

Molecular Orbital Approach to Cyclic Anionic Pentaoxysilicates, Fluorosilicates, and Isoelectronic Phosphoranes. Structural Comparisons^{1,2}

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Geometries and relative energies from *ab initio* calculations using Gaussian 92 on five-coordinated anionic cyclic pentaoxysilicates and isoelectronic cyclic pentaoxyphosphoranes containing saturated five- and six-membered rings in trigonal bipyramids (TBP) are compared with structural results from X-ray diffraction and VT NMR studies. The theoretical study is extended to cyclic $C_4H_4SiF_3^-$, $C_4H_8SiF_3^-$, and isoelectronic phosphorus species in trigonal-bipyramidal geometries. In agreement with structural results, the saturated five- and six-membered rings in pentaoxy species are located on the potential energy surface as local energy minima with the rings occupying axial–equatorial (a–e) sites. In the cyclic anionic organofluorosilicates and organofluorophosphoranes, the five-membered saturated rings reside in diequatorial (e–e) sites, whereas the five-membered unsaturated rings are located in (a–e) sites. It is suggested that these cyclic derivatives provide useful models for nucleophilic displacement reactions. Low calculated axial bond overlap populations found for anionic silicon compared to isoelectronic phosphorus entities correlate with accompanying longer axial Si–O and Si–F bond lengths. It is concluded that the long axial bond lengths accompany weaker bond strengths, as indicated by the *ab initio* results and represent a major factor responsible for enhanced reactivity of five-coordinated anionic organosilicon compounds. This bond length factor, associated with the reduced nuclear charge on silicon, suggests greater fluxional character, which is consistent with the lower ligand exchange activation energies involving ring reorientations found for five-coordinated silicon compared to that for phosphorus. Bond-lengthening effects are found in the series $RR'SiF_3^-$ that correlate with the bulkiness of the organo substituents. Structural nonrigidity leads to axial bond shortening as the structure traverses from trigonal bipyramidal to square pyramidal, a feature which may reduce reactivity in nucleophilic displacement reactions for pentacoordinated molecules thus displaced.

Introduction

Hypervalent phosphorus^{4–7} and silicon^{7–9} compounds provide excellent models for proposed intermediates and activated states in nucleophilic displacement reactions. With cyclic components, X-ray structural work has been largely confined to examples with five-membered rings in oxyphosphoranes.^{4,7}

Pentaoxyphosphoranes with six-membered rings are of particular interest in cyclic adenosine monophosphate (cAMP) reactions.⁶ A knowledge of their structural consequences under a variety of conditions has an important bearing on the mechanisms associated with enzymatic reactions utilizing cAMP. A cyclic pentaoxyphosphorane activated state of cAMP with the six-membered ring in axial–equatorial (a–e) sites of a TBP has been implicated at the active site in hydrolytic cleavage reactions by phosphodiesterases,^{10–12} whereas in the activation of protein kinases, a TBP pentaoxy state of cAMP with the phosphorinane ring occupying diequatorial (e–e) sites has been advanced in the literature.^{10,13–15}

To address this problem, syntheses and structural studies have concentrated in the last few years on cyclic

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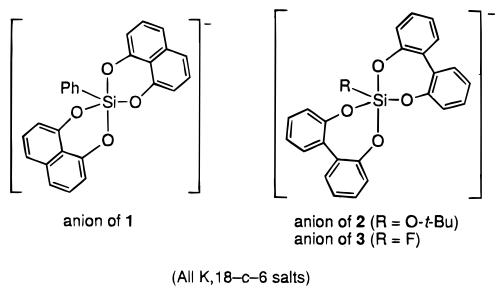
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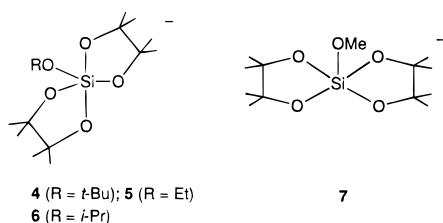
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oxyphosphoranes with phosphorinane rings to ascertain geometrical and ring conformational requirements to obtain a-e and e-e ring orientations.^{6,16-26} In this effort, studies have been extended to include a wide range of oxyphosphoranes possessing seven- and eight-membered rings.^{6,16,18-20,27-31}

In the less-advanced area of related silicon chemistry, the first anionic five-coordinated silicates with six- and seven-membered oxygen-containing rings, **1-3**, were isolated in 1991.³² Only 2 years earlier, the first X-ray



structures of cyclic anionic pentaoxysilicate compounds with five-membered rings, obtained using syntheses from Frye's work,³³ were reported:^{34,35} trigonal-bipyramidal (TBP) **4-6** and square-pyramidal (SP) **7**. Sili-



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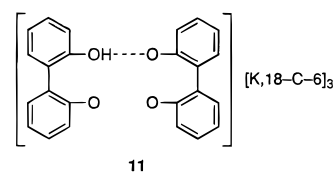
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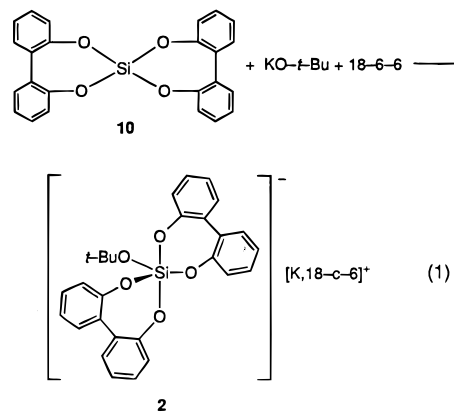
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ates **4**³⁴ and **6**³⁵ are K⁺, 18-crown-6 salts, while **5**³⁴ and **7**³⁴ are salts of *n*-BuNH₃⁺. In addition, the related bicyclic anionic tetraoxysilicates TBP [(CF₃)₂CO]₂-SiC₆H₁₁[[Et₄N] (**8**) and SP [(C₆H₄O)₂SiC₆H₁₁][Me₂NH₂] (**9**), have had their X-ray structures determined.³⁵

In the area of hypervalent silicon chemistry, enhanced reactivity is found for a variety of reactions involving species of this type.^{8,9} For example, immediate hydrolysis takes place on addition of Bu₄NF in THF to bis(2,2'-biphenoxy)silane (**10**) at room temperature or on addition of KO-*i*-Pr and 18-c-6 to 2,2'-biphenoxydiisopropoxysilane, whereas the silanes are much more hydrolytically stable under these conditions.³² The products isolated are anionic organic entities, e.g.,

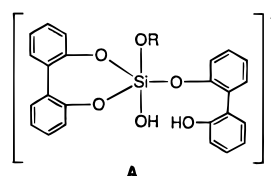


This type of reaction may be followed by solution ²⁹Si NMR in the case of the more stable derivatives **2** and **3**.³² For example, with **2**, prepared according to eq 1,



initially one signal appears at ~ -125 ppm, attributable to pentacoordinate silicon. This signal decreases with time as a signal at ~ -52 ppm in the tetracoordinate region increases.

The hydrolysis presumably is initiated by attack at silicon by a water molecule, resulting in the formation of a hexacoordinated activated state, which undergoes Si-O bond cleavage and yields a postulated intermediate of the type **A**. Repetition of the process is envisioned



to lead to the organic products. The enhanced reactivity of pentacoordinated anionic silicates compared to their four-coordinated silane precursors represents a growing but little-understood field of research. In related work, Kira et al.³⁶ found pentacoordinate anionic allyl derivatives containing the same ring system as is present in **2** and **3** to show a greater reactivity with benzaldehyde than that of the tetracoordinate silicon analogues.

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In the present work, we employ *ab initio* molecular orbital methods to assist in delineating the mechanistic problems described above. Calculations are performed to determine energies, and associated geometries of anionic five-coordinated pentaoxosilicates containing five- and six-membered rings are compared with that previously reported^{37a} for isoelectronic cyclic pentaoxyphosphoranes. For simplicity, these compositions are represented by the general formulations SiO_5^- and PO_5 , respectively. The calculations are extended to include five-membered carbon-containing rings, both saturated and unsaturated, for species of the types C_2SiF_3^- and C_2PF_3 , where these representations indicate the bonds attached to silicon and phosphorus, respectively. The results of the theoretical studies are compared with existing structural data from X-ray analysis, electron diffraction, and VT NMR data on ligand exchange barriers for these classes of hypervalent compounds.

Previous theoretical work has emphasized the lower silicon–ligand bond strengths^{37b} and greater positive charge at silicon^{37c} in the pentacoordinated anionic state compared to that in the tetracoordinate state as factors influencing enhanced reactivity of acyclic five-coordinated anionic silicon, $[\text{SiH}_n\text{F}_{5-n}]^-$ vs $\text{SiH}_n\text{F}_{4-n}$. Similar calculations were performed for the related isoelectronic phosphorus series.^{37b}

In recent theoretical work on five-coordinated phosphorus and silicon, Moc and Morokuma^{38a} employed *ab initio* methods to compare structures and energies of XH_5 species going down the main group VA period, where X is P, As, Sb, and Bi. They conclude that the D_{3h} structures represent local minima while the higher energy C_{4v} structures represent transition states for Berry pseudorotation.^{38b} Barriers of about 2 kcal/mol are obtained at their best MP4/ECP, level which reflect a remarkable insensitivity to the kind of central atom present. Also, electron correlation and effective core potentials showed little influence on these structures.

In related calculations, Gordon and co-workers^{38c} employed *ab initio* and semiempirical calculations to treat the SiH_5^- anion, which is isoelectronic with PH_5 . Both AM1 and MP2/6-31++G(d,p) calculations predict a 2.4 kcal/mol barrier for Berry pseudorotation involving the lower energy D_{3h} structure traversing via the higher energy C_{4v} square-pyramidal transition state into an equivalent D_{3h} trigonal bipyramid.

In the present work, we explore a considerably more formidable problem involving cyclic species. Our aim is to focus attention on a comparison of silicon–ligand and phosphorus–ligand bond effects as determinants in stabilizing rings in axial–equatorial vs diequatorial sites of trigonal-bipyramidal minima.

Computational Method

Full geometry optimization of all cyclic pentacoordinated species was carried out. Optimization was done at trigonal-bipyramidal minima with rings located either at axial–equatorial sites (a–e) or diequatorial locations (e–e). Calculations were carried out at the Hartree–Fock level with the program GAUSSIAN 92³⁹ at the San Diego Supercomputer

Center. For the cyclic SiO_5^- molecules, the basis set was 3-21G* (split-level valence with polarization functions on second-row atoms). For the anionic cyclic C_2SiF_3^- molecules, basis sets of 3-21G* and 3-21+G* were used, while the basis set for the isoelectronic cyclic C_2PF_3 molecules was 3-21G*. The latter has diffuse orbitals added to the basis sets for all non-hydrogen atoms as appropriate for anionic species. For the cyclic SiO_5^- molecules, single-point calculations were performed at the 6-31+G**/3-21G* level to provide the final energies. For the isoelectronic cyclic PO_5 molecules, on the basis of earlier work,^{2,37} the calculations were performed at the 3-21G* level with single-point calculations at 6-31G**/3-21G*. The nature of the stationary points was determined by frequency calculations. Minima have no imaginary frequencies, whereas transition structures have one imaginary frequency indicative of a saddle point. The use of different basis sets for phosphoranes and anionic silicates in this way introduces a measure of uncertainty in making comparisons between the two. However, in previous work with acyclic phosphoranes and analogous anionic silicates,⁴⁰ in general we found that relative differences of calculated isomeric energies maintained their order independent of whether the same basis set was used or not. In the present case, it was necessary to limit the calculations in this way for these cyclic derivatives, as the computational time becomes prohibitive otherwise. Although the *ab initio* calculations all refer to local energy minima, some of these, as illustrated in Figures 1 and 2, are used from an experimental point of view to mean activated states appearing along a potential surface governing intramolecular ligand exchange phenomena, *i.e.*, well-known pseudorotational behavior.

Results

Table 1 lists computed energy differences for TBP species between the higher energy (e–e) five- and six-membered-ring orientations relative to a–e ring orientations for cyclic SiO_5^- entities (**12–15**). Final energies were obtained using single-point calculations at the 6-31+G**/3-21G* level. These energies are compared with previously reported^{2,37a} *ab initio* calculations for the isoelectronic cyclic PO_5 species **16–19**, obtained at the 3-21G* and 6-31G**/3-21G* levels. The six-membered rings in a–e orientations have a boat conformation. In e–e ring orientations, the six-membered ring is in a chair conformation. Table 2 reports the results of similar calculations for cyclic C_2SiF_3^- and the isoelectronic cyclic C_2PF_3 species in TBP geometries. Here, the basis sets were 3-21G* and 3-21+G*.

The geometries reported represent stationary points on the potential surface which are local energy minima (with no imaginary frequencies) or local energy first-order saddle points (with one and only one negative eigenvalue). For example, the optimized geometry reported for the isomer with an axial–equatorial ring, **20**, corresponds to a local energy minimum, while that reported for the diequatorial ring isomer **21** corresponds to a first-order saddle point. In general, for members of the cyclic silicates and cyclic phosphoranes listed in Tables 1 and 2, we find that the lower energy structures with no imaginary frequencies are the ones observed

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Table 1. Minimum Energies of Optimized TBP Geometries of Cyclic SiO₅⁻ and Isoelectronic PO₅ Species with Rings in e-e Orientations Relative to a-e Orientations^a

	entry, ^b M = Si	energy, kcal/mol	entry, ^{b,e} M = P	energy, kcal/mol
	12	0	16	0
	13	18.5, ^c 18.1 ^d	17	20.1, ^{c,e} 22.9 ^f
	14	0	18	0
	15	7.6, ^c 6.7 ^d	19	6.6, ^{c,e} 8.7 ^f

^a As shown in the Supporting Information, the nonbonding hydrogen to oxygen distances fall in the range 2.01–3.96 Å, thus ruling out any effective hydrogen-bonding interactions which might influence the computed geometry. ^b The silicon species are anionic, whereas the isoelectronic phosphorus species are neutral. The isomers of lower energy, **12**, **14**, **16**, and **18**, are the ones observed by our X-ray studies. These represent minima in the *ab initio* study, whereas the higher energy isomers represent transition-state geometries. ^c Basis set 3-21G*. ^d Basis set 6-31+G*/3-21G*. ^e Reference 37a. ^f Basis set 6-31G*/3-21G*.

Table 2. Minimum Energies of Optimized TBP Geometries of C₂SiF₃⁻ and Isoelectronic C₂PF₃ Species with Five-Membered Rings in e-e Orientations Relative to a-e Orientations

	entry, ^a M = Si	energy, kcal/mol	entry, ^a M = P	energy, kcal/mol
	20	0	24	0
	21	15.3, ^b 10.8 ^c	25	13.2 ^b
	22	0	26	0
	23	3.8, ^b -0.2 ^{c,d}	27	-4.2 ^{b,d}

^a The Si species are anionic, whereas the P species are neutral. See footnote a to Table 1. ^b Basis set 3-21G*. ^c Basis set 3-21+G*. ^d Negative values mean that the e-e ring orientation is more stable.

by our X-ray studies. In the case of first-order saddle points (*i.e.*, the structures such as **17**, **19**, and **21**, which are the isomers of higher energy as compared to **16**, **18**, and **20**), we have observed that if the geometry of higher energy is not constrained, the structure will undergo Berry pseudorotation to give the more stable isomer in a downhill reaction path; thus, these structures represent transition states.

Values of Si–O bond distances are summarized in Table 3 for the computed TBP geometries of the cyclic SiO₅⁻ entries **12**–**15** listed in Table 1. These data are listed alongside previously reported P–O bond distances

that were computed for the cyclic PO₅ geometries **16**–**19** of Table 1. Comparison is made with experimental Si–O bond lengths obtained from three TBP molecular structures of pentaoxysilicates by X-ray diffraction.^{34,35} Average values are listed at the bottom of Table 3 along with average P–O bond distances from X-ray studies of a larger number of cyclic pentaoxyphosphoranes.^{18,19,21}

Table 4 reports calculated silicon–ligand and phosphorus–ligand bond distances for the TBP geometries associated with cyclic C₂SiF₃⁻ and C₂PF₃ species, obtained at the 3-21+G* and 3-21G* levels, respectively. These data are compared, where possible, with bond distances resulting from diffraction studies.^{41,42} For this class of substances, the surprising feature is that a similar number of structural data are available for the silicon compounds for comparison with the theoretical results as for the phosphorus derivatives. In any event, structural data for these types of derivatives are sparse.

Computed bond overlap populations are listed in Tables 6 and 7 for the cyclic MO₅ and cyclic C₂MF₃ formulations (M = Si, P), respectively, while Table 8 compares these terms for axial bonds of ground-state TBP geometries.

Figure 1 portrays the calculated isomer energy differences for the silicon and phosphorus ring systems listed in Table 1, and Figure 2 represents calculated isomer energy differences for silicon and phosphorus ring systems listed in Table 2.

Discussion

Energies of Cyclic SiO₅⁻ and PO₅ Species. It is apparent from the relative isomer energies listed in Table 1 that five- and six-membered saturated rings at e-e sites in TBP geometries are less stable than rings at a-e sites for cyclic SiO₅⁻ and PO₅ species. Also, the six-membered e-e ring orientation is greatly stabilized relative to the a-e ring location in that the higher energy e-e orientation is now much closer in energy to the a-e orientation for both phosphorus and silicon, in contrast to what was found for the five-membered rings in these two orientations. This is illustrated for the SiO₅⁻ species in Figure 1. As discussed in a previous publication³⁷ dealing with these cyclic PO₅ species **16**–**19**, the lower strain energy is cited as a principal factor in accounting for the much smaller energy encountered in placing a six-membered ring diequatorially in a TBP compared to that for a five-membered ring. These results agreed well with activation energies for pseudorotation obtained from VT ¹⁹F NMR studies⁴³ on pentaoxyphosphoranes **30A** and **30B** containing these rings, considering the compositional differences that are involved (Figure 4). The ligand exchange process^{44a} leads to promotion of the ground-state a-e ring location to e-e sites in each case. In this pseudorotational mechanism, a square-pyramidal (SP) state is traversed.^{44b}

Since the potential energy surface for such an exchange process is somewhat complicated, a direct comparison of isomer energy differences in Figure 1 from *ab initio* calculations with activation energies in Figure 4 from a VT NMR study is subject to qualification. This

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Table 3. Comparison of Calculated and X-ray Bond Parameters of Cyclic SiO₅⁻ and PO₅ Species^a

Calculated SiO ₅ ⁻ Bond Parameters							
entry ^b	ring size	Si-O bond dist (Å)				ring bond angle (deg) O-Si-O	
		ring		Si-OH			
		ax	eq	ax	eq		
12	5	1.840	1.700	1.694	1.683 1.683	86.0	
13	5		1.711 1.711	1.728 1.728	1.701	93.2	
14	6	1.730	1.712	1.761	1.681 1.681	91.0	
15	6		1.702 1.702	1.736 1.736	1.700	101.7	
Experimental SiO ₅ ⁻ Bond Parameters (Average Values) ^c							
Si-O bond distances (Å)							
five-membered rings ^d		Si-OR ^{d,e}		ring bond angle (deg) O-Si-O			
ax	eq	eq					
1.754(4)	1.697(4)	1.666(4)		88.5(1)			
Calculated PO ₅ Bond Parameters ^f							
entry ^b	ring size	P-O bond dist (Å)				ring bond angle (deg) O-P-O	
		ring		P-OH			
		ax	eq	ax	eq		
16	(5)	1.643	1.625	1.673	1.593 1.593	88.2	
18	(6)	1.631	1.612	1.681	1.601 1.592	92.8	
Experimental PO ₅ Bond Parameters (Average Values) ^c							
five-membered ring ^g			six-membered ring ^h			P-OXyl ⁱ	
P-O dist (Å)		O-P-O angle (deg)	P-O dist (Å)		O-P-O angle (deg)	ax	eq
ax	eq		ax	eq			
1.716(4)	1.636(4)	89.5(2)	1.636(4)	1.589(4)	96.4(2)	1.665(6)	1.612(6)

^a Calculated distances from minimized structures at the 3-21G* level. ^b Refer to Table 1 for the structural representations. Entries **12**, **13**, and **16** have five-membered rings, while **14**, **15**, and **18** have six-membered rings attached to the central atom. Of the six-membered rings, **14** and **18** have boat conformations in a-e orientations, and **15** has a chair form in e-e sites. ^c Numbers in parentheses are standard deviations. ^d From refs 34 and 35. Three X-ray structures of cyclic pentaosilicates with rings in a-e orientations, **4-6**. ^e R varies from Et (**5**³⁴) to *i*-Pr (**6**³⁵) to *t*-Bu (**4**³⁴) in three cyclic SiO₅⁻ derivatives with Si-OR distances of 1.661(4), 1.667(3), and 1.670(3) Å, respectively. ^f The calculated cyclic PO₅ geometries were previously reported³⁷ but are summarized here for convenience. ^g From refs 18 and 21. Four X-ray structures of cyclic pentaoxyphosphoranes with rings in a-e orientations. ^h From refs 18-21. Six X-ray structures of cyclic pentaoxyphosphoranes with rings in a-e orientations with boat forms. ⁱ From refs 18-21. Ten X-ray structures of cyclic pentaoxyphosphoranes with acyclic xylyloxy groups.

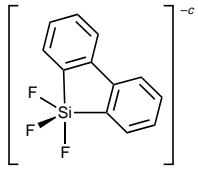
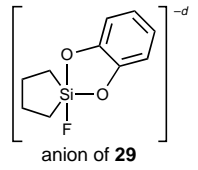
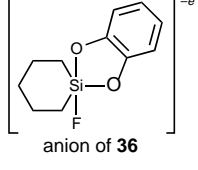
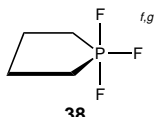
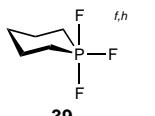
arises due to a lack of knowledge about the barrier state reflected by the experimental activation energies, *i.e.*, whether a SP or TBP represents the barrier state. In the case of **30A** of Figure 4 containing five-membered rings, application of a well-parameterized calculational model^{45ab} including this type of oxyphosphorane gives values of the respective relative isomer energies of 17.0 kcal/mol (**30A**), 28.7 kcal/mol (**a**), and 33 kcal/mol (**b**). This analysis, which has been used on a wide variety of phosphoranes and gives activation energies to within ±2.5 kcal/mol of actual values, suggests that the e-e ring TBP **b** is a good representation of the barrier state; *i.e.*, the energy difference between **b** and **30A** of 16 kcal/mol compares well with 17.4 kcal/mol observed experimentally from a VT NMR study. Thus, we gain some measure of confidence that the activation energy for the related six-membered ring derivative **30B** similarly may reflect the e-e ring TBP geometry **d** as representative of a close approximation to the barrier state. Applying

this parameterized model to the pseudorotational process involving **30B**, one obtains a barrier energy for **d** as the barrier representation of 5 kcal/mol. This again is in good agreement with the experimentally determined value of 6.1 kcal/mol and suggests that, in these cases, the barrier is represented by a TBP with e-e ring orientations rather than the preceding square pyramids **a** and **c** of Figure 4. In further comparisons with other cyclic PO₅ and SiO₅⁻ species, we make this same type of assumption in comparing experimental and theoretical results. These results are in accord with the theoretical treatment, which shows that the trigonal-bipyramidal species with e-e ring orientations (Table 1) are represented as transition states.

Although this paper confines most of the comparisons to five- and six-membered cyclic pentacoordinated systems, it is good to have in mind the order of ring strain as a function of ring size for phosphorus obtained from NMR activation energies for intramolecular ligand exchange^{45a,c,d} and application of the aforementioned parameterized empirical calculational model.^{45a,b} In Figure 5 the amount of strain for rings positioned at diequatorial sites of a TBP is seen to progressively

(45) (a) Reference 5, pp 32-83. (b) Holmes, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 433-446. (c) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 8096. (d) Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 1243.

Table 4. Calculated Bond Parameters for Cyclic C₂SiF₃⁻ and Isoelectronic Cyclic C₂PF₃ Species: Comparison with Bond Parameters from X-ray Studies of Cyclic Fluorosilicates and Electron Diffraction Studies of Cyclic Fluorophosphoranes in TBP Geometries^a

Calculated					
entry ^b	bond dist (Å)				bond angle (deg) C-Si-C
	ring Si-C		Si-F		
	ax	eq	ax	eq	
20	1.990	1.911	1.652	1.624	84.6
21		1.898	1.718	1.662	91.7
22	1.956	1.918	1.712	1.670	89.8
23		1.897	1.735	1.660	99.7
		1.897	1.735		
Experimental					
entry ^b	bond dist (Å)				bond angle (deg) C-Si-C
	ring Si-C		Si-F		
	ax	eq	ax	eq	
 anion of 28 ^c	1.958(6)	1.885(6)	1.698(3)	1.606(4) 1.620(4)	85.5(2)
 anion of 29 ^d		1.901(6) 1.862(4)	1.699(3)		96.2(2)
 anion of 36 ^e		1.877(5) 1.873(5)	1.715(3)		107.3(2)
Calculated					
entry ^b	bond dist (Å)				bond angle (deg) C-P-C
	ring P-C		P-F		
	ax	eq	ax	eq	
24	1.855	1.787	1.597	1.568	89.0
25		1.783	1.612	1.572	95.3
26	1.840	1.812	1.606	1.574	92.2
27		1.790	1.622	1.568	104.1
		1.790	1.622		
Experimental					
entry ^b	bond dist (Å)				bond angle (deg) C-P-C
	ring P-C		P-F		
	eq		ax	eq	
 38 ^{f,g}	1.788(4)		1.635(3)	1.547(8)	103.5(8)
	1.788(4)		1.635(3)		
 39 ^{f,h}	1.789(4)		1.637(3)	1.562(6)	115.7(8)
	1.789(4)		1.637(3)		

^a Calculated bond parameters from minimized structures at the 3-21+G* level for silicon and at the 3-21G* level for phosphorus.

^b Refer to Table 2 for the structural representations of **20**–**27**. ^c Reference 41. The cation is [K,18-c-6]⁺. Compare the bond parameters for **28** with theoretical results for **20**. ^d Reference 41. The cation is [K,18-c-6]⁺. Compare the bond parameters for **29** with calculated results for **23**. ^e Reference 41. The cation is [K,18-c-6]⁺. ^f Reference 42, an electron diffraction study. ^g Compare the bond parameters for **38** with calculated results for **27** and with experimental values for the silicon analog **29**. ^h Compare the bond parameters for **39** with experimental values for the silicon analog **36**.

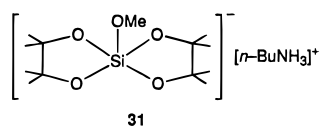
Table 5. Average M–X Bond Distance (Å) Comparison between Pentacoordinated Anionic Silicates and Isoelectronic Phosphoranes

Cyclic SiO ₅ ⁻ and PO ₅ Species			
	Si–O	P–O	diff
calcd ^a	1.717	1.624	0.093
exptl ^b	1.714	1.638	0.076
Cyclic C ₂ SiF ₃ ⁻ and C ₂ PF ₃ Saturated Species			
	Si–F	P–F	diff
calcd ^c	1.710	1.604	0.106
exptl ^d	1.697	1.609	0.085
	Si–C	P–C	diff
calcd ^c	1.897	1.790	0.107
exptl ^d	1.885	1.788	0.097
Cyclic C ₂ SiF ₃ ⁻ Unsaturated species ^e			
	Si–F	Si–C	
calcd ^f	1.633	1.951	
exptl ^g	1.641	1.922	

^a The average M–O bond distance values refer to the data for computed structures **12** and **14** of Table 3 for silicon and **16** and **18** of Table 3 for phosphorus. ^b The average M–O bond distance values refer to the data for structures **4–6** for silicon summarized in Table 3 and to structures cited in footnotes *g*, *h*, and *i* of Table 3 for phosphorus and summarized therein. ^c The average M–F and M–C bond distance values refer to the data for structure **23** of Table 4 for silicon and **27** of Table 4 for phosphorus. ^d The average M–F and M–C bond distance values refer to the data for structure **37**⁴¹ depicted schematically earlier for silicon and to **38** and **39** of Table 4 for phosphorus. It is noted that if the silicon structures **29** and **36**, whose values are listed in Table 4, are included in the Si–F and Si–C averaging, the final average values listed here do not change significantly. ^e No comparable structural data are available for phosphorus. ^f The average Si–F and Si–C bond distance values are from structure **20** (Table 4). ^g The average Si–F and Si–C bond distance values are from structure **28** (Table 4).

decrease (in kcal/mol) from five- to eight-membered. These ring types when a–e positions of a TBP are occupied are deemed to be essentially strain-free. Sufficient data are lacking for pentacoordinated silicon to construct such a scale at present.

The smaller relative energies calculated for cyclic SiO₅⁻ species relative to those obtained for the PO₅ systems are indirectly a reflection of the lower nuclear charge on silicon compared to that on phosphorus. This effect manifests itself in several ways. Major among these are longer bond distances, smaller activation energies determined by VT NMR, greater fluxional character, and enhanced reactivity for pentacoordinated silicon compounds. For example, unlike cyclic PO₅ compounds with saturated five-membered rings,^{4,7} an X-ray structure of the bicyclic pentaoxysilicate **31**³⁴ is a rectangular pyramid (RP). The structure is displaced from the TBP toward the RP by 71%, as measured by the dihedral angle method.⁴⁶ For square or rectangular



pyramids to form with pentaoxyphosphoranes, two unsaturated five-membered rings are required.^{47,48} A

Table 6. Comparison of Calculated Mulliken Overlap Populations on Cyclic SiO₅⁻ and Isoelectronic Cyclic PO₅ Formulations^a

M = Si				
Mulliken overlap pop. ^b				
	12	13	14	15
ring				
Si–O _{ax}	0.21		0.28	
Si–O _{eq}	0.30	0.29	0.28	0.29
OH				
Si–O _{ax}	0.33	0.29, 0.30	0.27	0.27, 0.30
Si–O _{eq}	0.32, 0.34	0.31	0.34, 0.33	0.31
M = P				
Mulliken overlap pop. ^c				
	16	17	18	19
ring				
P–O _{ax}	0.30		0.30	
P–O _{eq}	0.30	0.30	0.31	0.31
OH				
P–O _{ax}	0.26	0.30, 0.28	0.26	0.26, 0.30
P–O _{eq}	0.34, 0.35	0.32	0.33, 0.35	0.32

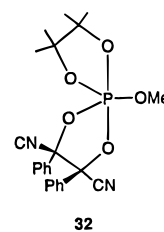
^a The Si formulas are anionic, whereas the P ones are neutral. ^b Basis set 3-21+G*. ^c Basis set 3-21G*.

Table 7. Comparison of Calculated Mulliken Overlap Populations on Cyclic C₂SiF₃⁻ and Isoelectronic Cyclic C₂PF₃ Formulations^a

M = Si				
Mulliken overlap pop. ^b				
	20	21	22	23
Si–C _{ax}	0.27		0.05	
Si–C _{eq}	0.38	0.13	0.06	-0.06
Si–F _{ax}	0.05	0.24	0.09	0.16
Si–F _{eq}	0.23	0.18	0.20	0.19
M = P				
Mulliken overlap pop. ^c				
	24	25	26	27
P–C _{ax}	0.22		0.25	
P–C _{eq}	0.25	0.19	0.21	0.22
P–F _{ax}	0.26	0.28	0.26	0.24
P–F _{eq}	0.32	0.33	0.31	0.33

^a The Si formulas are anionic, whereas the P ones are neutral. ^b Basis set 3-21+G*. ^c Basis set 3-21G*.

related example is **32**,^{7,49} a TBP which is displaced



toward a RP by only 10%. This greater stereochemical flexibility for hypervalent silicon may be viewed as a

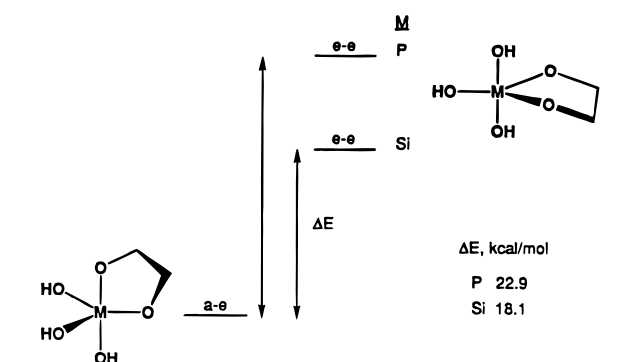
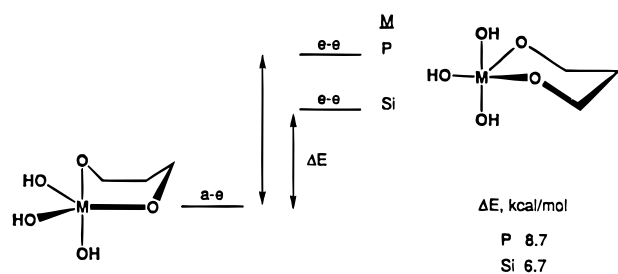
(46) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318–3326.

Table 8. Comparison of Calculated Mulliken Bond Overlap Populations for Minimum Energy Cyclic C_2MF_3 and Cyclic MO_5 Geometries of Silicon and Phosphorus^{a,b}

	M = Si (20)	M = P (24)	M = Si (23)	M = P (27)
Bond Distance, Å				
M-F _{ax}	1.652	1.597	1.735	1.622
Mulliken Overlap Population				
M-F _{ax}	0.05	0.26	0.16	0.24

	M = Si (12)	M = P (16)	M = Si (14)	M = P (18)
Bond Distance, Å				
M-O _{ax} (ring)	1.840	1.643	1.730	1.631
Mulliken Overlap Population				
M-O _{ax} (ring)	0.21	0.30	0.28	0.30

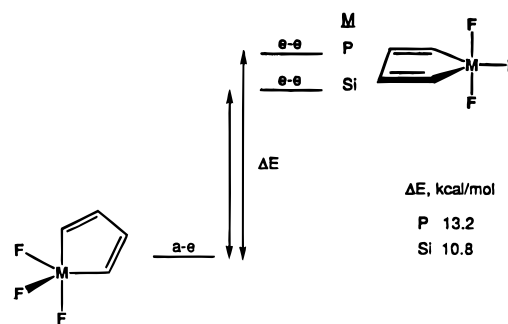
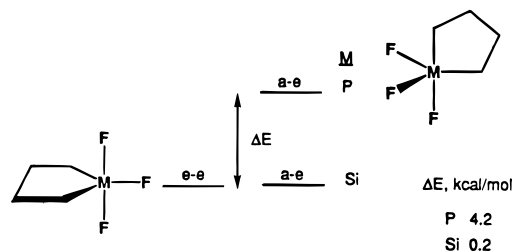
^a The Si formulas are anionic, whereas the P ones are neutral.
^b Basis set 3-21+G* for Si and 3-21G* for P.

(a) Ab-Initio Calculation - Five-Membered Saturated Ring**(b) Ab-Initio Calculation - Six-Membered Saturated Ring**

(6-31+G**/3-21G* Basis Set for SiO_5^- Species; 6-31G**/3-21G* for PO_5)

Figure 1. Computed relative energies, ΔE (kcal/mol), at the 6-31+G**/3-21G* level for silicon and at the 6-31G**/3-21G* level for phosphorus, of SiO_5^- and PO_5 species in TBP geometries: (a) containing saturated five-membered rings, silicates **13** (e-e) ring, minus **12** a-e ring, compared to phosphoranes³⁷ **17** (e-e) ring, minus **16** a-e ring; (b) containing saturated six-membered rings, silicates **15** (e-e) ring, chair form, minus **14** a-e ring, boat form, compared to phosphoranes³⁷ **19** (e-e) ring, chair form, minus **18** a-e ring, boat form.

manifestation of the lower activation energies associated with pseudorotation processes for pentacoordinated silicon species compared to that for phosphorus.

(a) Ab-Initio Calculation - Five-Membered Unsaturated Ring**(b) Ab-Initio Calculation - Five-Membered Saturated Ring**

(3-21+G* Basis Set for $C_2SiF_3^-$ Species; 3-21G* for C_2PF_3)

Figure 2. Computed relative energies, ΔE (kcal/mol), of TBP geometries: (a) containing five-membered unsaturated rings for cyclic $C_2SiF_3^-$ and C_2PF_3 species, silicates **21** (e-e) ring, minus **20** a-e ring, compared to phosphoranes **25** (e-e) ring, minus **24** a-e ring; (b) containing saturated five-membered rings for cyclic $C_2SiF_3^-$ and C_2PF_3 species, silicates **22** a-e ring, minus **23** (e-e) ring, compared to phosphoranes **26** a-e ring, minus **27** (e-e) ring. The basis sets for silicon (3-21+G*) and phosphorus (3-21G*) were used.

While no activation barriers have been obtained for the anionic cyclic pentaosilicates of this class, silicate **6** shows a ^{13}C NMR spectrum³⁵ indicative of rapid pseudorotation, whereby ring interchanges are indicated to occur between a-e positions of a TBP. This is so because only two of the four ^{13}C signals expected for the ring methyl groups, $C(CH_3)_2$, and only one of the two types of ring carbon signals, CMe_2 , are observed. Furthermore, the NMR spectrum remains invariant from -70 to 20 °C.

Numerous pentaoxyphosphoranes with either five- or six-membered rings exhibit this type of ligand exchange, which also is not slowed at low temperatures.^{18-20,50} Hence, additional studies of exchange phenomena by VT NMR on cyclic SiO_5^- systems are needed before an adequate comparison is possible with the *ab initio* results in Table 1. However, of the three TBP cyclic pentaosilicates with five-membered saturated rings that have had their structures **4-6**^{34,35} established by X-ray analysis, all have the rings occupying a-e sites, in agreement with the minimum energy representation from the *ab initio* calculation that is depicted in Figure 1. In addition, the X-ray structure of **1**,³² the only five-coordinated anionic silicate with six-membered rings, has the rings in a-e positions of a TBP.

In fact, no X-ray structure of either a pentaoxyphosphorus or a pentaoxy silicon compound has been re-

(47) Holmes, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 5379-5385.

(48) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257-265.

(49) Willson, M.; Mathias, F.; Burgada, R.; Enjalbert, R.; Bonnett, J. J.; Galy, J. *Acta. Crystallogr.* **1978**, *B34*, 629.

(50) Reference 4, p 177.

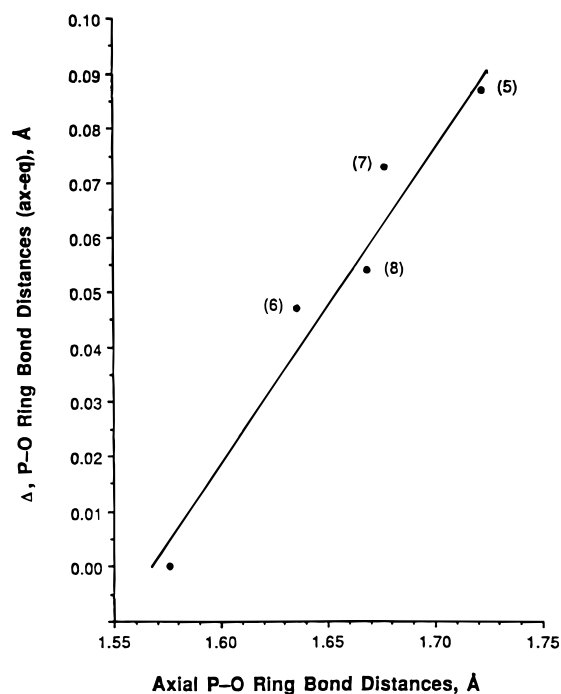


Figure 3. Difference in axial and equatorial ring bond distances (Å), Δ , from ideal values for a TBP vs the axial P-O ring bond distance (Å) for ring sizes of TBP pentaoxyphosphoranes varying from five- to eight-membered, as indicated by numbers in parentheses. The point at $y = 0$ represents a value of the P-O ring bond distance for four-coordinated cyclic phosphates.

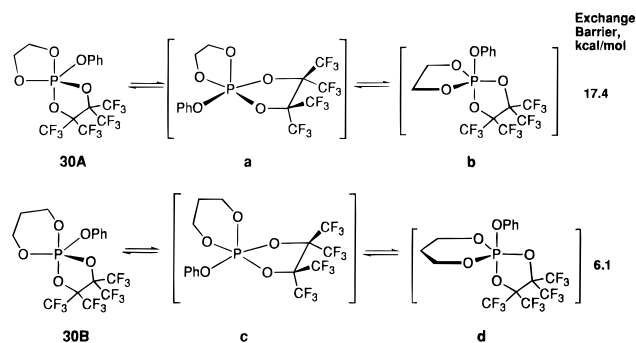


Figure 4. Intramolecular ligand exchange activation energies of **30A** and **30B** from VT ^{19}F NMR spectra.⁴³

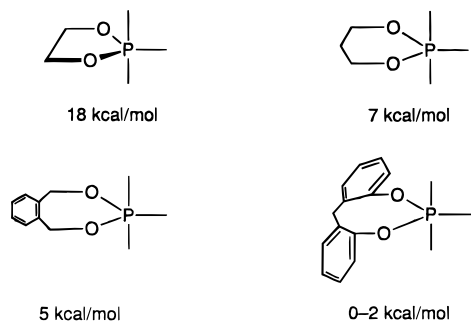
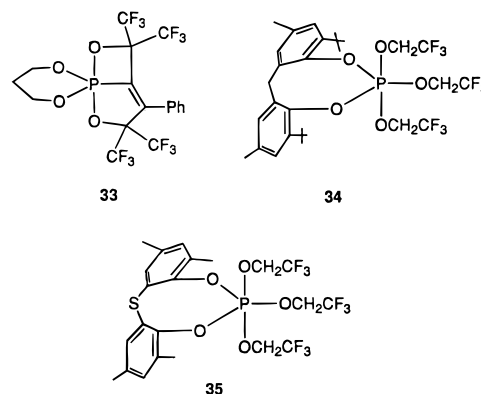


Figure 5. Relative values of strain for diequatorially positioned rings varying in size from five- to eight-membered for TBP phosphoranes (kcal/mol).⁴⁵

ported where a five- or six-membered ring occupies diequatorial sites. On the basis of the theoretical results reported here, the best chance for this to occur should be an anionic pentaosilicate derivative containing a saturated six-membered ring. The *ab initio* results indicate a modest 7 kcal/mol higher energy for this e-e ring orientation for pentaosilicon in a TBP geometry relative to an a-e ring arrangement. In a practical

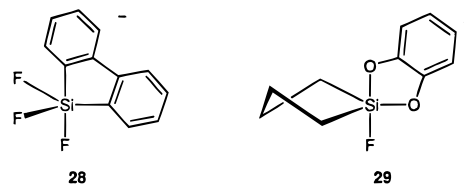
sense, since experimentally handling these somewhat elusive entities is more difficult in the case of silicon, it is more likely that the right compositional environment will be found to induce a cyclic pentaoxyphosphorane to assume this ring orientation.

Using a special ring constraint, Bentrude and co-workers²⁶ have isolated a tetraoxyphosphorane (**33**) with a six-membered ring that was shown by X-ray analysis to have the ring in e-e sites of a TBP. In the case of an eight-membered ring, X-ray studies have revealed e-e site occupancy in pentaoxyphosphoranes (**34**,²⁷ **35**²⁹) for the first time.

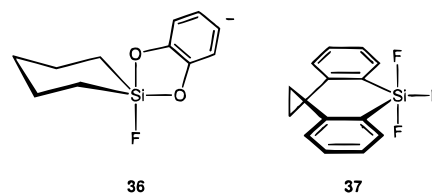


Energies of Cyclic C_2SiF_3^- and C_2PF_3 Species.

The calculated energies for these species in Table 2 provide interesting comparisons with structural results from X-ray and electron diffraction studies. The *ab initio* calculations support a structure with an a-e ring arrangement for an unsaturated carbon-containing five-membered ring, whereas the e-e ring arrangement is favored for a saturated ring of this type in TBP geometries for both the cyclic C_2SiF_3^- and C_2PF_3 species. This agrees with our experimental results on the structures⁴¹ of the anionic pentacoordinated cyclic organofluorosilicates **28** and **29**, which have five-mem-



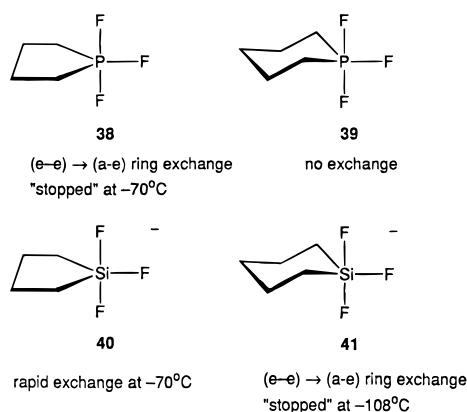
bered carbon-containing unsaturated and saturated rings, respectively. Their structures conform to the theoretical predictions. The fluorosilicate analogous to **29** with a six-membered ring, i.e., **36**, and one with a seven-membered ring, **37**, also have TBP structures⁴¹ with the carbon-containing rings in e-e locations. All are salts of $[\text{K}, 18\text{-c-}6]^+$.



Our computational prediction is consistent with the experimental finding for **28**, whereby a fluorine atom is displaced from its favored axial position of a TBP. The 13-atom ring fragment of **28**⁴¹ is highly planar (the atoms are coplanar to within ± 0.069 Å). The relief of ring strain for this moiety largely dictates the structure

found for **28**. The ^{19}F NMR spectrum of **28** remains invariant down to -80°C .⁴¹ One type of fluorine atom is present and indicates rapid ligand exchange. Consistent with this observation, application of an empirical model approximation⁵¹ gives an estimation of an a-e ring arrangement about 8 kcal/mol more stable than the structure with the ring in e-e sites. This compares with 10.8 kcal/mol obtained from the *ab initio* calculation portrayed in Figure 2. For **29**, **36**, and **37**, the rings have greater conformational flexibility and are more readily accommodated in e-e positions of a TBP.⁴¹ For example, in **29** the saturated five-membered ring is in a twist configuration and has a C-Si-C ring angle of $96.2(2)^\circ$, whereas for **28**, this angle is $85.5(2)^\circ$.

The structures of the related fluorophosphoranes **38** and **39** are known from electron diffraction studies⁴² and from VT ^{19}F NMR measurements⁵² to be TBP, with the ring occupying e-e sites, the same as that found for the fluorosilicates **29**, **36**, and **37**. The trifluorosilicates



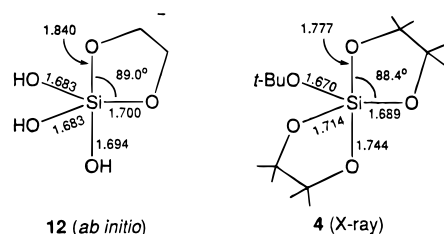
$(\text{CH}_2)_4\text{SiF}_3^-$ (**40**) and $(\text{CH}_2)_5\text{SiF}_3^-$ (**41**), analogous to the phosphoranes **38** and **39**, have been prepared as $[\text{K}, 18\text{-c-6}]^+$ salts and studied by VT ^{19}F NMR.⁵³ Whereas ligand exchange was "stopped" at -70°C for **38** and revealed a low-temperature pattern consistent with an e-e ring arrangement,⁵² the fluorines remained equivalent even at -70°C for the corresponding silicate **40**.⁵³ The exchange process outlined involves an intermediate with the ring in an a-e orientation. Similarly, the cyclic phosphorane **39** with a ground-state e-e ring arrangement is more rigid than the corresponding silicate **41**. The latter undergoes ligand exchange at room temperature,⁵³ whereas no exchange is observed for the analogous phosphorus compound **39**.⁵² At -108°C , a low-temperature pattern for **41** results for the silicate, consistent with the ring in e-e sites of a TBP. Retention of Si-F coupling throughout shows the process is intramolecular.⁵³

These data on ligand exchange showing that the phosphorus compound **38** has a higher barrier compared to that for the silicate **40** fully support the calculations portrayed in Figure 2 for these saturated five-membered-ring systems. For the analogous six-membered-ring derivatives, again the phosphorus compound (**39**) is indicated to have a ligand exchange barrier higher than that for the silicon compound (**41**).

On consideration of these cyclic silicates as a function of ring size, it is noted that the activation energy for **41** has been determined from line shape analysis of the VT

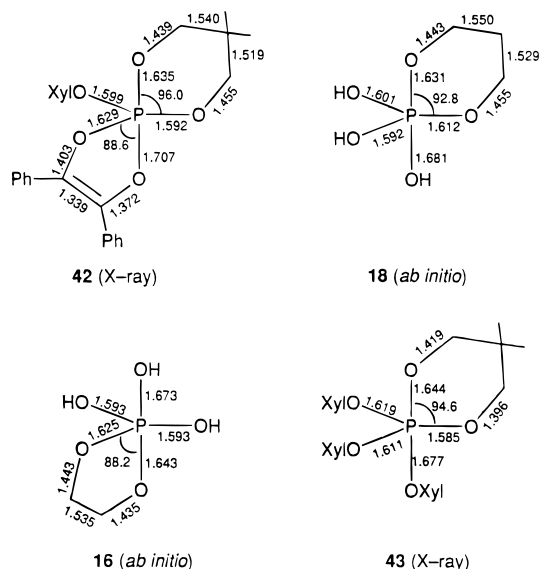
NMR spectra to be 9.1 kcal/mol.⁵³ A value for this same process for silicate **37** with a seven-membered ring is estimated as 10.5 kcal/mol.⁴¹ This is entirely reasonable. Much lower values, as suggested by the theoretical results for five-membered rings in this structural form, are consistent with the large degree of ring strain present in the e-e ring orientation compared to that for six- or seven-membered rings occupying e-e positions in experimentally established TBP geometries.⁴¹

Bond Parameter Comparisons of Cyclic SiO_5^- and PO_5^- Species. The only comparison at present for the cyclic SiO_5^- system is between the geometry calculated for **12** and the three anionic pentaoxosilicates **4-6**.^{34,35} The average bond parameters for the latter



set listed in Table 3 show particularly good agreement with **12**, other than that for the computed Si-O_{ax} bond distance for the five-membered ring. As a representative member, the comparison of parameters for **4** with those for **12** is shown here.

Pertinent calculated P-O bond parameters, previously reported, also are summarized in Table 3 for a-e five- and six-membered-ring arrangements in the TBP geometries **16** and **18**, respectively. These are compared with results of ten X-ray structures on this class of cyclic pentaoxyphosphoranes.¹⁸⁻²¹ Again, excellent agreement is noted between calculated and experimental results, especially considering the differences in the composition of the compounds analyzed by X-ray means and the models used in the computations. For example, the specific bond parameters for the bicyclic phosphorane **42**¹⁸ containing both a five- and a six-membered ring and the monocyclic derivative **43**¹⁹ with a six-membered ring are compared with calculated parameters for **16** and **18**. A remarkable similarity is seen for all of the ring bonds for the six-membered ring in the X-ray structure of **42** when compared with the *ab initio* results for the boat form for **18**.

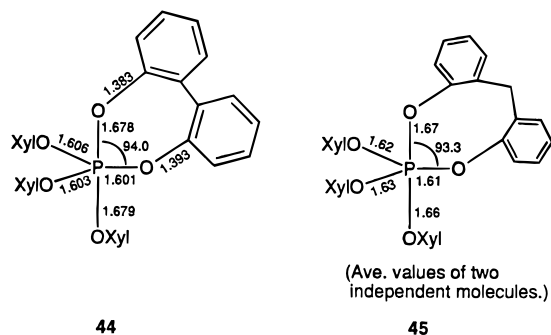


(51) Reference 5, p 32.

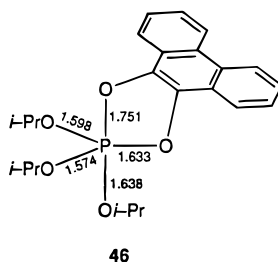
(52) Muettterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613.

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It is instructive to compare parameters for larger ring pentaoxyphosphoranes with the calculated parameters for **18**, possessing a saturated six-membered ring. Structures of **44**¹⁹ and **45**¹⁹ recently were studied by X-ray diffraction and have monocyclic compositions very similar to **43**. The ring axial P–O bond distance is most



sensitive to structural variations. The higher ring strain in the five-membered ring is alleviated by allowing the weaker ring P–O axial bond to lengthen relative to the equatorial one.⁴⁷ Not that the ring strain for an a–e orientation in a TBP is great, but a consistent pattern is evident. In the bicyclic derivative **42**, one notes the longer axial distance in the planar five-membered unsaturated ring (1.707(2) Å) compared to the P–O axial distance in the more flexible boat form of the saturated six-membered ring (1.635(2) Å). For **44** and **45**, containing quite flexible seven- and eight-membered rings, respectively, the P–O axial ring bonds are almost the same as that found for the opposite axial P–O bond to the acyclic OXyl group. This feature is indicative of the lack of any significant ring strain in these larger ring systems. This is illustrated in Figure 3, where we show the difference between axial and equatorial P–O ring bond distances, $\Delta P-O(ax-eq)$, vs axial P–O bond distances as a function of ring size (indicated in parentheses) for the cyclic pentaoxyphosphoranes whose structures were studied by X-ray diffraction.^{18–21,54,55} A linear correlation is obtained, $y = 0.594x - 0.932$, where the axial–equatorial bond distances decrease as ring size changes along the series 5, 7, 8, 6 for the particular rings that comprise the available TBP structures. The lower point at $y = 0$ refers to the average P–O bond distance (1.576(4) Å) obtained from three X-ray studies of four-coordinate phosphate structures^{30,56,57} containing eight-membered rings of the type that are present in the five-coordinated structures. There is no significant difference in the P–O ring bond distances for these structures (1.576 ± 0.004 Å). The differences were all within the standard deviation of the average P–O bond distance. In this regard, the longest P–O axial bond distance, 1.751(7) Å, is found in the monocyclic derivative **46**,^{54,55} which has a constrained five-membered ring and sterically larger isopropoxy groups instead of xyloxy groups attached to phosphorus. Here, the difference between the ring and nonring axial P–O distances is 0.113(6) Å.



A similar comparison is not possible, due to the limited structural data available on cyclic anionic pentaoxysilicates.^{34,35} It is notable both in the *ab initio* results and the existing X-ray data that the lengths of the Si–O bonds are longer than those of the P–O bonds in every case (Table 3). The average increase for all of the bond distance differences, (Si–O) – (P–O), is 0.093 Å from the theoretical calculations and 0.076 Å from the experimental values (Table 5). The sum of the single-bond covalent radii for silicon and oxygen vs phosphorus and oxygen,⁵⁸ when corrected for electronegativity differences,⁵⁹ gives about the same value for the Si–O and P–O bond lengths.

Table 6 compares calculated Mulliken bond overlap populations for minimum energy structures of cyclic pentaoxy anionic silicates and isoelectronic pentaoxyphosphoranes. In general, the axial ring Si–O overlap population is less than that for the axial ring P–O bonds. This comparison is emphasized for the lower energy structures in Table 8 (**12**, **14**, **16**, and **18**), which shows that the lower axial bond overlaps for silicates accompany longer ring Si–O_{ax} distances relative to ring P–O_{ax} bond lengths. Hence, in view of the longer Si–O bonds compared to P–O bonds cited above, the implication is that five-coordinated anionic pentaoxysilicates have inherently weaker bonds compared to their isoelectronic pentaoxyphosphorane counterparts. This observation provides evidence to support the enhanced reactivity found for five-coordinated silicon species, particularly in nucleophilic displacement reactions.^{8,9} Mechanistically, it is expected that the axial bonds would serve as the sites of greater reactivity due to their expected weaker and longer attachments to silicon.

Although we are dealing with structures that are being used for models of activated states in nucleophilic substitution reactions, there is the danger that these thermodynamic considerations do not necessarily imply a kinetic reactivity. However, as has been amply demonstrated, at least in the case of the reactivity of tetracoordinated phosphorus,⁵ a strong correlation exists in associating reactivity with the entrance of an attacking nucleophile and departure of the leaving group from the longer, weaker axial positions of trigonal bipyramids that serve as model intermediates.

Bond Parameters of Cyclic C₂SiF₃[–] and C₂PF₃ Species. The comparisons for this class of cyclic compounds between calculated and experimental bond parameters may be made for both organofluorosilicates and organofluorophosphoranes. Pictured here are the calculated minimum energy geometries for **20** and **23** compared with the X-ray structures⁴¹ of **28** and **29**. Also included are the related structures⁴¹ **36** and **37**, with six- and seven-membered rings, respectively. The X-ray structures all are of [K,18-c-6]⁺ salts.

The experimental distances at silicon for **28** agree with the calculated values for **20** to ±0.025 Å, which indicates a very satisfactory correspondence for this level of theory. The agreement is also good for the

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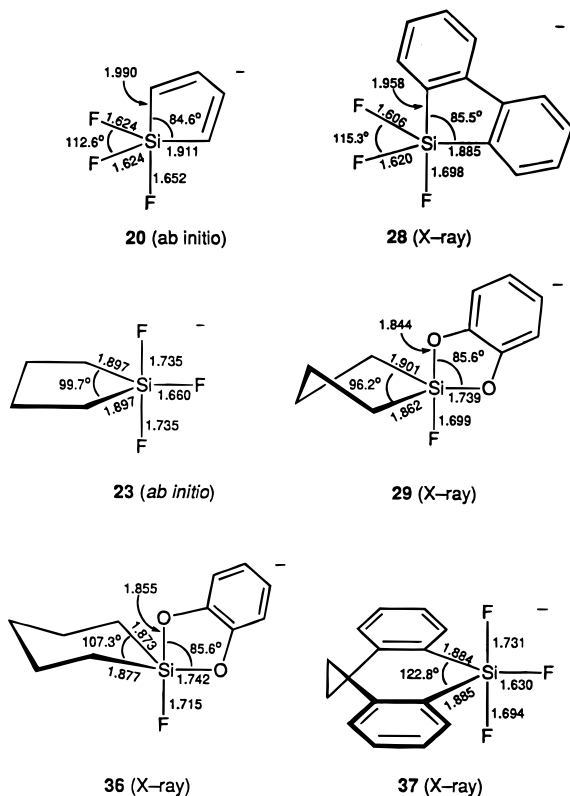
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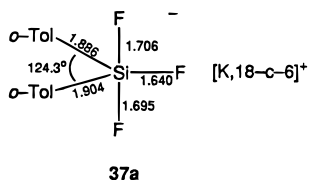
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calculated geometry of the fluorosilicate with a saturated five-membered ring, **23**, when compared with related experimental bond distances for the partially analogous structure **29**. There is not much change in respective bond distances that can be compared between the X-ray structures **29**, **36**, and **37**, other than to note an increase in the C–Si–C ring angle as ring size increases from five- to six- to seven-membered along this series.

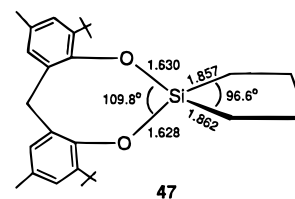
Actually, the structure of **37** shows a high degree of correspondence with the bond parameters of the acyclic analog **37a**.⁵³ The agreement in bond distances is



$\pm 0.011(3)$ Å. This indicates that ring strain effects are not significant for **37**, especially since the C–Si–C angle is similar in each. However, a study of acyclic members of the series R_2SiF_3^- demonstrates the presence of a modest steric effect due to the *o*-tolyl groups.⁵³ This steric contribution (Δ) as measured by the sum of the differences of the bond angles $\text{F}_{\text{ax}}\text{--Si--F}_{\text{ax}}$ and $\text{C}_{\text{eq}}\text{--Si--C}_{\text{eq}}$, respectively, from the 180 and 120° angles of the TBP is 9.9° for **37**, the same as that for the *o*-tolyl derivative **37a**.

The long axial Si–O ring bond distances in **29** and **36**, 1.844(3) and 1.855(3) Å, respectively, result from the presence of the cyclic components containing equatorial carbon atoms.⁴¹ In the cyclic SiO_5^- series, the longest axial Si–O bond distance is 1.777(3) Å,³⁴ nearly 0.08 Å shorter than that for **36**.⁴¹ In a related four-coordinated

cyclic silane derivative, **47**,⁶⁰ the Si–O bond distances



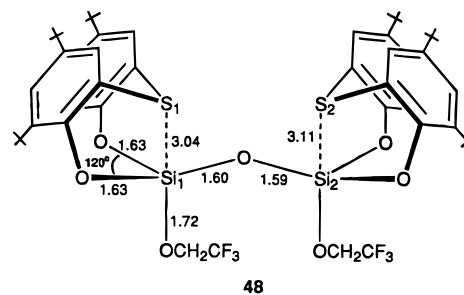
average 1.629(3) Å, i.e., 0.226 Å less than that cited for **36**. In terms of the VSEPR theory,⁶¹ the electron density is increased toward silicon in the presence of directly bonded elements of low electronegativity and, as a result of electron pair repulsions, the inherently weaker axial silicon–ligand bonds increase in length. Other elements of low electronegativity are expected to have a similar axial bond-lengthening effect, e.g., hydrogen in hydrosilicates. However, structures are not available for anionic silicates of the latter type to confirm this effect.

Table 7 compares calculated Mulliken bond overlap populations for minimum energy structures of cyclic anionic organotrifluorosilicates and isoelectronic organotrifluorophosphoranes. Similar to that discussed with the cyclic pentaoxy derivatives, the silicon species have lower Si– F_{ax} overlap populations compared to the corresponding values for the axial P– F_{ax} bond. Specific to lower energy isomeric structures, Table 8 highlights this comparison, showing that the lower bond overlap populations for axial fluorine atoms are accompanied by longer Si– F_{ax} bond distances compared to P– F_{ax} bond lengths.

We conclude that the increased axial bond lengths and, hence, accompanying weakened bond strengths expected for anionic five-coordinated organosilicate derivatives such as **28**, **29**, **36**, and **37** are judged to be a major factor accounting for enhanced reactivity for hypervalent silicon species compared to tetracoordinate members in nucleophilic displacement reactions. For example, PhMeSiF_3^- and $\text{Ph}_3\text{SiF}_2^-$ are much more reactive than PhMeSiF_2 and Ph_3SiF with RMgBr to give PhMe(F)SiR and Ph_3SiR , respectively, as reported by Corriu and co-workers.⁶² Many other reactions concerning this topic have been discussed extensively elsewhere.^{8,9}

In this same context, the Si–C ring bond distance in the cyclic silane **47**⁶⁰ averages 1.860(4) Å, whereas a much longer axial Si–C distance of 1.958(6) Å is present in the five-coordinated anionic silicate **28**.⁴¹

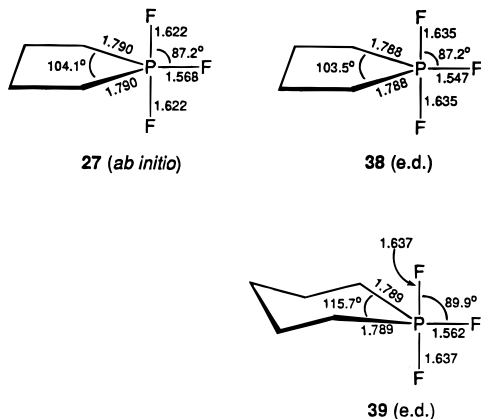
On this point, the cyclic disiloxane **48**⁶⁰ is most instructive regarding a model for a nucleophilic displacement reaction. As is apparent, the sulfur atom is



(60) Day, R. O.; Prakasha, T. K.; Holmes, R. R.; Eckert, H. *Organometallics* **1994**, *13*, 1285.

/poised for incipient nucleophilic attack at silicon, approximately halfway between a van der Waals distance (3.90 Å⁶³) and a covalent bond distance (2.20 Å⁵⁸), entering the coordination sphere of silicon along an axial direction, i.e., a face of the silane tetrahedron.

For the calculation on the cyclic diorganotrifluorophosphorane **27** (Table 4), a direct comparison of bond parameters with this same formulation, **38**, is available from an electron diffraction study by Oberhammer.⁴² It



is seen that the agreement is excellent and gives bond parameter comparisons between the theoretical and experimental values that are equivalent within the standard deviation of the data (i.e., within about 0.01 Å and 1° for bond distances and angles, respectively, for each structure). This agreement lends confidence to the energy calculations indicating that the diequatorial ring arrangement for **27** (= **38**) is more stable than axial-equatorial ring placement. Table 2 lists a 4.2 kcal/mol advantage for the e-e ring orientation. This is fully consistent with the temperature-dependent ¹⁹F NMR study performed some time ago⁵² indicating that the e-e ring placement for **38** was the correct geometry, as deduced from the observation of separate axial and equatorial fluorine resonances at -70 °C, where rapid intramolecular ligand exchange was "stopped"

As with the pentaoxy derivatives of phosphorus and silicon discussed earlier, an expansion of bond distance values is found for the isoelectronic cyclic anionic diorganofluorosilicates relative to the related phosphorus species; cf. the geometries of silicates **23**, **29**,⁴¹ **36**,⁴¹ and **37**⁴¹ discussed above with the phosphorus entities **27**, **38**,⁴² and **39**.⁴² This amounts to an average bond distance increase for all the Si-F values over all the P-F values from the theoretical calculations of 0.106 and 0.085 Å from the experimental values. In a similar fashion, it is found that the average Si-C bond distances exceed the average P-C values for the computed structures by 0.107 Å and for the experimental struc-

tures by 0.092 Å. Table 5 lists these average bond distances. When the single-bond covalent radii⁵⁸ are corrected for electronegativity differences,⁵⁹ the silicon-ligand bond lengths do not differ appreciably from those for phosphorus-ligand bonds. Thus, most of the increase in calculated and experimental values for these distances found in the pentacoordinated molecules listed in Table 5 appears to be due to the extra "looseness" inherent in the silicon species relative to phosphorus, as we discussed in a previous section.

Conclusions

The theoretical calculations and structural results on cyclic five-coordinated anionic silicates and isoelectronic phosphoranes are in accord with establishing preferred TBP geometries for SiO₅⁻, PO₅, C₂SiF₃⁻, and C₂PF₃ cyclic systems. The bond parameter and energy comparisons between theory and experiment show that the bond distances for silicon-ligand bonds are uniformly longer than those for phosphorus-ligand bonds. This is particularly so for silicon-ligand axial bonds compared to phosphorus-ligand axial bonds for TBP geometries. This correlates with lower axial bond overlap populations for the cyclic anionic silicates compared to those for the isoelectronic cyclic phosphoranes. These features act to lower energies between the normally less stable cyclic SiO₅⁻ systems having e-e ring orientations relative to those in a-e ring orientations compared to those for PO₅ TBP systems. As a consequence, the silicon systems assume more structural nonrigidity and support enhanced reactivity of silicon compounds in nucleophilic displacement reactions where higher coordinate species are involved as important mechanistic intermediates or activated states. Similar conclusions from theory and experiment result for cyclic C₂SiF₃⁻ and C₂PF₃ systems where unsaturated five-membered rings are in a-e sites of a TBP.

For saturated rings in anionic diorganofluorosilicates and diorganofluorophosphoranes, the lower energy structure has the rings occupying e-e sites in a TBP for both the silicon and phosphorus species considered. The consequence of this as models in nucleophilic substitution reactions where the ring is maintained intact is that retention of configuration is expected for unsaturated five-membered rings in TBP intermediates and inversion of configuration is expected for saturated rings in such intermediates.⁴¹

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Supporting Information Available: Tables of Cartesian coordinates and distances for molecules **12**-**19** that are depicted in Table 1 (14 pages). Ordering information is given on any current masthead page.

OM960198P

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