exhibited in their mass spectra a high-intensity molecular ion, and the breakdown patterns were consistent with the arrangements. In each case, a prominent ion was observed corresponding to loss of a methyl group and ammonia. Ions derived by loss of ammonia were absent in the mass spectra of **1** and **2**, which is to be expected due to the absence of NH₂ groups. Neither compound exhibited an infrared absorption at ~1100 cm⁻¹, confirming the absence of NHSiMe₃ groups; both had very strong bands in the vicinity of 1600 cm⁻¹, characteristic of a NH₂ deformation mode. The ¹H NMR of **3** showed two resonances at δ 0.18 (CH₃) and 1.63 (NH₂); for **4** three resonances were observed at δ 0.18 (CH₃), 2.31 (NH₂), and 2.84 (NH), confirming the presence of the three different NH protons. The ¹¹B NMR signal was broader in **4** than in **3**, which is to be expected. The chemical shifts, 31.8 and 33.0 ppm, respectively, are consistent with the literature data.[20]

Only preliminary thermal stability studies were performed on **4**. The material was recovered essentially unchanged when exposed to 150 °C for 20 h. However, after 20 h at 200 °C, no starting material was recovered. The two borazines [(Me₃Si)₂NBNH]₂[(Me₃Si)HNBNH] and [(Me₃Si)₂NBNH]₃ were produced in approximately equal proportions, together with a small amount of [(Me₃Si)₂NBNH][(Me₃Si)HNBNH]₂.
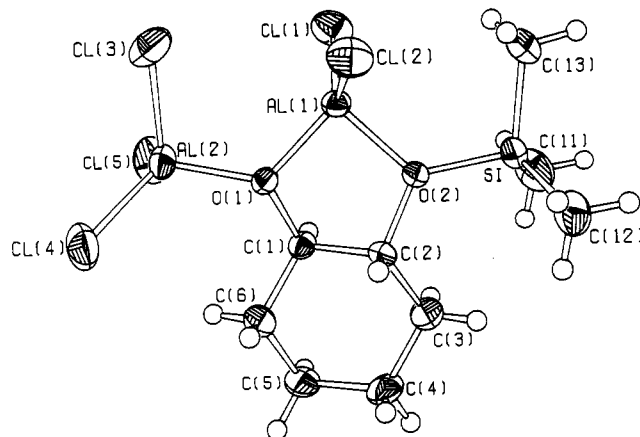

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Complex of a Silyl Ether with a Dichloroaluminum Alkoxide. Reaction of the Bis(trimethylsilyl) Ether of *trans*-1,2-Cyclohexanediol with Aluminum Chloride

Vijay Sharma, Michel Simard, and James D. Wuest*

In attempting to prepare dichloroaluminum alkoxide **1**, a novel bidentate Lewis acid,[1] we added the bis(trimethylsilyl) ether **2**[2] of *trans*-1,2-cyclohexanediol to a suspension of 2 equiv of aluminum chloride in CH₂Cl₂ at 25 °C. This reaction yielded a crystalline compound that was not the expected product **1** of complete desilylation. Instead, its ¹H NMR spectrum showed a single trimethylsilyl signal shifted 0.56 ppm downfield from that of starting material **2**, and its elemental analysis confirmed that

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(1) For references to related work on multidentate Lewis acids, see: Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955–958. Galeffi, B.; Simard, M.; Wuest, J. D. *Ibid.* **1990**, *29*, 951–954. Bélanger-Gariépy, F.; Hoogsteen, K.; Sharma, V.; Wuest, J. D. *Ibid.*, submitted for publication. Bachand, B.; Bélanger-Gariépy, F.; Wuest, J. D. *Organometallics* **1990**, *9*, 2860–2862.
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Figure 1. ORTEP drawing of the structure of the chloroaluminum alkoxide **3**. Non-hydrogen atoms are represented by ellipsoids corresponding to 50% probability, and hydrogen atoms are shown as spheres of arbitrary size.

Table I. Crystallographic Data for the Chloroaluminum Alkoxide **3** and Experimental Parameters

formula	C₉H₁₉Al₂Cl₅O₂Si
fw	418.564
cryst syst	monoclinic
space group	P2₁/c
cell const	
a, Å	8.817 (2)
b, Å	13.729 (5)
c, Å	19.485 (5)
β, deg	126.63 (2)
cell volume (Å³)	1892.8
Z	4
T (K)	190
ρ_{calcd}, g cm⁻³	1.469
μ_{calcd}, cm⁻¹	9.20
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)
cryst dimens, mm	0.28 × 0.36 × 0.70
scan width	1.00 + 0.35 tan θ
$2\theta_{max}$, deg	50.0
data collcn range	±*h,k,l*
no. of reflcns collcd	3598
no. of reflcns retained	2759 (*I* ≥ 3.00σ(*I*))
no. of params refined	208
goodness-of-fit	2.08
R	0.031
R_w	0.036

only 1 equiv of chlorotrimethylsilane had been lost. Structure **3** is consistent with these observations but includes two unusual features: coordination of a silyl ether by a Lewis acid[3] and a trans junction of five- and six-membered rings.
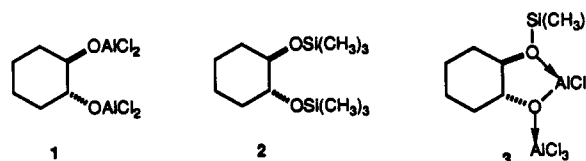
An X-ray crystallographic study confirmed this assignment and provided the structure shown in Figure 1. Crystallographic data

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Table II. Coordinates (×10⁵; C and O ×10⁴) and Equivalent Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for the Non-Hydrogen Atoms of the Chloroaluminum Alkoxide 3

atom	x	y	z	U_{eq}
Al(1)	15060 (9)	59180 (5)	41720 (4)	25
Al(2)	14778 (10)	52568 (5)	25942 (4)	34
Cl(1)	−14256 (9)	59893 (6)	34691 (4)	48
Cl(2)	29989 (10)	48775 (5)	51321 (4)	44
Cl(3)	6718 (13)	40221 (5)	29561 (5)	64
Cl(4)	36022 (11)	49096 (6)	24555 (5)	55
Cl(5)	−7936 (10)	59759 (6)	14917 (4)	58
Si	24380 (10)	76867 (5)	54535 (4)	32
O(1)	2260 (2)	6058 (1)	3493 (1)	26
O(2)	2504 (2)	7125 (1)	4662 (1)	27
C(1)	2783 (5)	7064 (3)	3515 (2)	24
C(2)	3779 (5)	7417 (3)	4430 (2)	26
C(3)	4242 (4)	8482 (2)	4517 (2)	43
C(4)	5444 (6)	8661 (3)	4221 (3)	45
C(5)	4587 (6)	8272 (3)	3313 (3)	41
C(6)	4024 (4)	7233 (2)	3235 (2)	40
C(1')	3622 (9)	6912 (5)	3832 (5)	31
C(2')	2988 (9)	7637 (5)	4156 (4)	28
C(4')	4819 (11)	8886 (6)	4002 (6)	47
C(5')	5385 (10)	8126 (6)	3658 (5)	51
C(11)	1042 (5)	8810 (2)	4977 (2)	58
C(12)	4899 (4)	7864 (3)	6402 (2)	60
C(13)	1224 (4)	6821 (2)	5693 (2)	53

Table III. Selected Bond Lengths (Å) and Angles (deg) in the Chloroaluminum Alkoxide 3

	Bond Lengths		
Al(1)–Cl(1)	2.0838 (12)	Al(2)–Cl(5)	2.1134 (10)
Al(1)–Cl(2)	2.0820 (9)	Al(2)–O(1)	1.820 (2)
Al(1)–O(1)	1.811 (2)	Si–O(2)	1.756 (2)
Al(1)–O(2)	1.852 (2)	Si–C(11)	1.842 (3)
Al(2)–Cl(3)	2.1151 (12)	Si–C(12)	1.843 (3)
Al(2)–Cl(4)	2.1007 (15)	Si–C(13)	1.836 (4)

	Bond Angles		
Cl(1)-Al(1)-Cl(2)	119.61 (5)	O(2)-Si-C(11)	106.70 (13)
Cl(1)-Al(1)-O(1)	111.53 (7)	O(2)-Si-C(12)	107.61 (13)
Cl(1)-Al(1)-O(2)	108.56 (7)	O(2)-Si-C(13)	105.59 (13)
Cl(2)-Al(1)-O(1)	114.74 (7)	C(11)-Si-C(12)	115.32 (16)
Cl(2)-Al(1)-O(2)	107.43 (7)	C(11)-Si-C(13)	110.76 (16)
O(1)-Al(1)-O(2)	90.75 (8)	C(12)-Si-C(13)	110.28 (16)
Cl(3)-Al(2)-Cl(4)	111.33 (5)	Al(1)-O(1)-Al(2)	123.06 (10)
Cl(3)-Al(2)-Cl(5)	114.21 (5)	Al(1)-O(1)-C(1)	109.2 (2)
Cl(3)-Al(2)-O(1)	99.98 (7)	Al(2)-O(1)-C(1)	122.4 (2)
Cl(4)-Al(2)-Cl(5)	110.62 (5)	Al(1)-O(2)-Si	126.24 (10)
Cl(4)-Al(2)-O(1)	113.95 (7)	Al(1)-O(2)-C(2)	107.2 (2)
Cl(5)-Al(2)-O(1)	106.32 (7)	Si-O(2)-C(2)	124.9 (2)

and experimental parameters are summarized in Table I, atomic coordinates are listed in Table II, and selected bond lengths and angles are compiled in Table III. The six-membered ring adopts a normal chair conformation, while the oxygen, aluminum, and silicon atoms associated with the five-membered ring lie close to a common plane. Both oxygens are nearly trigonal, while silicon and both aluminums are approximately tetrahedral. As expected, the silicon–oxygen bond of the coordinated trimethylsiloxy group is significantly longer (1.756 (2) Å) than those of normal trimethylsilyl ethers (1.62–1.66 Å).[4] The three aluminum–oxygen bond lengths vary little (1.811 (2)–1.852 (2) Å) and resemble standard values,[5] so the conventional representation of dative and covalent bonds in structure 3 is somewhat misleading.[6]

One major species, presumably similar to structure 3, is present in solution, since the proton-decoupled ¹³C NMR spectrum of a

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0.21 M solution in CD_2Cl_2 at −85 °C consists of only seven peaks. Similarly, ¹H NMR spectra recorded at +25 and −78 °C in CD_2Cl_2 are simple, nearly identical, and inconsistent with extensive dissociation or redistribution. These spectra show that no planes of effective symmetry are present, so the two oxygens do not become equivalent by rapid intramolecular or intermolecular exchanges of the $(CH_3)_3Si$ and $AlCl_3$ groups under these conditions. In addition to the expected signals, ¹H and ¹³C NMR spectra of compound 3 also reveal traces of chlorotrimethylsilane, which may result from partial decomposition in solution. Direct evidence that the primary species in solution is similar to structure 3 is provided by ²⁷Al NMR spectra in CH_2Cl_2 at 0.014 and 0.21 M. At 25 °C, one major signal appears at δ 99 ($w_{1/2}$ = 200 Hz) in the region characteristic of tetracoordinate aluminum,[7] and a broad, partly overlapping peak can be detected at δ 91 ($w_{1/2}$ = 800 Hz). These peaks broaden further and can no longer be distinguished when the temperature is decreased to −78 °C. The presence of these signals indicates that the tetrahedral aluminums found in compound 3 in the solid state are also present in solution. In addition, a very minor peak appears at δ 52 in the region characteristic of pentacoordinate aluminum.[7] We suggest that this signal corresponds to small amounts of products derived from compound 3 by decomposition, redistribution, or dissociation.

Compound 3 is significant because normal silyl ethers are too weakly basic and too reactive to form stable adducts with Lewis acids.[3] Coordination of the trimethylsiloxy group in compound 3 by the adjacent trans dichloroaluminum alkoxide is possible presumably because it is intramolecular. We suggest that the interaction is not strong enough to provoke immediate desilylation, but nevertheless prevents cleavage by external aluminum chloride. Alternatively, the arrangement of chlorine, aluminum, oxygen, and silicon atoms may be stereoelectronically unsuitable for desilylation. It is also noteworthy that a five-membered ring containing two oxygens and one aluminum can be trans-fused to a six-membered ring. This is permissible largely because the endocyclic O–Al–O angle can contract to 90.75 (8)° and because the two endocyclic Al–O–C bond angles can accept an average value (108.2 (2)°) much smaller than the trigonal ideal. We conclude that the five-membered ring found in compound 3 is a basic structural motif likely to be favored in the bidentate dichloro alkoxide 1 and related compounds of aluminum.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer. A Varian VXR-300 spectrometer was used to obtain ¹H nuclear magnetic resonance (NMR) spectra at 300 MHz, ¹³C NMR spectra at 75.4 MHz, and ²⁷Al NMR spectra at 78.2 MHz. Low-temperature ¹H NMR spectra were recorded on a Bruker WH-400 spectrometer at 400 MHz. ¹H and ¹³C NMR chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ), and ²⁷Al chemical shifts are relative to an external 1.5 N solution of $Al(NO_3)_3$ in D_2O. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus and are not corrected. Dichloromethane was dried by distillation from CaH_2, and pentane was dried by distillation from the sodium ketyl of benzophenone. Aluminum chloride was purified twice by sublimation in vacuo.

Reaction of the Bis(trimethylsilyl) Ether 2² of *trans*-1,2-Cyclohexanediol with Aluminum Chloride. A stirred suspension of aluminum chloride (0.827 g, 6.20 mmol) in dichloromethane (2 ml) was cooled to −78 °C under dry Ar and treated dropwise with a solution of bis(trimethylsilyl) ether 2² (0.807 g, 3.10 mmol) in dichloromethane (2 mL). The cooling bath was removed and the mixture was kept at 25 °C for 24 h. Volatiles were then removed by evaporation in vacuo, the solid yellow residue was redissolved in dichloromethane (11 mL), and a layer of pentane (22 mL) was carefully added. Slow diffusion at 25 °C induced the formation of colorless crystals of the chloroaluminum alkoxide 3 (1.07 g, 2.56 mmol, 82.6%): mp 136–137 °C; IR (Nujol mull) 1270, 1260, 1010, 975, 885, 850, 820, 710, 635, 620 cm⁻¹; ¹H NMR (300 MHz, $CDCl_3$) δ 0.67 (s, 9 H), 1.43 (m, 2 H), 1.75 (m, 1 H), 1.97 (m, 3 H), 2.50 (d, 1 H), 2.87 (d, 1 H), 4.42 (m, 2 H); ¹³C NMR (75.4 MHz,

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CD_2Cl_2, −85 °C) δ 85.6, 81.4, 31.1, 30.6, 23.1, 22.6, 1.1; ^{27}Al NMR (78.2 MHz, CH_2Cl_2 containing 10% CD_2Cl_2, 30 °C) δ 99 ($w_{1/2}$ = 200 Hz), 91 ($w_{1/2}$ = 800 Hz), 52. Anal. Calcd for $C_9H_{19}Al_2Cl_5O_2Si$: C, 25.83; H, 4.58. Found: C, 24.81; H, 4.99.

X-ray Crystallographic Study of the Chloroaluminum Alkoxide 3. Crystallographic data and experimental parameters are summarized in Table I. A single crystal of compound **3** was mounted quickly in air on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 25 well-centered reflections in the range 10° < θ < 11°. The structure was solved by using direct methods (SHELXS86) and difference Fourier calculations (SHELX76).[8] Full-matrix least-squares refinement converged at *R* = 0.031 and R_w = 0.036. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found by difference-Fourier synthesis and/or were calculated at idealized positions. The final Δ*F* map showed three peaks of 0.28–0.58 e Å⁻³ within 0.95 Å of Cl, and the general background was below ±0.31 e Å⁻³. Scattering curves for the non-hydrogen atoms[9] and hydrogen atoms[10] were taken from standard sources.

Disorder was introduced to account for the large anisotropic thermal parameters for C(1), C(2), C(4), and C(5), and for the short C(1)–C(2) distance of 1.37 Å found at the end of the initial refinement. Occupancy was refined as 65% for the structure shown in Figure 1 and 35% for the closely related structure shown in Figure 2 of the supplementary material. The major occupant is derived from (1*R*,2*R*)-1,2-cyclohexanediol, whereas the minor occupant is derived from the (1*S*,2*S*) isomer.

Atomic coordinates and isotropic thermal parameters for both structures are listed in Table II, and selected bond lengths and angles are compiled in Table III. Tables of complete bond lengths and angles, anisotropic thermal parameters, fixed hydrogen atom coordinates, and observed and calculated structure factors are included as supplementary material.

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On the Rapid, Monophasic Reaction of the Rabbit Liver Metallothionein α-Domain with 5,5′-Dithiobis(2-nitrobenzoic acid) (DTNB)

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Introduction

Since its detection in 1957, metallothionein (MT) has been the subject of a great deal of research. Although the structure and composition of mammalian MTs are now well understood,[1] their

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chemical reactivity and the relationship of reactivity to function are just now being explored.[2] MT is a low molecular weight protein (around 6800) containing 61 amino acids, of which 20 are cysteines. These highly conserved cysteines form metal–thiolate complexes with essential metals (such as Zn and Cu), toxic metals (Cd, Hg), and therapeutic metals (Au, Pt). Thus, MT appears to have significant roles in metal storage and transfer and in the detoxification of toxic metals.

In mammalian MTs, 7 equiv of Zn(II) or Cd(II) are bound and each metal ion is tetrahedrally coordinated to four thiolate ligands. Homonuclear ^{113}Cd decoupling experiments deduced that MT contains two distinct metal–thiolate clusters, one (cluster A) containing four and the other (cluster B) containing three Cd(II) ions.[3] The models proposed from these studies are shown below. Their validity is also supported chemically from the observation that under appropriate conditions subtilisin can be used to isolate the two fragments.[4] The β-domain consists of the amino terminal fragment from residues 1–30 containing 9 cysteines and binding 3 metals (cluster B), and the α-domain consists of the carboxyl terminal fragment from residues 31–61 containing 11 cysteines and binding 4 metals (cluster A). The isolated α-domain gave an ^{113}Cd NMR spectrum similar to that of cluster A in uncleaved MT.[5]

Cluster A   Cluster B
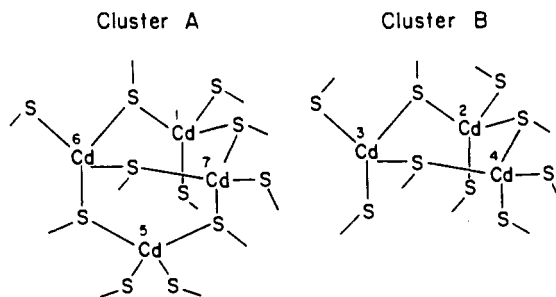
In an effort to relate the inorganic chemistry of MT to its biological function(s) and role(s) in cells, reactions of MT with a variety of ligands were studied.[2,6,7] Among them DTNB (5,5′-dithiobis(2-nitrobenzoic acid)) was studied extensively.[6,8] This electrophile undergoes slow thiol–disulfide interchange with the metal-coordinated thiols of MT, releasing the chromophore 5-thio-2-nitrobenzoate, TNB (λ_{max} = 412 nm). The reaction kinetics are biphasic with fast and slow steps, each displaying first- and second-order components.[6] One postulated explanation is that this behavior is due to differential reactivity of the two clusters, which predicts that isolated clusters will display cooperative, monophasic kinetics. Another possibility is that the terminal and bridging thiolates might react with distinctly different rates of reaction, which predicts that each cluster should react biphasically. In order to test these mechanistic possibilities, we isolated the α-Cd_4MT-II cluster and examined its reaction with DTNB.

Materials and Methods

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