

$\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ (0.26 g) was suspended in methanol (10 ml) and reacted under carbon monoxide with sodium iodide (0.35 g). By vigorous stirring the $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ slowly dissolved to give a yellow-green solution whose ir spectrum showed the presence of the $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ dianion. After 4 h stirring the suspension was filtered and precipitated by addition of a concentrated solution of tetraethylammonium chloride in methanol (10 ml). The resulting green-violet precipitate was filtered, washed with aqueous methanol, and dried under vacuum (yield 0.15 g).

(b) In THF, $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ (0.302 g) was suspended in anhydrous THF (10 ml) and reacted under carbon monoxide with 0.2 g of sodium iodide. By vigorous stirring the suspension turned blue-green and the ir spectrum showed the presence of the $[\text{Pt}_3(\text{CO})_6]_4^{2-}$ dianion. After 3 h stirring, the suspension was filtered and evaporated to dryness under vacuum. The residue was dissolved in methanol (15 ml) and solid tetraphenylphosphonium chloride was added to give 0.21 g of $[\text{PPh}_4]_2[\text{Pt}_3(\text{CO})_6]_4$.

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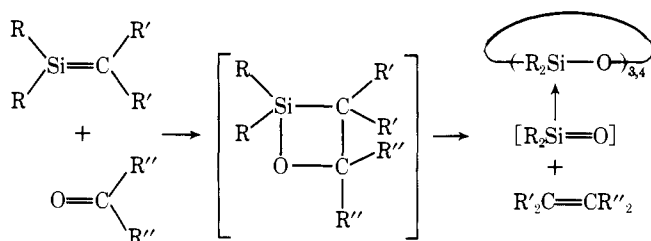
Reaction of a Disilene and Benzaldehyde¹

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Abstract: Tetramethyldisilene, $\text{Me}_2\text{Si}=\text{SiMe}_2$, was generated from the decomposition of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes⁴ at 480–500 °C in a flow system in the presence of excess benzaldehyde. The major products are *trans*-stilbene, hexamethylcyclotrisiloxane, and octamethylcyclotetrasiloxane. While these products clearly implicate the intermediacy of dimethylsilanone, $\text{Me}_2\text{Si}=\text{O}$, its origin is unclear. Several mechanistic possibilities were examined. That both stilbene and dimethylsilanone arise from a single, common intermediate, 5,6-diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (**12**), must be considered as a mechanistic possibility.

In recent years it has been amply demonstrated that transient silenes ($\text{R}_2\text{Si}=\text{CR}'_2$) are very efficiently trapped by the carbonyl group of aldehydes and ketones.² It is generally agreed that this reaction proceeds through cycloaddition of the silene to the carbonyl group to produce an unstable silaoxetane

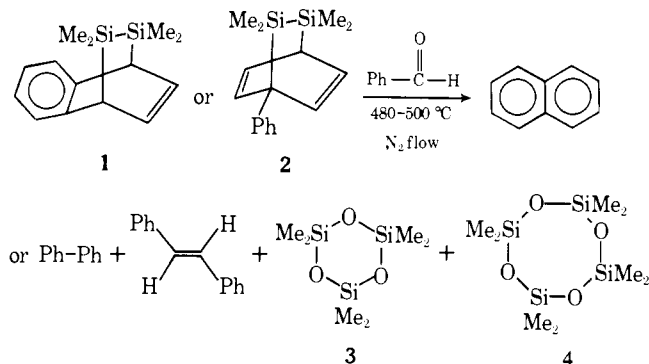


which thermally decomposes to an olefin and a silanone ($\text{R}_2\text{Si}=\text{O}$) which undergoes cyclic oligomerization. This initial addition is in accord with the predictions of Curtis³ that silenes should be highly polar, $\text{R}_2\text{Si}^{\delta+}=\delta-\text{CR}_2$.

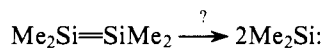
In contrast to the rather extensive studies of the chemistry of the silicon-carbon double bond,² very little is known about the behavior of disilenes, $\text{R}_2\text{Si}=\text{SiR}_2$. Roark and Peddle⁴ have reported strong evidence that 7,8-disilabicyclo[2.2.2]octa-2,5-dienes, **1** and **2**, thermally aromatize through extrusion of a disilene. The descriptive chemistry of disilenes has been limited to a few Diels-Alder reactions, internal rearrangements,⁴ and the addition to an alkyne.⁵ We have begun to examine the reactions of disilenes with various possible trapping reagents. In view of the above mentioned efficiency of silene trapping by ketones and aldehydes, the carbonyl group is an

obvious choice for such a study. Benzaldehyde was chosen as a trap since it is a nonenolizable aldehyde,⁶ had already proven to be an excellent silene trap,⁷ and is a liquid and thus could act as a solvent for the reaction. This ability to act as the solvent was particularly useful as the reactions were done in a vertical pyrolysis column under nitrogen flow.

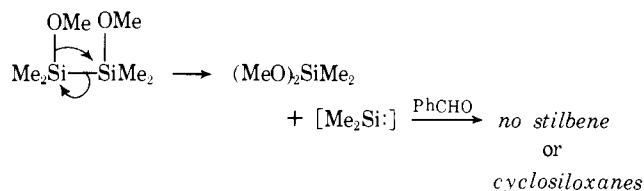
2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**1**) was dissolved in excess benzaldehyde (20:1) and the solution was pyrolyzed by slowly dripping it through a packed vertical pyrolysis column under a constant nitrogen flow at 500 °C. The isolated products included naphthalene, *trans*-stilbene (21.4%), hexamethylcyclotrisiloxane (**3**) (14.1%), and octamethylcyclotetrasiloxane (**4**) (10.2%). Likewise 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**2**) was copyrolyzed with benzaldehyde at 480 °C to afford biphenyl, *trans*-stilbene (23.9%), **3** (16%), and **4** (13.8%).



Focusing attention first on the product, *trans*-stilbene, it was first shown that a separate flow pyrolysis of neat benzaldehyde produced none of this olefin. Thus the observed products arise from reaction between benzaldehyde and **1** or **2** or something derived from **1** or **2**. Since it has been rather conclusively established that **1** and **2** thermally extrude tetramethyldisilene,⁴ it is reasonable to assume that the initial reaction is between benzaldehyde and the disilene. However, it was also possible that the reaction was actually that of a silylene (R₂Si:) derived from decomposition of the disilene.

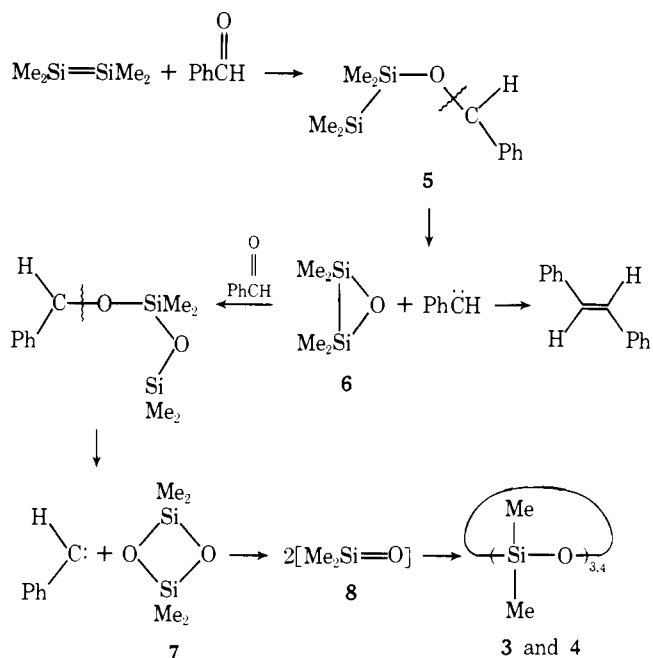


We know of no evidence for this decomposition but recently Gaspar⁸ has presented evidence for the reverse reaction—the gas phase dimerization of dimethylsilylene—and it therefore must be considered. When 1,1,2,2-tetramethyl-1,2-dimethoxydisilane, a well-established thermal generator of dimethylsilylene,⁹ was pyrolyzed with benzaldehyde in a nitrogen flow system at 500 °C the products included dimethyldimethoxysilane (the normal α -elimination product) some polysilanes, and benzaldehyde but no stilbene or cyclodisiloxanes. Thus a silylene is not involved in the reaction of **1** or **2** with benzaldehyde.



The possibility that *trans*-stilbene arises from dimerization of phenylcarbene must also be considered. Indeed a reasonable route can be written (Scheme I) by assuming stepwise attack by disilene on carbonyl followed by homolytic rupture of the carbon-oxygen bond to yield phenylcarbene. The resulting disilaoxirane (**6**) could react with benzaldehyde in an analo-

Scheme I



gous fashion to yield a second molecule of phenylcarbene and a cyclodisiloxane (**7**) which would be expected to cleave to two molecules of silanone **8** and then oligomerize.

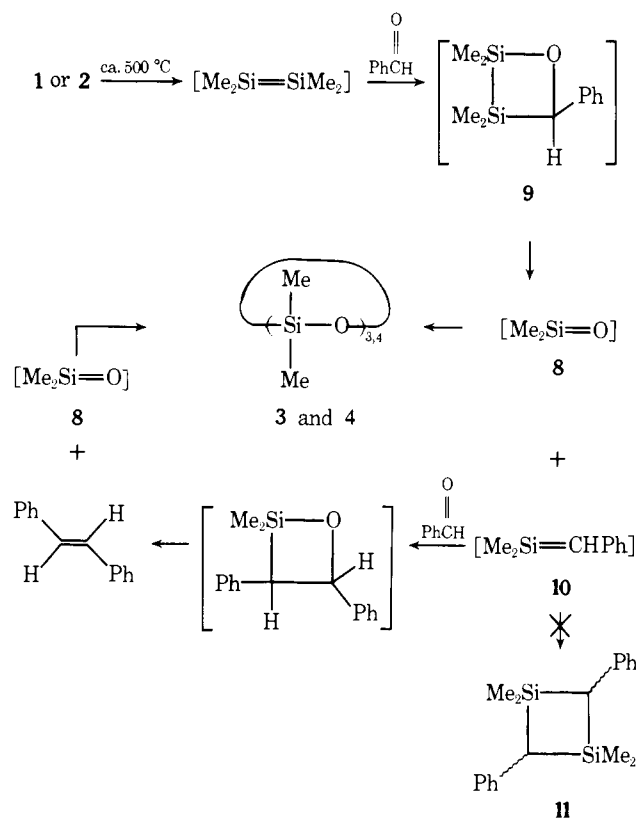
It is well established that in the gas phase phenylcarbene undergoes ring expansion to cycloheptatrienyldiene at temperatures below 600 °C. This is most easily detected by the fact that cycloheptatrienyldiene undergoes dimerization to heptafulvalene. Pyrolysis of the sodium salt of benzaldehyde tosylhydrazone (250 °C, N₂ flow, 40 Torr) is reported to afford 15% stilbenes and 30% heptafulvalene.¹⁰ Our product mixture (trapped at -196 °C) was only slightly yellow, both before and after warming under nitrogen, thus indicating an absence of the highly chromophoric heptafulvalene which was confirmed by NMR.¹¹ Thus the absence of the normal gas-phase isomerization product of phenylcarbene from our reaction mixture is considered sufficient for exclusion of this intermediate from mechanistic consideration.

In view of the generally accepted mechanism for silene reactions with ketones and aldehydes, the mechanism shown in Scheme II is a logical extrapolation. Here the initially formed tetramethyldisilene cycloadds (presumably stepwise) to benzaldehyde to form an intermediate disilaoxetane (**9**). Thermal cleavage of **9** would generate both silanone **8**, which can then oligomerize to **3** and **4**, and silene **10**. Since silenes are known to react with benzaldehyde to yield olefins and cyclic siloxanes,⁷ one would certainly expect **10** to react with benzaldehyde to ultimately yield the observed products.

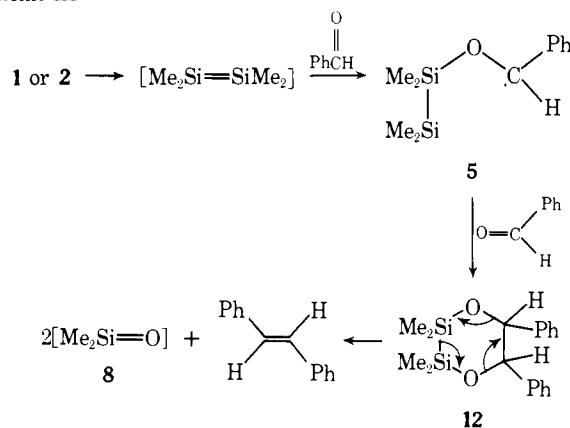
Other than explaining all of the observed products, the mechanism of Scheme II is attractive because it nicely correlates the chemistry of disilenes and silenes. A key intermediate in this route is 1,1-dimethyl-2-phenyl-1-silaethylene (**10**). Since silenes are known to readily dimerize in the gas phase² to 1,3-disilacyclobutanes, one test of this mechanism would be the isolation of 1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane (**11**). The ratio of benzaldehyde to **1** was lowered to 2:1 and finally to 1:1 but no evidence for **11** could be found. While in itself this negative evidence was not especially damning, it was sufficient to cause us to examine a final alternative.

It is entirely possible that an initially formed 1,4-diradical (**5**) does not suffer homolytic cleavage as was suggested in Scheme I or close to **9** as is implied in Scheme II but instead adds a second molecule of benzaldehyde to form the 2,3-disila-1,4-dioxane (**12**). While **12** has never been observed as a

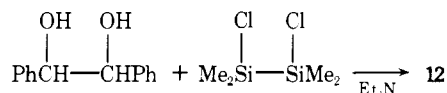
Scheme II



Scheme III



product in this reaction, its concerted, six-electron decomposition would afford stilbene and two molecules of silanone **8** (Scheme III). Thus intermediacy of **12** would explain all of the observed products. To test this possibility we synthesized what we believe to be **12** from the reaction of 1,1,2,2-tetramethyl-1,2-dichlorodisilane with dihydrobenzoin in the presence of triethylamine. The disiladioxane was pyrolyzed at 500 °C in a nitrogen flow system to yield *trans*-stilbene (73%), **3** (28%) and **4** (17%).



The available evidence therefore provides no clear, definitive choice between these two mechanisms (Schemes II and III). Both routes involve key intermediates which have now been shown to give the observed products under the same reaction conditions. The absence of **11** under conditions favorable for its formation argues against Scheme II but is certainly not

unequivocal proof. Perhaps as the chemistry of these intriguing π -bonded silicon compounds continues to unravel a method for making this mechanistic distinction will appear. Perhaps most exciting is the possibility that disiladioxanes like **12** will make it more practical to study the chemistry of the silicon-oxygen π -bond and our attention will be placed there in the immediate future.

Experimental Section

Infrared spectra (ir) were recorded on a Beckman 18A spectrophotometer. Routine NMR spectra were determined on a Varian Model A-60 or Hitachi R20-B spectrometer, and chemical shifts are reported as parts per million (δ scale) from tetramethylsilane as an internal standard. Routine mass spectra were obtained on an Atlas CH-4 spectrometer and an MS-902 spectrometer. High resolution mass spectra were run on the MS-902. Gas chromatographic/mass spectral (GCMS) analysis was done on a Perkin-Elmer 270 mass spectrometer. Routine analytical and preparative gas chromatography (GC) was done with an F & M 500 gas chromatograph.

Yields, unless otherwise indicated, were done by GC analysis. A known amount of a standard was added to the reaction mixture and used to calculate yield. The exception to this procedure was for reactions of the disilene generators. In these cases the yield of naphthalene or biphenyl was assumed quantitative, and yields were based on them. In all cases, corrections were made for differences in thermal conductivities.

Flow pyrolysis was done by dripping the desired solution through a vertical tube (10 m \times 30 cm) packed with quartz chips. The solutions were dripped through the tube at a rate of 0.33 ml/min. The reactions were done under a nitrogen flow at 1 ml/s. The products were trapped in a liquid nitrogen cooled trap for analysis and separation.

2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (1). 2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was prepared according to the method of Roark and Peddle.⁴ This procedure was sometimes modified to use sodium in place of lithium.

1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (2). 1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was prepared according to the method of Roark and Peddle⁴ with sodium used in place of lithium.

Preparation of Cyclosiloxanes. Hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and decamethylcyclopentasiloxane were made according to the method of Patnode and Wilcock.¹²

Pyrolysis of 1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (2) with Benzaldehyde. A solution of 0.450 g (1.06 mmol) of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene and 3.5 g (33 mmol) of benzaldehyde was degassed via the freeze-thaw technique. The solution was dripped (1/3 ml/min) through a vertical pyrolysis column heated to 480 °C under a nitrogen flow of 1 ml/s. The products were collected in a liquid nitrogen trap. Analysis and separation were done by gas chromatography. The products were *trans*-stilbene (23.9%—identification by matching GC retention time, NMR, and mass spectra with authentic sample), hexamethylcyclotrisiloxane (16%), and octamethylcyclotetrasiloxane (13.8%) (siloxanes identified by matching GC retention time, infrared, and mass spectral comparison with authentic samples).

Pyrolysis of 2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (1) with Benzaldehyde. 2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (0.122 g, 0.5 mmol) was dissolved in 1.06 g (10 mmol) of benzaldehyde. The solution was degassed and pyrolyzed in a nitrogen flow system at 500 °C. The products were isolated and analyzed by gas chromatography. Products included naphthalene, *trans*-stilbene (12.4%), hexamethylcyclotrisiloxane (14.1%), and octamethylcyclotetrasiloxane (10.2%). All products were identified by GC retention time, NMR, infrared, and mass spectra comparison with authentic samples. An NMR of the product solution shows no evidence for heptafulvalene (olefin H's at δ 5.88¹⁰) but does show a peak for *trans*-stilbene δ 6.93.

Pyrolysis of 2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (1) with Benzaldehyde and Cyclohexene. 2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (0.244 g, 1 mmol) was added to 0.42 g (4 mmol) of benzaldehyde and 0.82 g (10 mmol) of cyclohexene. The solution was degassed and pyrolyzed at 500 °C in a nitrogen flow system. The product was analyzed

by gas chromatographic mass spectroscopy. No evidence was found for 7-phenylnorcarane, nor any other $C_{13}H_{16}$ isomer.

Pyrolysis of 1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (2) in Hexene. 1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (0.1 g, 0.37 mol) was dissolved in 1.5 g (17.5 mmol) of hexane. The solution was pyrolyzed in a nitrogen flow system at 480 °C. Analysis by GC and GCMS showed neither *trans*-stilbene nor cyclic siloxanes. Gas chromatography and GCMS identified a quantitative yield of diphenyl along with several polysilanes.

Pyrolysis of Benzaldehyde. Benzaldehyde (1.75 g, 16.5 mmol) was pyrolyzed under nitrogen flow at 480 °C. Analysis of the product by NMR and GCMS showed only starting benzaldehyde (96% recovery) and no evidence for *trans*-stilbene.

Pyrolysis of 1,2-Dimethoxy-1,1,2,2-tetramethyldisilane with Benzaldehyde. Dimethoxydisilane⁹ (1.78 g, 0.1 mol) and 2.12 g (0.2 mol) of benzaldehyde were pyrolyzed in the flow system at 500 °C. The solution was analyzed by GC, and benzaldehyde (97%) was isolated (identified by GC retention time and GCMS). No evidence was found for *trans*-stilbene or cyclic siloxanes.

Preparation of 5,6-Diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (12). Dihydrobenzoin (2.0 g, 9.3 mmol) was dissolved in 250 ml of dry, deoxygenated benzene. Dry triethylamine (1.9 g, 18.8 mmol) and 1.75 g (9.3 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane were added, and the solution was refluxed under nitrogen for 12 h. The solution was filtered to remove triethylamine hydrochloride. The benzene was distilled from the filtrate under reduced pressure, and then under high vacuum. The residue was identified as disiladioxane **12** (80%): NMR (CCl_4) δ 0.30 (s, 12 H), 5.16 (s, 2 H), 6.92 (s, 10 H); infrared (CCl_4) 3080 (w), 3025 (w), 2950 (m), 2880 (w), 1410 (m), 1380 (w), 1250 (s), 1200 (w), 1105 (s), 1070 (b); mass spectrum (70 eV) *m/e* (rel intensity) 328 (1), 270 (17), 180 (100), 165 (25), 74 (28); mass spectrum calculated for $C_{18}H_{24}O_2Si_2$ *m/e* 328.1315; found, *m/e* 328.1310 \pm 0.0016. The synthesis of **12** is very erratic and only on two occasions has gone cleanly. The product has only been identified by the above spectroscopic means and is apparently *very* unstable to the atmosphere.

Pyrolysis of 5,6-Diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (12). 5,6-Diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (0.5 g, 1.5 mmol) (**12**) was dissolved in 10 ml of dry, deoxygenated benzene. The solution was dripped through a pyrolysis column at 500 °C under nitrogen flow. The products were separated by gas chromatography. They were *trans*-stilbene (73%) (identified by NMR and gas chromatographic comparison with authentic sample), hexamethylcyclotrisiloxane (28%), and octamethylcyclotetrasiloxane (17%) (siloxanes identified by GC and GCMS comparison of authentic samples).

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Stable Homopolyatomic Anions of the Post-Transition Metals. "Zintl Ions". The Synthesis and Structure of a Salt Containing the Heptantimonide(3-) Anion

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Abstract: The phenomenon of the formation of homopolyatomic or the so-called Zintl anions on solution of many alloys in liquid ammonia is considered, and a general route to the isolation of stable homopolyatomic anions illustrated in the case of antimony. The dark brown crystalline (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)sodium heptantimonide(3-), $(C_{18}H_{36}N_2O_6 \cdot Na^+)_3Sb_7^{3-}$, has been prepared from the reaction of a sodium-antimony alloy with $C_{18}H_{36}N_2O_6$ (2,2,2-crypt) in ethylenediamine. Lattice constants $a = 23.292$ (7) Å, $b = 13.791$ (6) Å, $c = 25.355$ (6) Å, and $\beta = 108.56$ (2)° with four molecules per unit cell in space group $P2_1/n$ were deduced from three-dimensional x-ray data collected from a single crystal of the compound on a four-circle diffractometer using Mo K α radiation. The problem was phased using direct methods. Stepwise full-matrix least-squares refinement of the ten heavy atoms with anisotropic thermal parameters and of the 78 light atoms of the crypts with isotropic temperature factors resulted in converged atomic parameters with $R = 0.111$ and $R_w = 0.134$. Three cryptated sodium cations in which the sodium ion occupies the central cavity of the macrobicycle occur together with the Sb_7^{3-} cluster anion, the first example of a well-characterized polyatomic anion for a metallic element. The polyantimony anion exhibits approximate C_{3v} symmetry as an end-capped trigonal prism with the capped face substantially expanded, analogous to the isoelectronic P_4S_3 . Bond distances in the cluster range from 2.693 (4) to 2.880 (4) Å. Possible geometries for several other reported Zintl ions of the group 5 elements are proposed on the basis of known isoelectronic ions or molecules.

The remarkable reaction of sodium and lead or their compounds with liquid ammonia to yield an intensely colored green solution was evidently first noted by Joannis¹ about 85 years

ago. Subsequent experimentation confirmed his observations and further established that the lead solute was anionic and contained about 2.25 lead atoms per charge² according to