

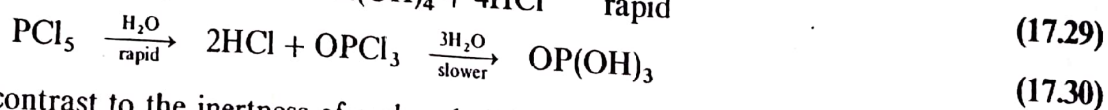
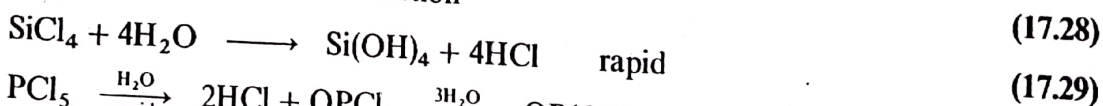
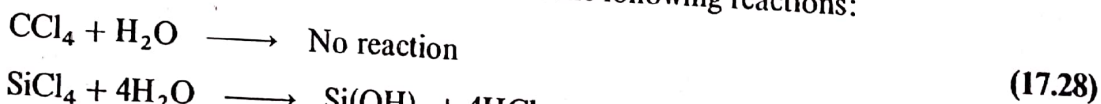
π bonding in the heavier congeners

In view of the uncertainty with which π bonding is known in the very well studied phosphorus and sulfur systems, it is not surprising that little can be said concerning the possibility of similar effects in arsenic, antimony, selenium, tellurium, etc. In general it is thought that the problems faced in phosphorus and sulfur chemistry concerning promotion energies and diffuse character may be even larger in the heavier congeners. In the latter regard it is interesting to note the apparent effectiveness of π bonding in metal complexes. To the extent that softness in a ligand can be equated with the ability to accept electrons from soft metal ions in $d_{\pi}-d_{\pi}$ "back bonds," information can be obtained from the tendency to complex with "b" metal ions (see p. 313): $P > As > Sb$. This order would indicate that the smaller phosphorus atom can more effectively π bond with the metal atom. With the halide ions the order is reversed: $I^{-} > Br^{-} > Cl^{-}$. Whether this is a result of the importance of polarizability in this series or more effective use of d orbitals by iodine is unknown.

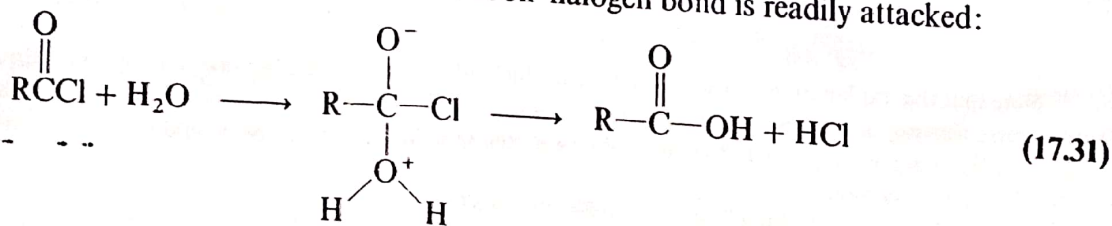
REACTIVITY AND d ORBITAL PARTICIPATION

It has been pointed out above that the elements of the second row (Li to F) not only resemble their heavier congeners to a certain extent (as far as formal oxidation state, at least) but also the lower right diagonal element (as far as charge, size, and electronegativity are concerned). For example, both silicon and phosphorus form hydrides that have some properties in common with alkanes, although they are much less stable. As a result of the electronegativity relationships the P—H bond more closely approaches the polarity of the C—H bond than does the Si—H bond. The resemblance of phosphorus to carbon has even been extended to the suggestion that a discipline be built around it in the same manner as organic chemistry is built on carbon.³⁰

There is one important aspect of the chemistry of both silicon and phosphorus which differs markedly from that of carbon. Consider the following reactions:

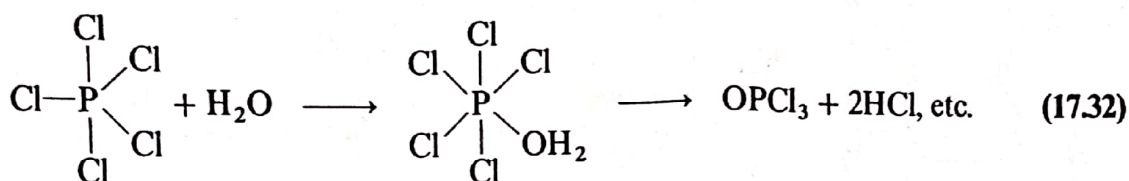


In contrast to the inertness of carbon halides, the halides of silicon and phosphorus are extremely reactive with water, to the extent that they must be protected from atmospheric moisture. A clue to the reactivity of these halides is provided by the somewhat similar reactivity of acid halides in which the carbon-halogen bond is readily attacked:



³⁰ J. R. Van Wazer, "Phosphorus and Its Compounds," Wiley (Interscience), New York, 1958, Vol. I, pp. vii-ix.

The unsaturation of the carbonyl group provides the possibility of the carbon expanding its coordination shell from 3 to 4, thereby lowering the activation energy. Carbon tetrahalide cannot follow a similar path, but the halides of silicon and phosphorus can employ $3d$ orbitals to expand their octets:

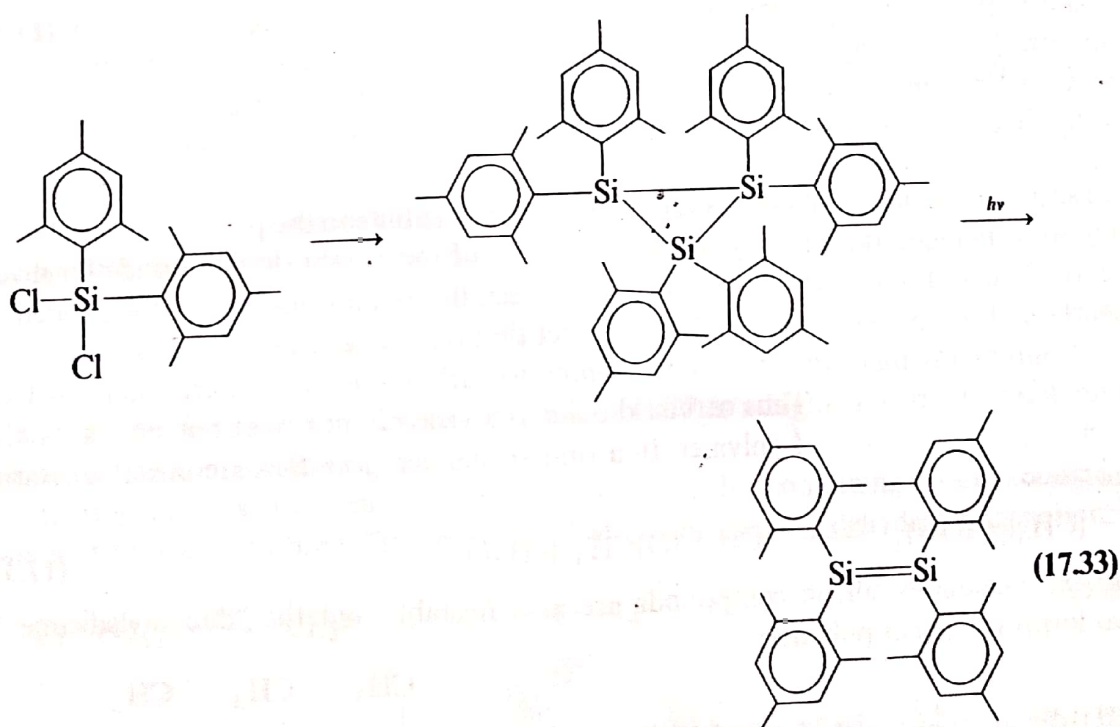


This enhanced reactivity of compounds of silicon and phosphorus is typical of all of the heavier nonmetals in contrast to the elements of the second row.

THE USE OF p ORBITALS IN π BONDING

Carbon-silicon similarities and contrasts

In view of the extensive chemistry of alkenes it was only natural for organic and inorganic chemists to search for analogous $\text{Si}=\text{Si}$ doubly bonded structures. For a long time such attempts proved to be fruitless. Recently the first stable $\text{C}=\text{Si}$ ³¹ and $\text{Si}=\text{Si}$ ³² compounds were synthesized. One synthesis involves the rearrangement of cyclotrisilane:

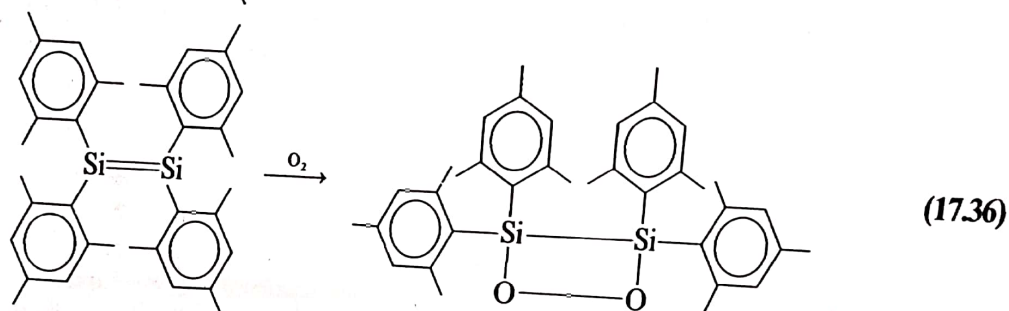
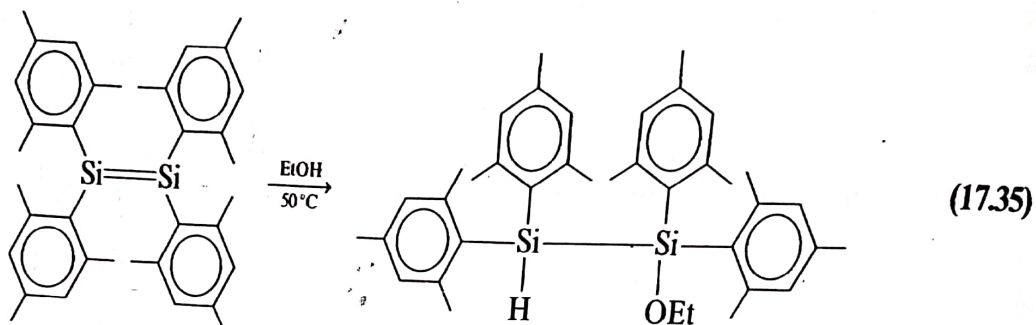
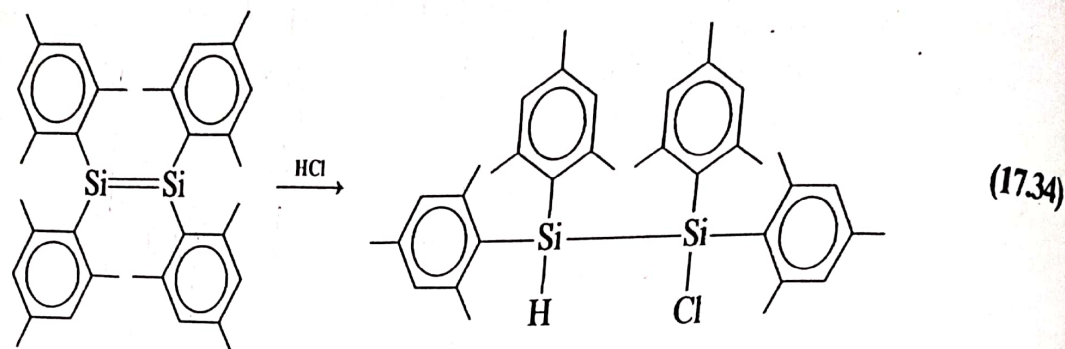


It is possible to add reagents across the $\text{Si}=\text{Si}$ double bond in some ways analogous to

³¹ A. G. Brook et al., *Chem. Commun.*, 1981, 191.

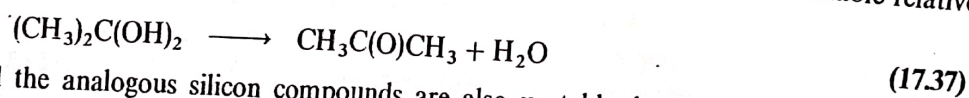
³² R. West et al., *Science*, 1981, 214, 1343; S. Matsumune et al., *J. Am. Chem. Soc.*, 1982, 104, 1153.

the C=C bond in alkenes:

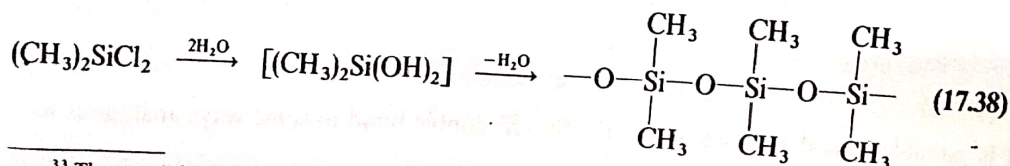


The successful isolation of these compounds is more a tribute to the persistence with which they were pursued than to any inherent stability of the Si=Si double bond. To invert George Leigh Mallory's remark about Mt. Everest, the extraordinary efforts expended on this class of compounds stemmed from the fact that they *weren't* there.

Compounds that are formally analogous to carbon compounds are found to have quite different structures. Thus carbon dioxide is a gaseous monomer but silicon dioxide is an infinite single-bonded polymer. In a similar manner, *gem*-diols are unstable relative to ketone



and the analogous silicon compounds are also unstable, but the "dimethylsilicone"³³ that forms is a linear polymer:



³³ The term "silicone" was coined by analogy to *ketone* under the mistaken belief that monomeric $\text{R}_2\text{Si}=\text{O}$ compounds could be isolated.

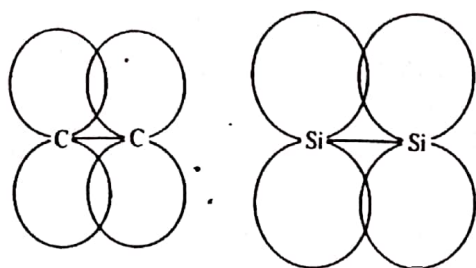


Fig. 17.7 Diagrammatic representation of the possibly poorer overlap of the p orbitals in C—C and Si—Si to form π bonds.

There are two possible sources of instability of doubly bonded silicon structures involving $p_{\pi}-p_{\pi}$ bonds. It may be that the longer σ bond in the silicon system reduces the sideways overlap of the p orbitals (Fig. 17.7). Mulliken has objected that the overlap is *not* reduced and has advanced the idea that d orbital participation may favor two "single" bonds over the one double bond. This viewpoint would emphasize that all Si—X bonds (where X = N, O, halogens) will have some double bond character (even though much less than that of a full bond) from back bonding using the d orbitals. Hence formal "single bonds" actually would be stronger than a simple σ bond and more than half as strong as the hypothetical $p_{\pi}-p_{\pi}$ double bonds.³⁴

Nitrogen-phosphorus analogies and contrasts

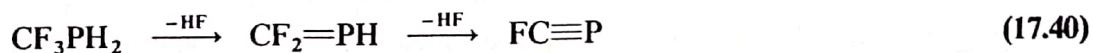
The stable form of nitrogen at room temperature is N_2 , which has an extraordinarily strong (946 kJ mol^{-1}) triple bond. In contrast, white phosphorus consists of P_4 molecules (see p. 723), and the thermodynamically stable form is black phosphorus, a polymer. At temperatures above 800°C dissociation to P_2 molecules does take place, but these are considerably less stable than N_2 with a bond energy of 488 kJ mol^{-1} . In this case, too, in the heavier element several single bonds are more effective than one multiple bond.

In 1961 the phosphorus analogue of hydrogen cyanide was prepared:³⁵



In contrast to the stability of hydrogen cyanide, HCP is a highly pyrophoric gas which polymerizes above -130°C .

During the past five years the number of molecules containing $\text{C}\equiv\text{P}$ bonds has increased to about a dozen. One method of obtaining them is dehydrohalogenation:³⁶

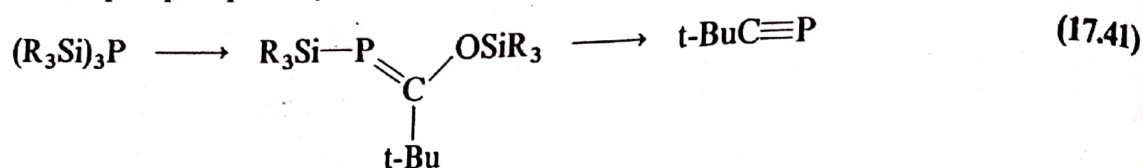


³⁴ For further discussion, see W. E. Dasent, "Nonexistent Compounds," Dekker, New York, 1965, Chap. 4; B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, 1968, 11, 249. For a discussion of bond energies in silicon compounds, see R. Walsh, *Acc. Chem. Res.*, 1981, 14, 246.

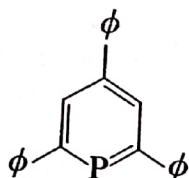
³⁵ T. E. Gier, *J. Am. Chem. Soc.*, 1961, 83, 1769.

³⁶ H. W. Kroto et al., *J. Am. Chem. Soc.*, 1978, 100, 446.

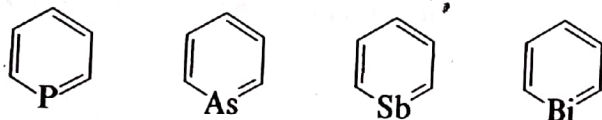
A stable, liquid phosphalkyne has recently been synthesized:³⁷



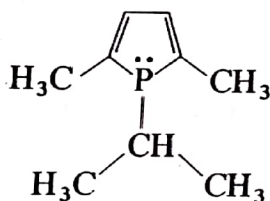
For a considerable period of time it seemed impossible to prepare doubly bonded phosphorus analogues of nitrogen. Finally, phosphorus analogues of pyridine of the type:



were synthesized,³⁸ and now all of the group VA analogues of pyridine have been prepared.³⁹



However, these compounds must be considered the exception rather than the rule as far as the heavier elements are concerned. In fact, when the barrier to inversion of the pyramidal phosphole:



was found to be only half as large as the usual value for pyramidal phosphines, R_3P , it was immediately reported as evidence that aromaticity (analogous to that of pyrrole) was responsible for lowering the activation energy. Note, however, that the aromatic stabilization is insufficient to keep the phosphole molecule planar—the ground state pyramidal with the lone pair localized on the phosphorus atom rather than delocalized in the π_p system.⁴⁰

³⁷ See H. W. Kroto and J. F. Nixon, "Phosphorus Chemistry," L. D. Quin and J. G. Verkade, eds., *ACS Symp. Ser. 171*, 1981, Paper 79.

³⁸ G. Märkl, *Angew. Chem. Int. Ed. Engl.*, 1966, 5, 846; A. J. Ashe, III, *J. Am. Chem. Soc.*, 1971, 93, 3293.

³⁹ A. J. Ashe, III, *J. Am. Chem. Soc.*, 1971, 93, 6690; A. J. Ashe, III, and M. D. Gordon, *J. Am. Chem. Soc.*, 1972, 94, 7596; A. J. Ashe, III et al., *J. Am. Chem. Soc.*, 1976, 98, 5451.

⁴⁰ W. Egan et al., *J. Am. Chem. Soc.*, 1970, 92, 1442. The evidence from the barrier to inversion is somewhat ambiguous—other factors may also be important (see R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, 1971, 93, 773).