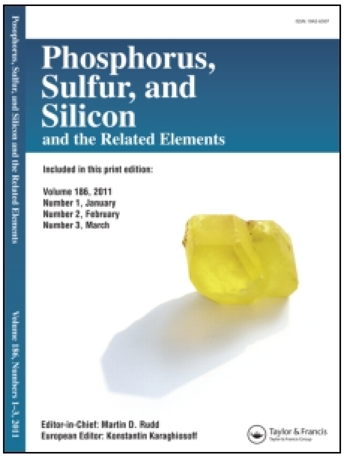

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J. C. Martin[a]; William H. Stevenson III[a]
[a] Roger Adams Laboratory, University of Illinois, Urbana, Illinois, U.S.A.

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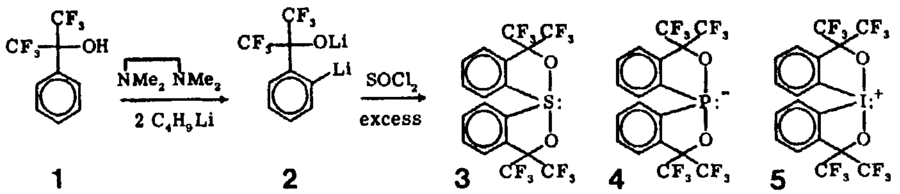
ORGANO-NONMETALLIC CHEMISTRY: PENTACOORDINATE, TEN-ELECTRON (10-X-5) COMPOUNDS OF SILICON, PHOSPHORUS AND SULFUR

J. C. MARTIN AND WILLIAM H. STEVENSON III
Roger Adams Laboratory, University of Illinois, Urbana,
Illinois 61801, U.S.A.

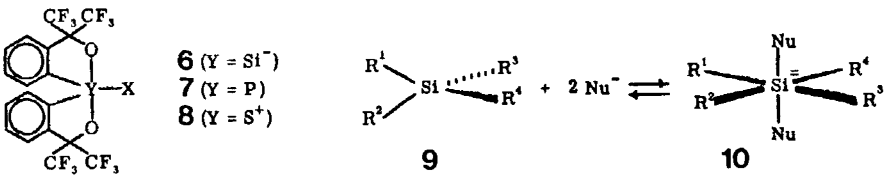
Abstract We have shown that ligands to nonmetals can be designed to stabilize five-coordinate species, relative to four- or six-coordinate ones. Nondissociative permutational isomerization of identically substituted hypervalent 10-Si-5 siliconate anions and neutral 10-P-5 phosphoranes is faster for the isoelectronic isostructural silicon species. Nucleophile mediated stereochemical inversion in silanes which are substituted by ligands which stabilize trigonal bipyramidal species is shown to proceed by pseudorotation of an intermediate 10-Si-5 species.

Over the past decade work in our laboratory has been directed toward the synthesis of organo-nonmetallic[1] compounds in which bonding about the central nonmetal involves, at least formally, expansion of the valence octet of electrons--compounds with the kind of electron-rich multicenter bonding which has been called hypervalent.[2] We have been successful in designing ligands which impart sufficient stability to these higher-valent species that many compounds with new hypervalent functional groups have been made available for study. The broad outline of our research in this area has been reviewed.[3]

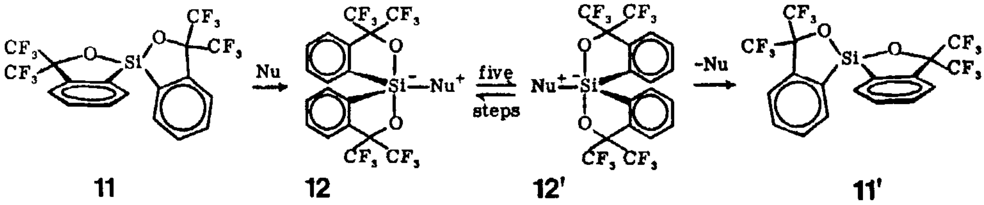
The three-centered four-electron apical bonds of ten-electron hypervalent trigonal bipyramidal (TBP) species place the extra pair of electrons in an orbital which is primarily a ligand orbital[2] creating relatively negative charge on the apical ligands and positive charge on the central atom. Ligands such as the bidentate ligand of 3, 4 and 5 stabilize this charge distribution by providing very electronegative fluoroalkoxy apical ligands and sigma-donor, carbon-centered equatorial ligands. The pictured reaction provides a convenient synthetic route to the remarkably stable[4] sulfurane 3,[5] a 10-S-4 species. (The 10-S-4 designation defines a system in which ten valence-shell electrons are formally involved in bonding four ligands to a central sulfur.) Closely parallel reactions provide the anionic 10-P-4 species 4 by reaction of 2 with PCl_3[6] and the cationic 10-I-4 species 5 by a sequence of steps[7] involving 2.



Similar triads of isostructural, isoelectronic 10-Y-5 species (anionic 10-Si-5,[5,8] neutral 10-P-5[5] and cationic 10-S-5[9]) have also been prepared. All of these species reflect the stabilizing influence of the bidentate ligand.



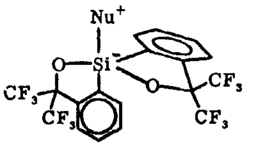
Both 10-Si-5 and 12-Si-6 species are well known, despite the two formal negative charges on silicon in the latter. Corriu[10] has shown, in a number of cases, that optically active silanes (9) undergo nucleophile promoted racemization by a process second-order in nucleophile (Nu^-). The two molecules of nucleophile in the transition state for this reaction are most probably in an achiral 12-Si-6 octahedral (Oc) geometry 10, or if 10 is an intermediate, a transition state resembling 10 in geometry.



Silane 11 has two bidentate ligands to silicon which are designed to stabilize the TBP species derived from 11 by reaction with a nucleophile, 12. It is therefore not surprising to find that 11 is very strongly electrophilic. Its racemization is catalyzed by a wide range of nucleophiles but the kinetics were always first order in nucleophile, never second order, in the cases studied.

The use of ^{19}F NMR methods to detect exchange of geminal CF_3 groups of 11 (or 12) provides no evidence for the involvement of a second molecule of nucleophile in an Oc, 12-Si-6 geometry analogous to 10, even with high concentrations of strong nucleophiles which give isolable 10-Si-5 species (12). The ligand set of 12 clearly provides more stabilization for the 10-Si-5 species than for the 8-Si-4 or 12-Si-6 species derived from 12 by the loss or gain of one nucleophile molecule.

The presence of low concentrations of weak nucleophiles such as benzaldehyde in solutions of 11 results in coalescence of the two ^{19}F NMR quartets into a sharp single peak via a process which is first order in benzaldehyde. In our preliminary communication of these results we suggested several possible mechanisms for the racemization of 11, including the inversion at the TBP silicon of 12 via the five-step pseudorotation route. We have now shown this to be the most likely mechanism. The highest energy geometry along the five-step pseudorotation pathway for inversion would be expected to resemble TBP species 13 with two energetically unfavored structural features--an apical carbon and a five-membered ring linking two equatorial sites.



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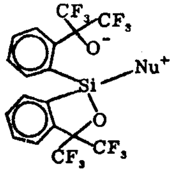

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The rate of inversion for a number of isolable siliconates 12 ($Nu^+ = p\text{-}C_6H_4X$) shows that electron-withdrawing substituents speed the reaction. A Hammett-Brown correlation (X = H; 3,5-bis(trifluoromethyl), 3-trifluoromethyl, and 4-OMe) for the rates of inversion of these siliconates shows a linear correlation (r = 0.9830) with σ^+, with $\rho^+ = 0.33$ at 150 °C. Correlation of $\Delta G^*_{150°}$ with σ^* for Nu^+ = n-butyl (28.7 kcal/mol), p-methoxyphenyl (26.6), phenyl 26.0, 3-(trifluoromethyl)phenyl (25.6), 3,5-bis-(trifluoromethyl)phenyl (25.5), pentafluorophenyl (22.0) and F^8 (17.5) is linear (r = 0.9899). The correlation with σ_I is also linear (r = 0.9955) over the range of $\Delta G^*_{150°} = 17.5$ (F) to 28.7 kcal/mol (n-butyl).

The driving force for rapid pseudorotation in siliconates of structure 12 in which Nu^+ is a very apicophilic substituent may therefore be postulated to come from the shifting of Nu^+ from an equatorial position in 12 to a more electron-rich apical position in transition state 13. These results rule out dissociative mechanisms, via silane 14, for the inversion at silicon.

Extrapolation of the σ_I correlation to an estimated value of σ_I of 0.75 to 0.90 for the very apicophilic oxonium substituent of 12 ($Nu^+ = \text{-O}\overset{+}{=}\text{CHC}_6\text{H}_4\text{-p-NMe}_2$) predicts a value of ΔG^*_{150} of only 8 - 12 kcal/mol for pseudorotation of this species. This 10-Si-5 species can be directly observed in solution at low temperature. We were able to measure rates of inversion at these temperatures using spin polarization transfer techniques[12] in ^{19}F NMR. The value of $\Delta G^*_{150°}$ determined by these studies, 10 kcal/mol, is in the range predicted for the pseudorotation mechanism pictured above for the conversion of 12 to 12'. The pseudorotation mechanism is therefore compatible with all data currently available.

Use of spin polarization transfer techniques[12] made it possible for us to measure rates of pseudorotation for both phosphorane 7 (X = Ph) and siliconate 6 (X = Ph, as its tetrabutylammonium salt). The ΔG^* for the siliconate anion at 150 °C (26.0 ± 0.1 kcal/mol) was lower than that for the isostructural, isoelectronic phosphorane (28.5 ± 0.4 kcal/mol) by 2.5 kcal/mol.

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