mol).[3c] The *N*-acyl compounds require the additional process of free rotation about the N-C bond for ring inversion to occur.

A set of parameters has previously been developed to describe the solid-state sturctural features of dibenzotricyclic systems.[10a,35] The values for these parameters are summarized in Table VII for 2 and 3 and are compared to those of related tricycles, silipramine,[36] and imipramine.[26] The replacement of nitrogen in 1 (X = NR) by the larger silicon center (1, X = SiRR′) results in flattening of the tricyclic framework as demonstrated by the increase in the bend angles relative to imipramine. The increase in the bend angle is paralleled by an increase in the distance between the benzo group centers. Addition of substituents in positions ortho to the silicon heteroatom flattens the framework further.

The skew distance, the difference between nonbonded benzo carbon distances across the central ring, is primarily a function of the covalent radius of X in 1.[35] The larger silicon atom provides a spacing closer to that of the ethano bridge and is reflected in the smaller skew distances relative to imipramine. The decreases in the skew distance through the sequence silipramine, 3, 2 result from a small increase in the endocyclic Si–C bond lengths through this series from 1.870 (4)[35] to 1.92 (1) Å.

The major difference between 2 and 3 in the solid state is an appreciable widening of the Si–Si–Si angle from a value of 112° in 3 to 124° and 125° in the two independent molecules of 2. The widening of the angle in 2 decreases the interaction of the exocyclic trimethylsilyl groups with ortho methyl substituents. Consistent with this observation are the longer Si–Si bond lengths in 2 relative to 3. Smaller substituents on the silicon heteroatom should exhibit a decreased interaction with the ortho methyl groups. To test this hypothesis, the silepin related to 2 with exocyclic methyl substituents, 4, was synthesized and indeed 4 undergoes rapid ring inversion down to 183 K. It is not clear how bulky the organic substituents on silicon must be to conformationally lock the tricylic framework. There is at least one report which demonstrates that a trimethylsilyl substituent behaves as a bulkier group than a *tert*-butyl group.[38] The series of compounds in this study demonstrate that to increase the barrier to ring inversion of a dibenzosilacycle will require the combination of a substituent in positions ortho to the silicon heteroatom and sufficiently bulky exocyclic substituents.

Acknowledgment. The Weldon Spring Fund of the University of Missouri—St. Louis is acknowledged for support of this work. The Hewlett-Packard 5988A GC/MS system was purchased with support of the National Science Foundation (Grant CHE-8813154). We appreciate helpful discussions with C. Maryanoff, B. Maryanoff, R. E. K. Winter, G. Anderson, S. Barcza, and F. Homan. We also appreciate the administrative assistance of R. Schneider and the technical assistance of J. Kramer.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen coordinates and thermal parameters and figures showing stereoviews (4 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Triazine Adducts of Dimethylzinc and Dimethylcadmium: X-ray Crystal Structure of $Me_2Zn[(CH_2NMe)_3]_2$

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Received January 16, 1991

The reaction of various triazines of the type $(CH_2NR)_3$ with dimethylzinc and dimethylcadmium yielded a series of adducts of the type $Me_2M[(CH_2NR)_3]_2$ (where M = zinc or cadmium and R = methyl, ethyl, or isopropyl), of which the methyl derivative of dimethylzinc has proved useful in the growth of high-quality ZnSe by metalloorganic vapor deposition (MOCVD). The X-ray crystal structure of $Me_2Zn[(CH_2NMe)_3]_2$ has been determined and shows the complex to consist of monomeric units of C_{2v} symmetry. The compound crystallizes in space group *Cmcm*, a = 13.553 (2) Å, b = 7.399 (2) Å, and c = 19.738 (4) Å, $\alpha = \beta = \gamma$ = 90°.

The adducts of group 12 metal alkyls were studied in a pioneering series of papers by Thiele.[1-5] A range of nitrogenous bases were used including monodentate ligands such as trimethyl- and triethylamine and potentially chelating ligands such as 1,10-phenanthroline, the latter being also studied by Coates.[6] The adducts with monodentate ligands were generally low boiling point liquids; those with the chelating ligands, volatile solids. Adducts of both 1:1 and 2:1 stoichiometries were formed by the monodentate amines. The tendency of many of the 2:1 adducts to dissociate into 1:1 species, in solution, in nondonor solvents such as benzene, was noted on the basis of cryoscopic molecular weight measurements. Dissociation

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Table I. Elemental Analyses and ^1H NMR Results[a]

compd	anal., %			^1H NMR δ, ppm	
	C	H	N		
$Me_2Zn[(CH_2NMe)_3]_2$	47.48 (46.99)	10.17 (10.20)	23.74 (23.08)	$(CH_2\mathrm{NMe})$	2.93 (s)
$C_{14}H_{36}H_6Zn$				$(\mathrm{CH_2N}CH_3)$	2.04 (s)
				$CH_3\mathrm{Zn}$	−0.39 (s)
$Me_2Zn[(CH_2NEt)_3]_2$	54.87 (54.91)	10.97 (10.87)	19.20 (19.33)	$(CH_2\mathrm{NEt})$	3.18 (s)
$C_{20}H_{48}N_6Zn$				$(\mathrm{CH_2NC}H_2\mathrm{CH_3})$	2.32 (q)
				$(\mathrm{CH_2NCH_2C}H_3)$	0.59 (t)
				$CH_3\mathrm{Zn}$	−0.44 (s)
$Me_2Zn[(CH_2N^iPr)_3]_2$	59.89 (61.26)	11.51 (12.07)	16.11 (16.46)	$(CH_2\mathrm{N^iPr})$	3.44 (s)
$C_{26}H_{60}N_6Zn$				$(\mathrm{CH_2NC}H\mathrm{(CH_3)_2})$	2.83 (m)
				$(\mathrm{CH_2NCH(C}H_3)_2)$	1.02 (d)
				$CH_3\mathrm{Zn}$	−0.32 (s)
$Me_2Cd[(CH_2NMe)_3]_2$	41.96 (41.79)	9.00 (9.34)	21.00 (21.25)	$(CH_2\mathrm{NMe})$	2.96 (s)
$C_{14}H_{36}N_6Cd$				$(\mathrm{CH_2N}CH_3)$	2.06 (s)
				$CH_3\mathrm{Cd}$	−0.39 (s)
$Me_2Cd[(CH_2NEt)_3]_2$[b]	52.75 (53.68)	10.55 (9.22)	18.46 (14.05)	$(CH_2\mathrm{NEt})$	3.10 (s)
$C_{20}H_{48}N_6Cd$				$(\mathrm{CH_2NC}H_2\mathrm{CH_3})$	2.29 (q)
				$(\mathrm{CH_2NCH_2C}H_3)$	0.91 (t)
				$CH_3\mathrm{Cd}$	−0.48 (s)
$Me_2Cd[(CH_2N^iPr_3]_2$[b]	57.95 (56.59)	11.14 (9.34)	15.60 (15.23)	$(CH_2\mathrm{N^iPr})$	3.46 (s)
$C_{26}H_{60}N_6Cd$				$(\mathrm{CH_2NC}H\mathrm{(CH_3)_2})$	2.82 (m)
				$(\mathrm{CH_2NCH(C}H_3)_2)$	1.01 (d)
				$CH_3\mathrm{Cd}$	−0.39 (s)

[a] Calculated values in parentheses. [b] Good analytical results are difficult to obtain for the cadmium complexes. These compounds yellowed on prolonged storage in sealed vials; the discrepancies in reported values are probably accounted for by some decomposition before the microanalysis was performed; the composition of all adducts has been confirmed as 1:2 by integration of the ^1H NMR spectra of freshly prepared samples.

was far more extensive for the cadmium complexes[4] than for those of zinc.[5] Repeated vacuum distillation of the 2:1 species also led to dissociation of such adducts to the 1:1 species. More recently, some cadmium adducts were studied by infrared spectroscopy.[7] The much decreased reactivity of such adducts toward both atmospheric oxygen and water, as compared to the parent metal alkyls, has been widely noted. Work in this area has been reviewed.[8]

We have recently shown[9] for the 2:1 adduct $Zn(Me)_2\cdot(NEt_3)_2$ that the vapor above the liquid consists almost entirely of the triethylamine ligand. The reduced reactivity of the system, on exposure to air, is hence readily explained in terms of the equilibrium

$$Zn(Me)_2\cdot(NEt_3)_2(liq) \rightleftharpoons Zn(Me)_2\cdot(NEt_3)(liq) + NEt_3(liq)$$

The triethylamine, being the most volatile component in the above scheme, dominates the vapor. These results are consistent with the early observations of Thiele.[1-5]

Metal alkyls are now used on a routine basis to grow II/VI materials by metalloorganic chemical vapor deposition (MOCVD),[10,11] and because of this, use there has been a substantial revival of interest in the chemistry of the adducts of group 12 alkyls.[12-21] Adducts have three distinct applications in precursor chemistry:

1. to control the vapor pressure of metal alkyls which are extremely volatile, e.g. dimethylzinc.[9,12-18]
2. in the purification of metal alkyls for MOCVD.[19-22] Alkyls are often purified by "cracking" an adduct. In this way unwanted volatile impurities can be removed. The methods are similar to those that have been particularly successful for the purification of group 13 alkyls such as trimethylindium.[22]
3. in the control of homogeneous reaction in MOCVD reactors. Adducts have been shown to be effective in eliminating or controlling such reactions.[13-18] The reasons for this are not as yet clear but may include the greater purity of alkyls as obtained from adducts and/or specific interactions with vapor-phase species in the MOCVD reactor.

The apparent absence of any structural information for adducts of the group 12 metals has been commented on.[23] In the present paper we describe the synthesis and characterization of a number of adducts of triazines with dimethylzinc and dimethylcadmium. The 2:1 adducts of the metal alkyls with the methyl triazine $(CH_2NMe)_3$ are crystalline solids, and the X-ray crystal structure of $Me_2Zn[(CH_2NMe)_3]_2$ is reported. A preliminary report of this work has appeared.[21]

Triazines are interesting molecules to study as ligands, having the potential to be two-, four-, or six-electron donors. The only adducts to have been studied with the triazine ligand are those of group 3 metal alkyls.[24] A recent crystallographic study of the methyl triazine adduct

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Table II. Crystallographic Data for $Me_2Zn[(CH_2NMe)_3]_2$

	Crystal Data		
stoichiometry	$C_{14}H_{36}N_6Zn$	space group	*CmCm*
MW	353.870	D_c, g cm^{-3}	1.19
a, Å	13.553 (2)	*Z*	4
b, Å	7.399 (2)	*F*(000)	768
c, Å	19.738 (4)	Mo Kα radiation, Å	0.71069
$\alpha = \beta = \gamma$, deg	90	μ, cm^{-1}	12.73
V, Å^3	1979.30		
syst	orthorhombic		
	Data Collection		
$\theta_{max/min}$, deg	1.5/25	total no. of unique data	940
temp, °C	room temp	total no. of data obsd	793
total no. of data measd	1042	significance test	$F_o > 3\sigma(F_o)$
	Refinement		
no. of params	97	final *R*	0.0309
abs corr	ψ-scan	final R_G	0.0394
g^a (weighting scheme)	0.000125		

^{a} $w = 1/[\sigma^2(F_o) + g(F_o)^2]$.

of trimethylindium shows the ligand to behave as a six-electron donor (with In–N 2.81 Å (twice) and 2.77 Å).[25]

Experimental Section

All experiments were performed in an atmosphere of oxygen-free nitrogen (Schlenk line or drybox). Amines were purchased from Aldrich, and metal alkyls were a gift from Epichem Ltd. ^{1}H NMR spectra were obtained by using a Bruker WP80 or WH400 FT spectrometer; infrared spectra were recorded with a Mattson Polaris FTIR instrument. Microanalyses were carried out by the Microanalytical Laboratory of University College, London. Microanalytical and ^{1}H NMR spectroscopic results are summarized in Table I.

The preparations of the adducts were similar in all cases and involved the stoichiometric reaction of the metal alkyl and amine; e.g. hexahydro-1,3,5-trimethyl-1,3,5-triazine (5 mL, 35.6 mmol) was slowly added to dimethylzinc (1.52 g, 15.9 mmol) at −196 °C, and the resulting mixture was allowed to warm to room temperature. Distillation or sublimation procedures are now indicated for each compound.

Dimethylzinc–Bis(hexahydro-1,3,5-trimethyl-1,3,5-triazine). The crude white, waxy solid product was sublimed (120 °C, 10^{-2} Torr) to give a white crystalline solid, 6.08 g, 99.4%. On leaving at ≈35 °C overnight, white crystals formed on the side of the flask. Diffraction-quality crystals of $Me_2Zn[(CH_2NMe)_3]_2$ were obtained by leaving a sample in a sealed Schlenk flask at about 30 °C for 2–3 weeks, during which time well-formed crystals sublimed from the mass of the compound to the edges of the flask (mp 37.1 °C).

Dimethylzinc–Bis(hexahydro-1,3,5-triethyl-1,3,5-triazine). The crude liquid product was distilled (140 °C, 10^{-2} Torr) to give a colorless liquid, 6.76 g, 98.8%.

Dimethylzinc–Bis(hexahydro-1,3,5-triisopropyl-1,3,5-triazine). The crude liquid product was distilled (140 °C, 10^{-2} Torr) to give a colorless liquid, 2.61 g, 95.6%.

Dimethylcadmium–Bis(hexahydro-1,3,5-trimethyl-1,3,5-triazine). The crude white solid product was sublimed (120 °C, 10^{-2} Torr) to give a white crystalline solid, 4.88 g, 98.9%, (mp 28.8 °C).

Dimethylcadmium–Bis(hexahydro-1,3,5-triethyl-1,3,5-triazine). The crude liquid product was distilled (140 °C, 10^{-2} Torr) to gove a colorless liquid, 23.62 g, 98.4%.

Dimethylcadmium–Bis(hexahydro-1,3,5-triisopropyl-1,3,5-triazine). The crude liquid product was distilled (140 °C 10^{-2} Torr) to give a colorless liquid, 5.11 g, 99.2%.

Crystallography. Samples for the structure determination were sealed in capillary tubes under an inert atmosphere.

All measurements were made by using a CAD4 diffractometer operating in the $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation, as described previously.[26] The structure was solved via standard heavy-atom procedures and refined by using full-matrix least-squares methods[27] with scattering factors calculated by using data from ref 28. All non-hydrogen atoms were refined with anisotropic displacement factors; hydrogen atoms were identified in difference maps and included with isotropic displacement factors. Crystal data and details of the intensity measurements and refinement are given in Table II. Positional parameters are given in Table III. Table of H atom coordinates, full lists of bond lengths and angles, anisotropic displacement factor coefficients and F_o/F_c values are included in the supplementary material.

Table III. Fractional Atomic Coordinates (×10^4) for $Me_2Zn[(CH_2NMe)_3]_2$^{a}

	x	*y*	*z*
Zn(1)	0*	280 (1)	7500*
N(1)	0*	2248 (3)	8473 (1)
N(2)	877 (1)	4487 (2)	9117 (1)
C(1)	1401 (4)	−513 (6)	7500*
C(2)	876 (2)	3386 (3)	8507 (1)
C(3)	0*	5606 (4)	9129 (2)
C(4)	0*	878 (5)	9019 (2)
C(5)	1761 (2)	5612 (4)	9137 (2)

^{a} Asterisks denote invariant positions.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Me_2Zn[(CH_2NMe)_3]_2$

N(1)–Zn(1)	2.410 (4)	C(1)–Zn(1)	1.987 (6)
C(2)–N(1)	1.456 (4)	C(4)–N(1)	1.479 (5)
C(2)–N(2)	1.453 (4)	C(3)–N(2)	1.448 (3)
C(5)–N(2)	1.460 (4)		
C(1)–Zn(1)–N(1)	100.3 (2)	C(2)–N(1)–Zn(1)	112.7 (2)
N(1)–Zn(1)–N(1a)	105.6 (2)	C(1)–Zn(1)–C(1a)	145.1 (2)
C(4)–N(1)–Zn(1)	99.5 (3)	C(4)–N(1)–C(2)	111.2 (3)
C(3)–N(2)–C(2)	109.5 (3)	C(5)–N(2)–C(2)	110.1 (3)
C(5)–N(2)–C(3)	110.3 (3)	N(2)–C(3)–N(2)	110.3 (3)
N(2)–C(2)–N(1)	111.3 (3)	C(2)–N(1)–C(2)	109.1 (3)

Results and Discussion

The series of compounds $Me_2M[(CH_2NR)_3]_2$ where M = Zn and Cd and R = CH_3–, CH_3CH_2–, and $(CH_3)_2CH$– have been prepared by the direct stoichiometric reaction of the ligand and metal alkyl. All the compounds prepared have properties similar to those of the adducts earlier prepared by Coates or Thiele, and their reduced reactivity toward atmospheric oxygen and water makes them much easier to handle than the base-free alkyl. NMR and microanalysis data are presented in Table I. The adducts of dimethylcadmium yellowed on prolonged storage and are more susceptible to decomposition on exposure to the air than the dimethylzinc adducts. This observation may reflect the lower polarizing effect of the cadmium center.

The methyl triazine derivatives of both the zinc and cadmium alkyls are low-melting crystalline solids whereas the higher alkyls are all involatile liquids. This is probably due to the steric bulk of the alkyl substituents preventing the close packing observed in the adduct of the methyl triazine with dimethylzinc (vide infra). Dimethylzinc or -cadmium in the presence of excess methyl triazine ([M$(CH_3)_2$]:[$(CH_2NMe)_3$] > 1:2) yields on removal of volatile material under reduced pressure the bis adduct; similar mixtures of triethyl- or trimethylamines and such metal alkyls approach a limiting 1:1 stoichiometry. The relative

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Table V. Important Bond Lengths (Å) and Angles (deg)

	$Zn[(CH_2)_3N(Me)_2]_2$ X-ray[34]	$Zn[(CH_2)_3N(Me)_2]_2$ GED[34]	$(CH_3)_2Zn[(CH_2NMe)_3]_2$ X-ray (this work)
Zn-C	1.984 (5)	1.991 (6)	1.987 (6)
Zn-N	2.307 (4)	2.392 (15)	2.410 (4)
C-Zn-C	156.4 (2)	152 (8)	145.1 (2)
N-Zn-N	109.7 (1)	117 (4)	105.6 (2)
N-Zn-C[a]	85.6 (1)	82 (2)	
N-Zn-C[b]	108.2 (1)	113 (4)	100.3 (2)

[a] Chelating. [b] Separate molecules.

Table VI. Growth Results Illustrating the Utility of $Me_2Zn[(CH_2NMe)_3]_2$ for the Growth of ZnSe[a]

precursor	material grown	growth temp, °C	n_{77K}, cm^{-3}	μ_{77K}, $cm^2\ V^{-1}\ s^{-1}$	comments
Me_2Zn	ZnSe	325	3.2×10^{15}	1708	prereaction[18]
$Me_2Zn(NEt_3)$	ZnSe	350	3.6×10^{14}	6455	no prereaction[18]
$Me_2Zn[(CH_2NMe)_3]_2$	ZnSe	350	layers depleted		no prereaction[18]

[a] By conventional atmospheric pressure MOCVD using H_2Se as the source of selenium.

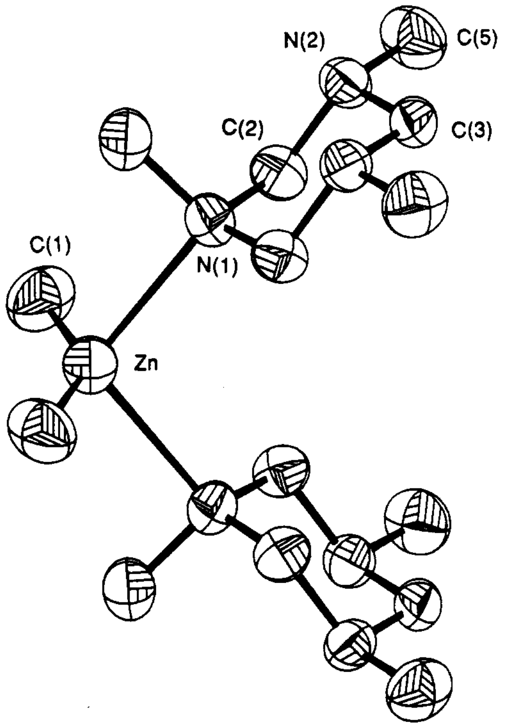

Figure 1. Molecular unit in the structure of $Me_2Zn[(CH_2NMe)_3]_2$.

volatilities of the amine and alkyl may, in part, account for this observation, but another factor is probably the polar nature of the triazine ligand, which leads to the facile formation of the solid species.

Structure of $Me_2Zn[(CH_2NMe)_3]_2$. The structure of $Me_2Zn[(CH_2NMe)_3]_2$, as determined by x-ray crystallography, is shown in Figure 1; selected bond lengths and angles are summarized in Table IV. The structure consists of molecular units with distorted tetrahedral coordination at zinc (the molecule has C_{2v} symmetry). The parent alkyl has, in the vapor phase, a linear carbon-metal-carbon unit,[29] with $Zn-CH_3$ being 1.95 Å; in the adduct each metal carbon bond is distorted by ≈18° and the $Zn-CH_3$ bond length is 1.98 Å. The angle between the C-Zn-C and N-Zn-N planes is determined by the symmetry of the structure as 90°. There are relatively few examples of crystallographically characterized zinc alkyl compounds[30] and only one example of a simple bis(alkyl), a rotoxane containing linear diethylzinc units[31] ($Zn-C_2H_5$, 1.98 Å).

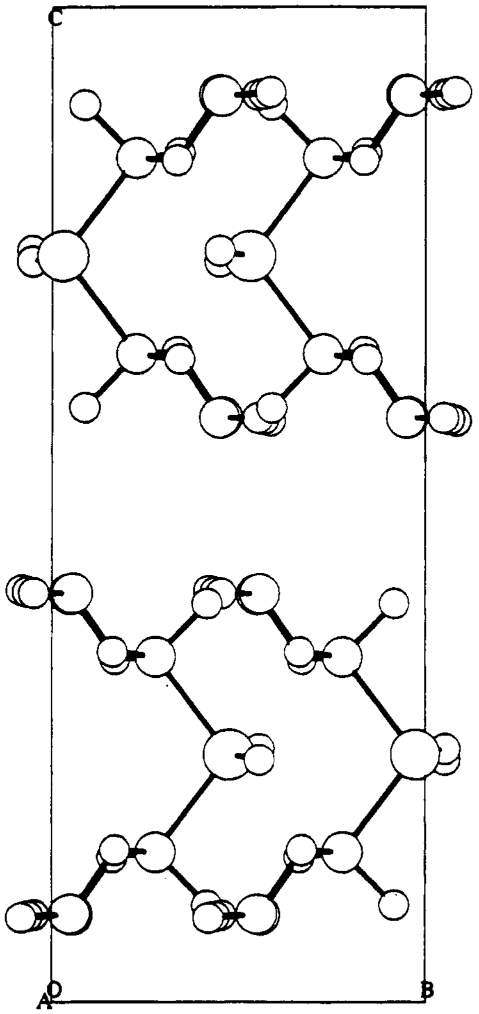

Figure 2. Packing diagram for $Me_2Zn[(CH_2NMe)_3]_2$.

Other recently characterized alkyls include a tris(pyrazolyl)borate[32] ($Zn-CH_3$, 1.89 Å) and a dimeric mixed methyl/diethylthiocarbamate[33] ($[MeZnS_2CNEt_2]_2$, $Zn-CH_3$ 1.96 Å). Consequently, the coordination of the amine and distortion of the alkyl-metal bond angle in $Me_2Zn[(CH_2NMe)_3]_2$ do not lead to any significant extension of the metal-to-carbon bond, which is not surprising; simple

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calculations suggest only slight changes in bond energy for substantial deviation of linearity of the C–Zn–C axis.[34] The packing of the molecule is interesting and consists of chains along the *b* axis, with the metal centers located above the below the *bc* plane in alternate molecules (Figure 2). There are no particularly short or unusual contacts between the molecules.

There are no other adducts with which the coordination geometry at zinc in the present compound can be compared; however a molecule with the same set of donor atoms, bis(3-(dimethylamino)propyl)zinc, $[Zn((CH_2)_3N(Me)_2)_2]$, has been studied in some detail by electron diffraction in the vapor phase (GED) and in the solid state by x-ray diffraction.[34] Bond lengths and angles at zinc for $[Zn((CH_2)_3N(Me)_2)_2]$ are tabulated in Table V to allow easy comparison with those for the adduct prepared in the present study. In the present, stable, solid crystalline adduct, the Zn–N distance is much greater than the sum of the covalent radii and suggests little or no covalent interaction between the nitrogen and metal. The reported[34] range of Zn–N bond lengths was previously from 1.82 Å in $[Zn(N(SiMe_3)_2)_2]$ to 2.32 Å in $[Zn((CH_2)_3N(CH_3)_2)_2]$ and is now extended to 2.41 Å.

The zinc adduct with the trimethyltriazine has been successfully used,[18,21] in combination with H_2Se, to grow high-quality layers of ZnSe by conventional atmospheric pressure MOCVD experiments[18] (see Table VI). Thin films of ZnSe grown from this precursor are essentially fully depleted and free from n-type dopants (such as iodide) which adversely effect the properties of this material. One reason for this observation may be that the adduct is extremely effective in removing traces of MeI from dimethylzinc.

Acknowledgment. We thank the SERC for a grant to P.O'B. and for their support of crystallography at QMW and Epichem for their support of work at QMW. J.R.W. thanks the SERC for a CASE studentship in association with Epichem. We thank Dr. P. J. Wright and Prof. B. Cockayne of RSRE for their collaboration in related growth studies and permission to reproduce the growth results in this paper.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, bond lengths and angles, and nonbonded distances (3 pages); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

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Role of Pentacoordinate Intermediates in the Hydrolysis Reaction of Organic Silicates

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Received February 27, 1991

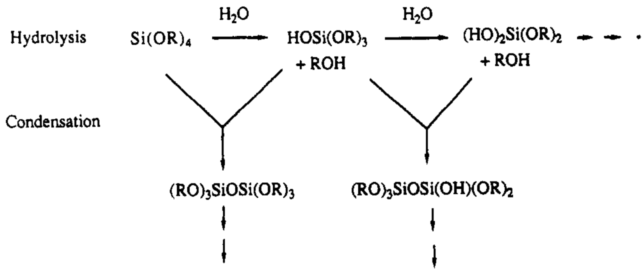
The alcoholysis and hydrolysis reactions of $XSi(OR)_3$, $XSi(OR)_3$ + 10% KOR (X = H, OR), and $K[XSi(OR)_4]$ (X = H) or [K,18-crown-6]$[XSi(OR)_4]$ (X = OR) were studied to approach the mechanism of the reaction. We found the following: (i) The first step of the process in the case of $XSi(OR)_3$ (X = H, OR) was the formation of a pentacoordinate intermediate by nucleophilic activation at silicon. (ii) The rate-determining step was the coordination of R'OH (R' = H, R) to the pentacoordinate silicon leading to a hexacoordinate intermediate (or transition state), which gave the product. (iii) A step by step nucleophilic substitution occurred on a pentacoordinate silicon derivative, $K[H_2Si(OR)_3]$ and $K[HSi(OR)_4]$, giving another pentacoordinate compound, $K[HSi(OR)_4]$ and [K,18-crown-6]$[Si(OR)_5]$, respectively.

Introduction

The hydrolysis of organic silicates, mainly $Si(OMe)_4$ and $Si(OEt)_4$, is the key reaction in the sol–gel process for preparation of silica. The mechanism of this reaction is complex because of competition between hydrolysis, condensation reactions, and redistribution reactions. The different reactions in the hydrolysis process are summarized in Scheme I.

The mechanism of the hydrolysis of silicon alkoxides depends on the reaction conditions (neutral or catalyzed with acids, bases, or nucleophiles) and has been studied by several groups.[1-7]

Scheme I



In the case of basic conditions, two mechanisms may be envisaged. In the more common mechanism (Scheme II)

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