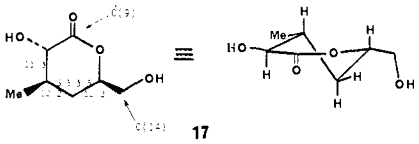
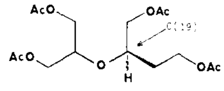
spectrum of **10**, only small and large vicinal couplings are observed, strongly suggesting that none of the substituents in the acyclic portions of the palytoxin molecule are gauche–gauche to other substituents or to cyclic ether oxygens in the fully extended conformations. Most the stereochemical assignments could be made from data obtained at 25 °C. Some of the couplings, however, were 5–5.5 Hz at 25 °C, and low-temperature studies were needed to make a decision. In the ^{1}H NMR spectrum of **13**, for example, couplings of 5.5 Hz for $J_{95,96}$, $J_{95',96}$, $J_{96,97}$, $J_{97,98}$, and $J_{98,99}$ suggested that the conformation in which C(93)–C(94)–C(95)–C(96)–C(97)–C(98)–C(99) is aligned with the methyl carbon on C(99) is also a prominent species in solution at 25 °C; at −40 °C, however, these coupling constants changed to larger and smaller values, indicating the predominance of a single conformer, presumably the one in which the carbon side chain is planar and fully extended with C(101)–C(102) in the tetrahydropyran ring.

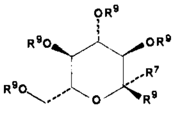
The absolute configurations of 60 of the 64 chiral centers in Hawaiian *P. toxica* palytoxin have been determined as follows. 10*S*,11*R*,13*R*: The δ-lactone **17** (from HCl hydrolysis of the corresponding diacetate[1]) has the absolute stereochemistry shown from NMR and CD data ($[\theta]_{224}{}^{\mathrm{EtOH}}$ +2300°).[8,9] 16*R*,17*R*,19*R*,20*R*,21*R*,22*S*,23*S*,24*R*,25*R*,26*R*,27*R*,28*R*: Periodate oxidation of palytoxin leads to **18**,[1] which has a CD curve ($[\theta]_{215}{}^{\mathrm{EtOH}}$ −100°) that is opposite in sign to that of *S*-**18** ($[\theta]_{215}{}^{\mathrm{MeOH}}$ +100), synthesized from periodate oxidation of **22** (glucose → **19** → **20** → **21** → **22**). The absolute configuration of C(19) in **11** is therefore *R*. 34*S*,36*R*,37*R*,39*R*,41*S*,49*S*: The absolute stereochemistries of these carbons are implied from X-ray studies of **4**.[6] 49*S*,51*R*,52*R*,53*R*,54*R*,55*S*: The chiralities of the R^3 groups in **9–11** are as shown since all have been related to C(49) by NMR. 64*R*,65*S*,66*R*,68*S*,69*R*,70*S*,72*S*,73*R*,75*R*,76*S*,77*R*,78*R*,79*S*,81*S*:[10] Compound **7** from ozonolysis of a previously described periodate oxidation product containing the cis, trans diene system[5] has a CD spectrum ($[\theta]_{213}{}^{\mathrm{EtOH}}$ −3900°) that is comparable in sign with that of **6** ($[\theta]_{215}{}^{\mathrm{EtOH}}$ −1100°), synthesized from **20**. 87*R*,89*R*: The ozonolysis product **23**[1] shows a maximum peak in its CD spectrum ($[\theta]_{210}{}^{\mathrm{EtOH}}$ +2000°) that is comparable in sign, position, and intensity to those of (2*R*,3*S*,4*R*)-1,2,3,4,6-pentaacetoxyhexane (from 2-deoxy-D-glucose) ($[\theta]_{212}{}^{\mathrm{MeOH}}$ +2500°) and (2*R*,3*R*,4*R*)-1,2,3,4,6-pentaacetoxyhexane (from 2-deoxy-D-galactose) ($[\theta]_{212}{}^{\mathrm{MeOH}}$ +2900°). 96*R*,97*S*,98*R*,99*S*,101*S*,102*S*,103*S*,104*R*,105*S*,108*S*,109*S*,111*R*,113*S*,115*R*,116*R*,119*R*,120*R*,122*S*: The absolute stereochemistry of **12** is implied from X-ray studies of **2**.[6] Detailed ^{1}H NMR analysis of **14**, which is actually a 1:1 mixture of C(93) epimers, correlates the relative stereochemistries of **12** and **13**.



17



18

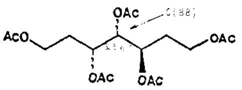


19 R^7 = H ; R^8 = Cl ; R^9 = CH_2Ph

20 R^7 = $CH_2CH{=}CH_2$; R^8 = H ; R^9 = CH_2Ph

21 R^7 = CH_2CH_2OH ; R^8 = H ; R^9 = CH_2Ph

22 R^7 = CH_2CH_2OH ; R^8 = H ; R^9 = H



23

Interestingly, the NMR signal for one of the protons on C(123) is clearly doubled, suggesting that C(123) and the epimeric C(93) are spatially close in the preferred conformation. A Dreiding model examination of **14** shows that this is the case when the carbons of all side chains are aligned in a fully extended and planar manner with two or three carbons in each of the ether rings: C(123) and C(93) do not come in contact, however, if the absolute stereochemistry of C(92)–C(106) is opposite that shown by **13**.

Acknowledgment. This research was supported by Grant CHE79-25416 from the National Science Foundation and Grant CA12623-09 awarded by the National Cancer Institute, Department of Health and Human Services. The 600-MHz ^{1}H NMR studies at Carnegie-Mellon University were supported by NIH Grant RR00292. ^{1}H NMR studies at 360 MHz were carried out at the Stanford Magnetic Resonance Laboratory under the auspices of NSF Grant GP-23633 and NIH Grant RR00711. The 500-mHz ^{1}H NMR studies at the California Institute of Technology were supported by NSF Grant CHE79-16324A1. We thank Dr. R. Bonjouklian for her assistance in the preparation of compound **20**. Recent 300-MHz ^{1}H NMR studies at the Univeristy of Hawaii were made possible by NSF Grant CHE81-00240.

Supplementary Material Available: High-field region of the 600-MHz ^{1}H NMR spectrum of **3** and simulated spectra of H_2, H_3, H_4, and H_5 resonances (Figure 1); low-field region of the 360-MHz ^{1}H NMR spectrum of **13** at 20, 3, −20, and −40 °C (Figure 2); low-field regions of the 600-MHz ^{1}H NMR spectra of **12**, **14**, and **15** (Figure 3) (4 pages). Ordering information is given on any current masthead page.

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[8] (a) Korver, O. *Tetrahedron* **1970**, *26*, 2391. (b) Cardellina, J. H., II; Moore, R. E.; Arnold, E. V.; Clardy, J. *J. Org. Chem.* **1979**, *44*, 4039.

[9] The enantiomer of **17** has been synthesized from (+)-pulegone: Thurkauf, A.; Tius, M. A., unpublished results.

[10] The same CD signs for **6** and **7** only suggest that the two compounds have the same absolute configurations. The absolute stereochemistry of the C(63)–C(82) portion of palytoxin is therefore tentative.

Ab Initio Study of Silylene Insertion into O–H Bonds. Stability of Zwitterionic Intermediates

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The current burst of activity in the study of silicon reactive intermediates[1] has brought to light increasing differences between the structural chemistry of silicon and carbon. The reluctance of silicon to form multiple bonds and its unusual preference to adopt divalent structures instead provide dramatic examples.[2] In this communication we point to another structural type, generally not adopted by carbon, that may be spectroscopically observable as a silicon compound.

We have carried out ab initio calculations with extended basis sets including significant electron correlation and zero-point energy corrections on all the stationary points of the two insertion-reaction

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(1) Review: Gaspar, P. P. In "Reactive Intermediates", Jones, M., Moss, R. A., Ed.; Wiley-Interscience: New York, 1978; Vol 1, pp 229–277.

(2) (a) Blustin, P. H. *J. Organomet. Chem.* **1976**, *105*, 161. Murrell, J. N.; Kroto, H. W.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1977**, 619. Barthelat, J.-C.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1979**, *101*, 3785. Hopkinson, A. C.; Lien, M. H. *J. Chem. Soc., Chem. Commun.* **1980**, 107. Gordon, M. S.; Pople, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 2939, 2945. Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F. *Ibid.* **1980**, *102*, 7644. (b) Multiply bonded silicon compounds are not unknown. For spectroscopic characterizations, see: Mahaffy, P. G.; Gutowsky, R.; Montgomery, L. K. *Ibid.* **1980**, *102*, 2854. Kreil, C. L.; Chapman, O. L.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 841. Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 52.

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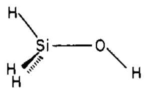
Table I. Energies[a] for Stationary Points on the Reaction Surface $SiH_2 + H_2O \rightarrow SiH_3OH$

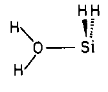
molecule	HF[b]	$\epsilon^{(2)b}$	$\epsilon^{(3)c}$	$\epsilon^{(4)}_{SDQ}{}^{c}$	$\epsilon^{(4)d}_{T}$	*E*(vib)[e]	*E*(rel)
H_2O+SiH_2	−366.025 97	−292.84	−24.48	−7.06	−2.78	21.7	0
1	−366.143 03	−300.11	−17.73	−6.33	−4.33	25.8	−70.1
2	−366.047 90	−300.12	−21.48	−6.45	−3.92	26.4	−12.1
3	−365.983 51	−323.23	−15.07	−8.01	−7.10	22.8	11.3

[a] Total energies in hartrees, correlation energies in mhartrees, vibrational and relative energies in kcal/mol. [b] Obtained with the 6-211G** basis. This basis set was formed by splitting the 31 part of the 6-31G** basis to 211. The scale factors were not changed. [c] Obtained with the 6-31G** basis. [d] Obtained with the 6-31G* basis. [e] Obtained with the 3-21G* basis.

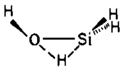
potential-energy surfaces: $^1SiH_2 + H_2O \rightarrow SiH_3OH$ and $^1SiH_2 + SiH_3OH \rightarrow (SiH_3)_2O$. Both reactions involve the formation of a donor–acceptor complex between two closed-shell fragments, followed by a 1,2-hydrogen shift. Correlated wave functions derived from a leading single determinant are known to give reliable energies for such reactions.[3] Our calculations which employ complete fourth-order Møller–Plesset perturbation theory[5] and large basis sets[6] (the computational details are summarized in ref 4) indicate **2** not only to be a stable complex formed from singlet silylene and water (complexation energy = 12.1 kcal/mol) but also to have a significant barrier (23.4 kcal/mol) to rearrangement to the more stable silanol (**1**). The carbon analogue of the zwitterionic structure **2** is the highly unstable oxonium ylid, which is indicated to rearrange without a barrier at comparable theoretical levels.[8,9]



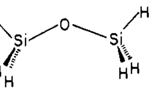
1(C_s)



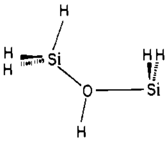
2(C_s)



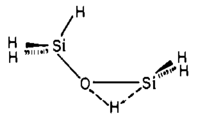
3(C_1)



4 (C_{2v})



5 (C_s)



6(C_s)

Zwitterionic intermediates similar to **2** have previously been proposed for the reaction of silylene with water, alcohols, oxetanes, and epoxides on the basis of detailed mechanistic studies by Weber and his associates.[10] The unusual solvent effect on the rates of silylene insertion into oxygen–hydrogen bonds, not observed in analogous carbene reactions, provides further support.[10a] Our results agree with the mechanistic proposals of Weber et al. and provide in addition detailed structural and energetic information.

The reaction between silylene and water (Table I) occurs with the initial formation of complex **2**, in which the vacant p orbital of SiH_2 is oriented for maximum interaction with the σ lone pair on the oxygen. **2** has the indicated C_s structure[18] with the lone pairs on the heavy atoms aligned orthogonal to each other. The coordination around oxygen is planar although no constraint was imposed during the optimization. This structural feature is not unusual since oxonium ions are generally calculated to be planar with split-valence basis sets that do not include d functions on oxygen.[11] The Si–O bond is long, 1.96 Å, compared to 1.63 Å in silanol. The rotational barrier about the Si–O bond in **2** is 3.0 kcal/mol (HF/3-21 G* level), fairly large in view of the large Si–O distance (for comparison, the rotational barrier in methylsilane is 1.8 kcal/mol).[12] The transition state of the rotational process has a C_s structure (not shown) with the two lone pairs in a slightly cis orientation. The long Si–O bond, 2.00 Å, reflects the lone-pair repulsion present in this geometry.

The transition state for the rearrangement of **2** to silanol is **3**, which possesses only C_1 symmetry.[18] The hydroxyl hydrogen is bent significantly out of the plane formed by the migrating hydrogen, Si, and O. The Si–O bond length of 1.81 Å in **3** is

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(3) Yoshioka, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1981**, *103*, 7367 and references cited therein. See also: Schaefer, H. F. *Acc. Chem. Res.* **1979**, *12*, 288. In the case of the closed-shell vinylidene–acetylene system, different electron correlation methods (MP4, GVB/POL-CI and SCEP) yield similar calculated barriers. See: Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7475.

(4) The first insertion-reation surface: All the geometries were obtained by analytical gradient optimization procedures at the Hartree–Fock level with the 3-21G* basis[6a] (a split-valence basis with d functions on silicon). Analytical second derivatives[7] obtained at this level were used to compute zero-point vibrational energies. Møller–Plesset perturbation theory[5] correct to fourth order within the space of single, double, and quadruple substitutions (SDQ) were carried out with the 6-31G** basis set[6b] (a split-valence basis including d functions on heavy atoms and p functions on hydrogens). The effect of triple substitutions (T) were evaluated with the 6-31G* basis[6b] (a split-valence basis with d functions on heavy atoms). The effect of larger basis sets were estimated by performing second-order perturbation (MP2) calculations with the 6-211G** basis (formed by splitting the 31 part of the 6-31G** basis to 211). The second insertion reaction surface: All the geometries were optimized with the 3-21G split-valence basis set[6a] at the HF level. Second-order Møller–Plesset perturbation theory (MP2) calcualtions were carried out at these geometries with the 6-31G** basis.[6b] Higher order effects of electron correlation, larger basis-set effects, and vibrational corrections were estimated from the computed results for the first insertion reaction. All calculations were performed with the GAUSSIAN 80 computer program on a Cray-1 computer at Bell Laboratories.

(5) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* **1975**, *9*, 229. Pople, J. A.; Binkley, J. S.; Seeger, R. *Ibid.* **1976**, *S10*, 1. Krishnan, R.; Pople, J. A *Ibid.* **1978**, *14*, 91. Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(6) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Chem. Phys.*, in press; Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.*, in press. (b) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.*, in press.

(7) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quant. Chem.* **1979**, *S13*, 225.

(8) Harding, L. B; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394. The oxonium ylid survives as a minimum if electron correlation is not included. See also: Eades, R. A.; Gassman, P. G.; Dixon, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 1066.

(9) Substituted oxonium ylids with highly stabilized carbanion moieties may, however, be involved in certain carbene-insertion reactions. Such a suggestion has been made for the insertion of cyclopentadienylidene in O–H bonds Kirmse, W.; Loosen, K.; Sluma, H.-D. *J. Am. Chem. Soc.* **1981**, *103*, 5935.

(10) (a) Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6095. (b) Gu, T.-Y. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7; *195*, 29; Steele, K. P.; Weber, W. P. *Inorg. Chem.* **1981**, *20*, 1302. Gu T.-Y. Y.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 1641. Tzeng, D.; Weber, W. P. *Ibid.* **1980**, *102*, 1451.

(11) Hydronium ion is calculated to be planar with the 3-21G basis. See: Carnegie-Mellon Quantum Chemistry Archive, 2nd ed.; Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. Carnegie-Mellon University, Pittsburgh, PA, 1981.

(12) Lowe, J. P. *Prog. Phys. Org. Chem.*, **1968**, *6*, 1.

(13) The Si–O–Si angle is disiloxane is calculated to be 180°, considerably larger than the electron diffraction value of 144°[15]. This is principally due to the neglect of d-type polarization functions on O in the optimization.[16] However, even optimization at the MP2/6-31G* level leads to a wide angle, 161°. This is larger than the value calculated by Ernst et al.,[16] and this aspect of the problem needs more investigation. however, in view of the extreme flatness of the bending potential surface,[16,17] the relative energies, in any case, are expected to be of quantitative accuracy.

(14) The insertion of SiH_2 into H_2 has also been recently calculated to have an activation barrier: Gordon, M. S. *J. Chem. Soc., Chem. Commun.* **1981**, 890.

(15) Almenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455.

(16) Ernst, C. A.; Allred, A. L.; Ratner, M. A.; Newton, M. D.; Gibbs, G. V.; Moskowitz, J. W.; Topiol, S. *Chem. Phys. Lett.* **1981**, *81*, 424.

(17) A variety of different bond angles have been observed for various substituted disiloxanes. See, for example: Glidewell, C.; Liles, D. C. *J. Chem. Soc., Chem. Commun.* **1977**, 633.

(18) The optimized geometries and vibrational frequencies are available from the authors on request.

Table II. Energies[a] for Stationary Points on the Reaction Surface $SiH_2 + SiH_3OH \rightarrow (SiH_3)_2O$

molecule	HF[b]	$\epsilon^{(2)b}$	E(rel)[c]
$SiH_3OH+SiH_2$	−656.14223	−366.08	0
4	−656.266 63	−372.75	−75.7
5	−656.162 45	−375.63	−12.8
6	−656.107 47	−397.78	4.9

[a] Total energies in hartrees, correlation energies in mhartrees, and relative energies in kcal/mol. [b] Obtained with the 6-31G** basis. [c] Higher order effects of electron correlation, larger basis set effects, and vibrational corrections were taken from the first insertion reaction.

intermediate between that in **1** and **2**. The relative energy of **3** is very sensitive to the inclusion of electron correlation. The overall activation energy for the formation of silanol from SiH_2 and H_2O is calculated to be 11.3 kcal/mol at the highest theoretical level. The exothermicity of the reaction, 70.1 kcal/mol, is considerably lower than the value of 94.9 kcal/mol computed for the corresponding carbene-insertion reaction.[8]

We have also examined the second insertion reaction, viz., the reaction between silanol and SiH_2 to yield the ultimate reaction product disiloxane, **4** (Table II). This reaction proceeds in a manner qualitatively analogous to the first reaction, with the initial formation of a complex, **5**,[18] between SiH_2 and the oxygen lone pair of silanol. The complexation energy of 12.8 kcal/mol is nearly the same value calculated for **2** at a similar level. However, the overall activation energy (4.9 kcal/mol) and the exothermicity (75.7 kcal/mol) of this step are calculated to be about 6 kcal/mol lower than the corresponding values for the initial insertion reaction. The key structural features of **1–3**, viz., the large variation in Si–O distance, wide angles at the oxygen bound to silicon,[13] and the low symmetry of the rearrangement transition state, are also found in the structures **4–6**.[18]

We are currently examining the insertion of silylene in a variety of σ bonds to probe the general stability of zwitterionic structures involving silicon and other heteroatoms.[14]

Acknowledgment. J. C. thanks Professor W. L. Jorgensen for encouragement and support.

Registry No. SiH_2, 13825-90-6; H_2O, 7732-18-5; SiH_3OH, 14475-38-8; $(SiH_3)_2O$, 13597-73-4.

Synthesis of Cesium 18-Crown-6: The First Single-Crystal Electride?

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A relatively stable crystalline compound between cesium metal and the crown ether 18-crown-6[1] has been synthesized. The optical, electrical, and magnetic properties suggest that it is an electride, $Cs^+18C6\cdot e^-$, although the ceside, $Cs^+(18C6)_2\cdot Cs^-$, cannot be ruled out. Electrides are salts in which the anion is a trapped electron.[2] They had previously been prepared only as films or powders by complete solvent evaporation from solutions that contained solvated electrons and alkali metal cations complexed by crown ethers or cryptands.[3-8] Thin films had also been prepared by direct vapor deposition.[9] Characteristic of all electrides is an intense optical absorption band at 1250–1800 nm.[3-6] Magnetic susceptibilities and EPR spectra of electride powders showed that they exhibit substantial spin pairing.[6-8] Numerous attempts to crystallize electrides from solution have failed. In "good" solvents such as methylamine or ammonia the solubility is too high, while "poor" solvents such as isopropylamine or diethyl ether always led to rapid decomposition. The key to the present synthesis is stabilization of the solutions by dissolved lithium.

Extensive studies of films and powders prepared from methylamine solutions of cesium and 18-crown-6 in various proportions[8] showed that when lithium was added the solutions were much more stable. In an attempt to prepare crystalline Cs18C6Li, analogous to the recently synthesized sodide salt $Cs^+18C6\cdot Na^-$,[10] we dissolved equimolar amounts of Cs, Li, and 18C6 in methylamine in a fused silica apparatus. The solution was evaporated to near dryness, and the crystallization solvent, an approximately equimolar mixture of isopropylamine and diethyl ether, was added.[11] When the solution was cooled to −78 °C, a crystalline precipitate formed. Microscopic examination of the ether-washed crystals from this preparation and from a second identical synthesis showed the presence of well-formed dark blue crystals. Mixed with the crystals were numerous irregularly shaped dark particles.[12] Analysis of selected crystals showed the stoichiometry to be essentially Cs18C6. In a third preparation the final solution was passed through a coarse frit at ∼−10 °C before crystallization in order to retain any precipitated lithium. Well-formed crystals resulted that showed little contamination by noncrystalline particles. After removal of the supernatant solution, the crystals were repeatedly washed with diethyl ether, vacuum-dried at room temperature, and transferred through a graded seal to Pyrex storage tubes.

The crystals are stable in vacuo for days at room temperature and below. They melt at ∼65 °C to yield an unstable deep blue liquid. Analysis of all three preparations showed the most likely stoichiometry to be simply Cs18C6. Surprisingly, lithium is not present in significant amounts, and that which was detected is probably adventitious lithium which adheres to the crystals. Complete analysis of a weighed sample from the third preparation was carried out as described elsewhere.[10] Reaction with water produces 0.5 mol of H_2 and 1 mol of OH^- per mol of reducing species. Titration of the OH^- was followed by flame emission analysis for alkali metals. The residue was dissolved in D_2O and was analyzed for 18C6 by ^1H NMR integration with an internal standard of potassium hydrogen phthalate. Crystals were also reacted directly with D_2O and examined by ^1H NMR. The spectrum showed the complete absence of methylamine, isopropylamine, and diethyl ether. The number of millimoles obtained by analysis of a mass equivalent to 0.246 mmol of Cs18C6 from the third synthesis were 0.124 (H_2), 0.252 (OH^-), 0.253 (Cs), 0.0033 (Li), and 0.258 (18C6). These results confirm the stoichiometry Cs18C6. Preliminary X-ray diffraction studies of three crystals yielded only diffuse spots, showing that the crystal quality was too poor for a structure determination.

Lithium seems to act as a scavenger for radicals produced by solvent and/or crown ether decomposition (possibly by forming lithium alkyls). When crystals were dissolved in isopropylamine in the absence of lithium in an attempt to recrystallize them, immediate decomposition occurred. Subsequent experiments have shown that lithium also stabilizes other alkali metal–crown ether

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(1) IUPAC: 1,4,7,10,13,16-hexaoxacyclooctadecane; abbreviation, 18C6.

(2) The trapped electrons may undergo spin pairing or even "dielectron" formation. Thus, the name "electride" refers to the stoichiometry, not the structure of the salt. The essential features are substantial electron localization and the absence of electron attachment to individual atoms or molecules to form conventional anions.

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(11) Pure isopropylamine can also be used, but the yields are lower.

(12) The low lithium content of the crystals and the low solubility of lithium in the crystallization solvent make it likely that these particles are precipitated lithium.

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