Chapter

10

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Msc II

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The Chemistry of the Main Group Elements: Periodicity

The most fascinating aspect of inorganic chemistry as well as its most difficult problem is the diversity of reactions and structures encountered in the chemistry of somewhat over one hundred elements. The challenge is to be able to treat adequately the chemistry of boranes and noble gas fluorides, transition metals and inner transition metals, cuprate superconductors and zeolites, all without developing a separate set of rules and theories for each element or system. Much of this book has been devoted to establishing relationships that connect various aspects of inorganic chemistry. The tool that the inorganic chemist uses to systematize elemental relationships is the periodic table, now somewhat over one hundred years old.[1] It is considered so essential that no general chemistry textbook would be complete without a discussion of the trends summed up in Chapter 2. Unfortunately, the impression left by these textbooks is often simply that all periodic properties vary smoothly.

Fundamental Trends

The basic trends of the periodic chart have been discussed in Chapter 2. They may be summarized as follows. Within a given family there are increases in size and decreases in ionization energy, electron affinity, electronegativity, etc. Increasing the atomic number across a given period results in concomitant increases in ionization, electron affinity, and electronegativity, but a decrease in size. The change in effective nuclear charge within a period is reasonably smooth, but the various periods differ in length (8, 18, and 32 elements). The properties of an element will depend upon whether it follows an 8, 18, or 32 sequence. One of the best known examples is the very close similarity in properties of hafnium, tantalum, tungsten, and rhenium to those of zirconium, niobium, molybdenum, and technetium, respectively, as a result of the lanthanide contraction and associated effects. These anomalies continue through the elements gold, mercury, thallium, and lead. Similar but smaller effects follow the filling of the 3d orbitals (rarely referred to as the "scandide" contraction).

Another area of the periodic chart revealing pronounced differences between similar elements is between the first ten, H—Ne, and those immediately following, Na—Ar. It is not completely obvious why this is true. Certainly the lighter elements utilize only the 1s, 2s, and 2p atomic orbitals in their ground states, and therefore

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[1] Periodic classifications of the elements by Dmitri Mendeleev and by Lothar Meyer appeared in 1869. For a centennial-celebrating discussion of the periodic table, see van Spronsen, J. W. The Periodic System of Chemical Elements; Elsevier: Amsterdam, 1969.

simple bonding theory, whether VB or MO, suggests four covalent bonds. In contrast, VB theory suggests that the presence of d orbitals in elements with $n \geq 3$ allows hybrids with more than four bonding oribitals. However, the use of d orbitals by nonmentals presents energetic problems, is unnecessary in the simplest molecular orbital approaches, and has been one of the most controversial topics in bonding theory. Before entering this theoretical discussion, a brief examination of chemical differences is appropriate.
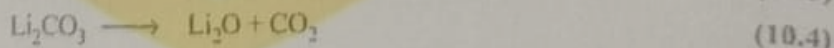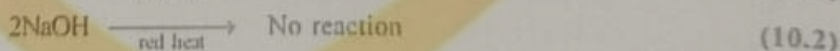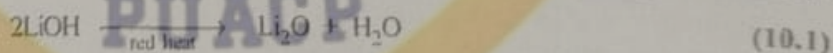
First- and Second-Row Anomalies

In many ways the first ten elements differ considerably from the remaining 99. Hydrogen is a classic example— it belongs neither with the alkali metals nor with the halogens although it has some properties in common with both. Thus it has a +1 oxidation state in common with the alkali metals but the bare H^+ has no chemical existence[2] and hydrogen tends to form covalent bonds that have properties more closely resembling those of carbon than those of the alkali metals. With the halogens it shares the tendency to form a -1 oxidation state, even to the extent of forming the hydride ion, H^-; however, the latter is a curious chemical species. In contrast to the proton which was anomalous because of its vanishingly small size, the hydride ion is unusually large. It is larger than any of the halide ions except iodide![3] The source of this apparent paradox lies in the lack of control of a single nuclear proton over two mutually repelling electrons. Since the hydride ion is large and very polarizable it certainly does not extend the trend of I^- through F^- of decreasing size and increasing basicity and hardness.

The elements of the second row also differ from their heavier congeners. Lithium is anomalous among the alkali metals and resembles magnesium more than its congeners. In turn, in Group IIA (2) beryllium is more closely akin to aluminium than to the other alkaline earths. The source of this efect is discussed below. We have already seen that fluorine has been termed a superhalogen on the basis of its differences from the remainder of Group VIIA (17).

On simple difference that the elements Li to F have with respect to their heavier congeners is in electron-attracting power. Thus fluorine is much more reactive than chlorine, bromine, or iodine; lithium is less reactive than its congeners.[4] The most electronegative and smallest element of each family will be the one in the second row.

The great polarizing power of the Li^+ cation was commented upon in Chapter 4. As a result of its small size and higher electronegativity this ion destablizes salts that are stable for the remaining alkali metals:

$$2LiOH \xrightarrow{\text{red heat}} Li_2O + H_2O \tag{10.1}$$

$$2NaOH \xrightarrow{\text{red heat}} \text{No reaction} \tag{10.2}$$

$$2LiSH \longrightarrow Li_2S + H_2S \tag{10.3}$$

$$Li_2CO_3 \longrightarrow Li_2O + CO_2 \tag{10.4}$$

In contrast, for the large polarizable hydride ion which can bond more strongly by a covalent bond the lithium compound is the most stable:

[2] Those who disapprove of writing H_3O^+ often point out that the hydration number of the H^+ is uncertain and "all cations are hydrated in solution." To treat H^+ (rather than H_3O^+) as a cation similar to Na^+, for example, is to equate nuclear particles with atoms, a discrepancy by a factor of about 10^5.

[3] Pauling (*The Nature of the Chemical Bond*, 3rd ed.; Cornell: Ithaca, NY, 1960; p 514) has provided an estimate of 208 pm for the hydride ion compared to 216 pm for I^-. To be sure, the existence of an unpolarized hydride ion is even less likely than a large unpolarized anion of some other kind, but insofar as ionic radii have meaning this would be the best estimate of the size of a free hydride ion.

[4] The inherent unreactivity of lithium is offset in aqueous solution by the exothermic hydration of the very small Li^+ ion. Nevertheless, in general, lithium is a less reactive metal than Na, K, Rb, or Cs.

$$LiH \xrightarrow{heat} \text{No reaction} \tag{10.5}$$

$$2NaH \xrightarrow{heat} Na_2 + H_2 \tag{10.6}$$
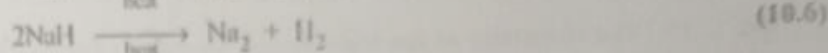
Size Effects in Nonmetals

One of the most obvious differences between the first ten elements and their heavier congeners is in their maximum coordination number, usually four or less in simple covalent molecules (Table 10.1). Arguments of the radius ratio type suggest that these atoms would have lower coordination numbers and that these steric effects would be relaxed for larger atoms. Table 10.1 can be readily interpreted in these terms. The smallest atoms have a maximum coordination number of four, larger atoms have coordination number six, and only the largest have coordination numbers as high as eight. In addition, the highest coordination numbers are found with the small fluorine atoms as ligand.[5] The hydroxy group, OH, is very similar in size, electronegativity, and other bonding properties to the fluorine atom, yet there are distinct differences between the oxygen and fluorine compounds of the nonmetals. The occurrence of molecules with the maximum number of hydroxy groups (the so-called ortho acids) is rare. Even the relatively small oxygen atom tends to result in lower coordination numbers. Thus, in contrast to the fluorides shown in Table 10.1, orthocarbonic acid, $C(OH)_4$, and orthonitric acid, $ON(OH)_3$, are unknown, the simple acids of these elements being three-coordinate, $O=C(OH)_2$ and O_2NOH.

The next two series of nonmetals, silicon through chlorine and germanium through krypton, show a maximum coordination number of six in hexafluoro anions, SF_6, and TeF_6. Even here the oxyacids and oxyanions typically show a coordination number of four as in H_3PO_4, $HClO_4$, and $HBrO_4$, and the silicates (see Chapters 11 and 12).

Table 10.1 Maximum coordination numbers of the nonmetals as shown by the fluorides

CF_4	NF_3[a]	OF_2	$FF(F_2)$
SiF_6^{2-}	PF_6^-	SF_6	ClF_5
			$IF_7(IF_8^-)$

[a] N, O, and other elements can achieve higher coordination in onium salts, e.g., NH_4^+.

The largest nonmetals show coordination numbers as high as eight in the octafluoroanions, IF_8^- and XeF_8^{2-} (see Chapter 12). The corresponding oxyacids and oxyanions show a maximum coordination number of six: $[Sb(OH)_6]^-$, $Te(OH)_6$, $OI(OH)_5$, and $[XeO_6]^{4-}$. Of these, apparently only iodine shows a maximum oxidation state with a coordination number as low as four: Periodic acid can exist as either $OI(OH)_5$ or HIO_4.

The Diagonal Relationship

It was mentioned previously that a strong resemblance obtains between Li and Mg, Be and Al, C and P, and other "diagonal elements," and it was pointed out that this could be related to a size-charge phenomenon. Some examples of these resemblances are as follows:

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[5] This is advantageous not only from the steric viewpoint but also from the fact that the redox behavior of fluorine is well suited to stabilize high oxidation states. To put it another, but equivalent, way: High oxidation state species are hard acids and the fluoride ion is the hardest possible base.

Lithium–Magnesium

There is a large series of lithium alkyls and lithium aryls which are useful in organic chemistry in much the same way as the magnesium Grignard reagents. Unlike Na, K, Rb, or Cs, but like Mg, lithium reacts directly with nitrogen to form a nitride:

$$3Li_2 + N_2 \longrightarrow 2Li_3N_2 \qquad (10.7)$$
$$6Mg + 2N_2 \longrightarrow 2Mg_3N_2 \qquad (10.8)$$
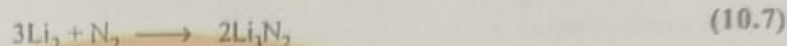
Finally, the solubilities of several lithium compounds more nearly resemble those of the corresponding magnesium salts than of other alkali metal salts.

Beryllium–Aluminum

These two elements resemble each other in several ways. The oxidation emfs of the elements are similar ($E^0_{Be} = 1.85$; $E^0_{Al} = 1.66$), and although reaction with acid is thermodynamically favored, it is rather slow, especially if the surface is protected by the oxide. The similarity of the ionic potentials for the ions is remarkable ($Be^{2+} = 48$, $Al^{3+} = 56$) and results in similar polarizing power and acidity of the cations. For example, the carbonates are unstable, the hydroxides dissolve readily in excess base, and the Lewis acidities of the halides are comparable.

Boron–Silicon

Boron differs from aluminum in showing almost no metallic properties and its resemblance to silicon is greater. Both boron and silicon form volatile, very reactive hydrides; the hydride of aluminum is a polymeric solid. The halides (except BF_3) hydrolyze to form boric acid and silicic acid. The oxygen chemistry of the borates and silicates also has certain resemblances.

Carbon–Phosphorus, Nitrogen–Sulfur, and Oxygen–Chlorine

All metallic properties have been lost in these elements, and so charge-to-size ratios have little meaning. However, the same effects appear in the electronegativities of these elements, which show a strong diagonal effect:[b]

$$C = 2.55 \quad N = 3.04 \quad O = 3.44 \quad F = 3.98$$
$$Si = 1.90 \quad P = 2.19 \quad S = 2.58 \quad Cl = 3.16$$
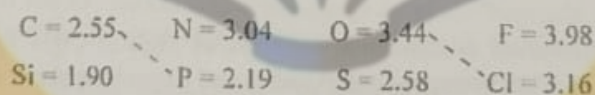
The similarities in electronegativities are not so close as that of the ionic potentials for Be^{2+} and Al^{3+}. The heavier element in the diagonal pair always has a lower electronegativity, but the effect is still noticeable. Thus when considering elements that resemble carbon, phosphorus is often as good a choice as silicon, and the resemblance is sufficient to establish a base from which notable *differences* can be formulated.[7]

The Use of p Orbitals in Pi Bonding

In view of the extensive chemistry of alkenes it was only natural for organic and inorganic chemists to search for analogous Si═Si doubly bonded structures. For a long time such attempts proved to be fruitless. The

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[b] These values are Pauling thermochemical electronegativities rather than those based on ionization energy–electron affinity. This choice of empirical values was made to obviate the necessity of choosing (arbitrarily) the proper valence state (hybridization).

[7] The diagonal relationship, like any other rule-of-thumb, can be seen from several viewpoints: in terms of unifying known facts (when it works), as a predictor of unknown properties (hoping it works), or in terms of the significance of its exceptions (when it does not work). See, for example, Feinstein, H. I. *J. Chem. Educ.* 1984, 61, 128. Hanusa, T. P. *J. Chem. Educ.* 1987, 64, 686–687.

first stable C=Si[8] and Si=Si[9] compounds were synthesized about a decade ago. One synthesis involves the rearrangement of cyclotrisilane:


(10.9)
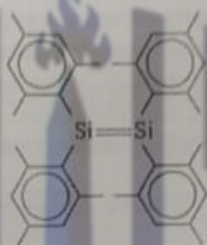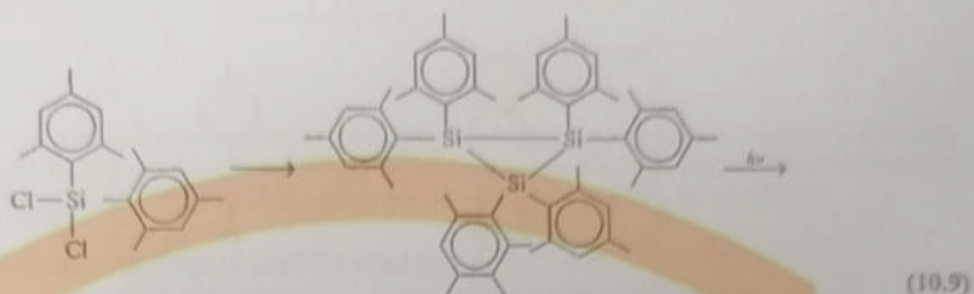
Carbon–Silicon Similarities and Contrasts

It is possible to add reagents across the Si=Si double bond in some ways analogous to the C=C bond in alkenes:


(10.10)

(10.11)
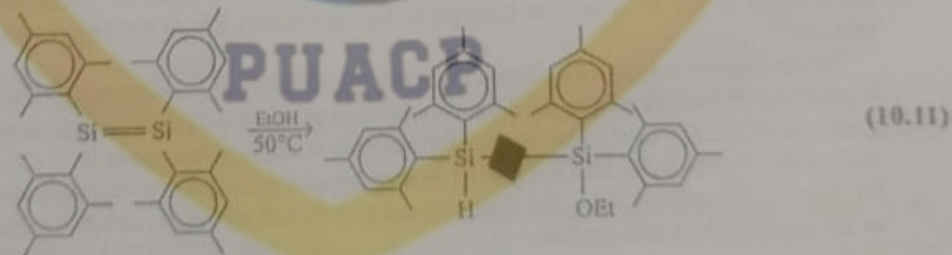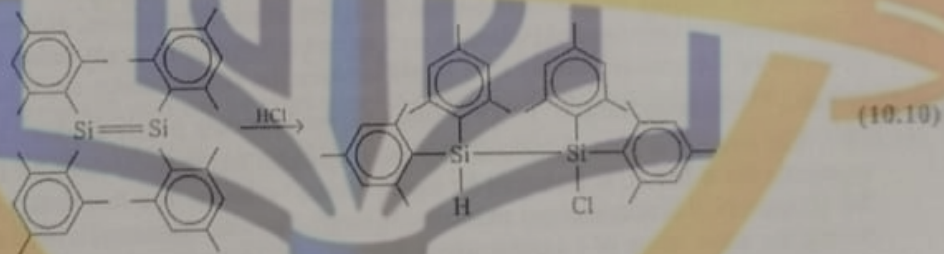
[8] Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Katlury, R. K. *J. Chem. Soc., Chem. Commun.* 1981, 191–192.
[9] West, R.; Fink, M. J.; Michi, J. *Science* 1981, *214*, 1343–1344. Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* 1982, *104*, 1150–1153. West, R. *Angew Chem. Int. Ed. Engl.* 1987, *26*, 1201.

$$(10.12)$$
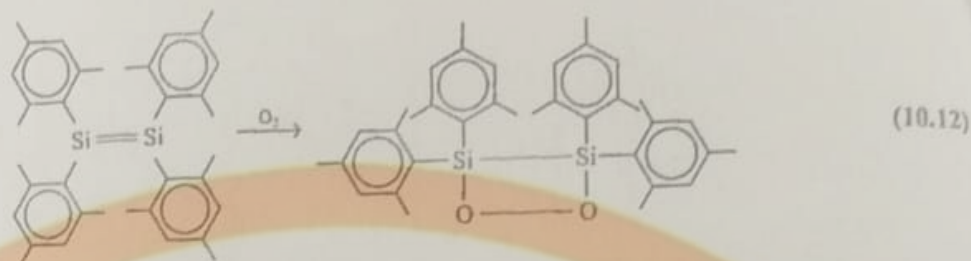
Compounds that are formally analogous to carbon compounds are found to have quite different structures. Thus carbon dioxide is a gaseous monomer, but silicon dioxide is an infinite single-bonded polymer. In a similar manner, *gem*-diols are unstable relative to ketones:

$$(CH_3)_2C(OH)_2 \longrightarrow CH_3C(O)CH_3 + H_2O \qquad (10.13)$$
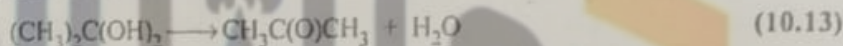
and the analogous silicon compounds are also unstable, but the "dimethylsilicone"[10] that forms is a linear polymer:

$$(10.14)$$
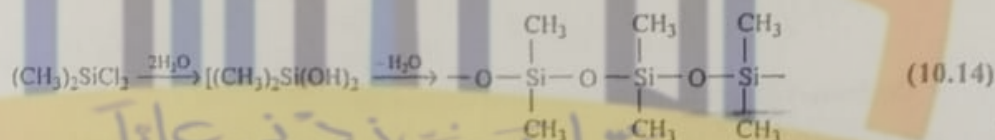
The contrast between the strengths of $2p_\pi$–$2p_\pi$ bonds and their higher-n congeners is responsible for much of the stability of groups important to organic chemistry: alkenes, aldehydes, ketones, and nitriles. It also permits doubly bonded molecules such as carbonic and nitric acids, rather than their ortho analogues. A source of the greater stability of π bonds between the smaller atoms could be better overlap of the $2p$ orbitals. The overlap integral $\int \Psi_A \Psi_B$ (see Chapter 5) is only poorly depicted by a drawing such as Fig. 10.1. The overlap is strongly affected by the *magnitude* of the wave function in the overlap region and, especially for π bonds, is increased by small, "dense" orbitals. The first time a given type of orbital ($2p$, $3d$, $4f$) appears, it is nodeless and anomalously small. The small size results from the absence of inner shells having the same value of l against which this set of orbitals must be orthogonal.[11] The $2p$ orbitals thus are as small as the $2s$ orbital, in contrast to the $3p$ orbitals which are larger and more diffuse than the $3s$ orbitals.[12]

For the heavier congeners in Group IVA (14), the differences are even more striking. Thus, although carbon is generally tetravalent except as transient carbene or methylene intermediates, it is possible to prepare divalent germanium, tin, and lead compounds. For example, if bulky substituents $[R = CH(SiMe_3)_2]$ are present, the compounds R_2Ge, R_2Sn, and R_2Pb exist as diamagnetic monomers in solution, although there is a tendency for them to dimerize in the solid. The molecular structure of the tin dimer has been determined and found to be in the trans conformation:

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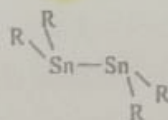
[10] The term "silicone" was coined by analogy to ketone under the mistaken belief that monomeric $R_2Si{=}O$ compounds could be isolated. See Chapter 11.

[11] Pyykko, P. *Chem. Rev.* 1988, *88*, 563–594.

[12] Walsh, R. *Acc. Chem. Res.* 1981, *14*, 246. West, R. *Angew. Chem. Int. Ed. Engl.* 1987, *26*, 1201–1211.
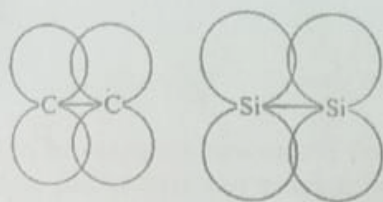
Fig. 10.1 Diagrammatic representaiton of the possibly poorer overlap of the p orbitals in Si—Si as compared with C—C.

In addition to being bent, in contrast to ethylene, the Ge—Ge and Sn—Sn bonds are not as short as expected for true double bonds.[13] Calculations indicate that p_π-p_π bonding is less important and other interactions may become increasingly important. Calculated bond orders are Ge—Ge = 1.61 and Sn—Sn = 1.46.[14]
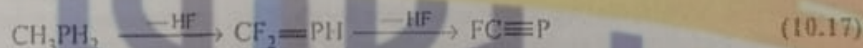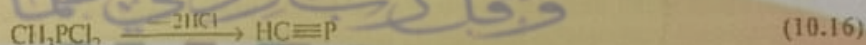
Nitrogen–Phosphorus Analogies and Contrasts

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 Chapter 11), 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 the multiple bond.
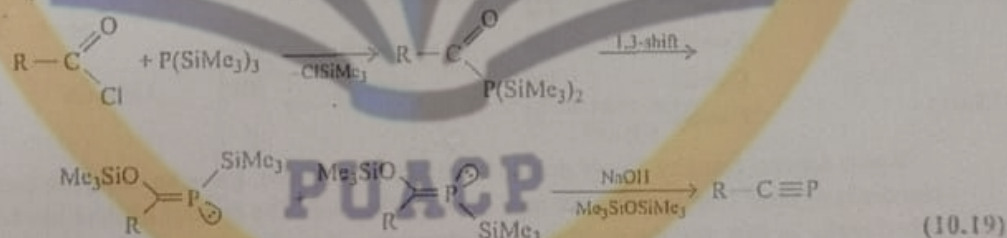
The phosphorus analogue of hydrogen cyanide can be prepared:

$$CH_4 + PH_3 \xrightarrow[\text{arc}]{\text{electric}} HC\equiv P + 3H_2 \qquad (10.15)$$
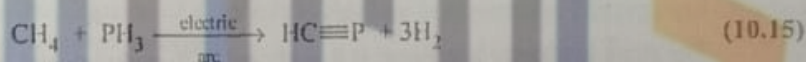
In contrast to stable hydrogen cyanide, HCP is a highly pyrophoric gas which polymerizes above −130 °C. In this decade the number of molecules containing C≡P bonds has increased to over a dozen. One method of obtaining them is by dehydrohalogenation:

$$CH_3PCl_2 \xrightarrow{-2HCl} HC\equiv P \qquad (10.16)$$

$$CH_3PH_2 \xrightarrow{-HF} CF_2\equiv PH \xrightarrow{-HF} FC\equiv P \qquad (10.17)$$

Kinetically stable phosphaalkynes can be synthesized if a sufficiently bulky substituent (R) is present:[16]

$$P_4 + 12Na/K + 12ClSiMe_3 \longrightarrow 4P(SiMe_3)_3 + 12(Na/K)Cl \qquad (10.18)$$

R—C(=O)Cl + P(SiMe₃)₃ →(−ClSiMe₃) R—C(=O)—P(SiMe₃)₂ →(1,3-shift)

Me₃SiO—C(R)=P(SiMe₃) / Me₃SiO—C(R)=P—SiMe₃ →(NaOH, −Me₃SiOSiMe₃) R—C≡P   (10.19)
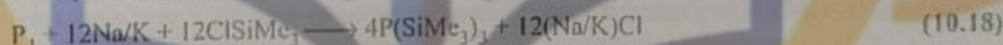
13 Davidson, P. J.; Harris, D. H.: Lappert, M. F. *J. Chem. Soc. Dalton Trans.* 1976, 2268–2274. Cowley, A. H., Norman, N. C. *Prog. Inorg. Chem.* 1986, *34*, 1–63.

14 Lendvay, G. *Chem. Phys. Lett.* 1991, *181*, 88–94. See also data on bond energies on page 865 and Grev, R. S. *Adv. Organomet. Chem.* 1991, *33*, 125–170.

15 Regitz, M.; Binger, P. *Angew. Chem. Int Ed. Engl* 1988, *27*, 1484–1508. Regitz, M. *Chem. Rev* 1990, *90*, 191. Maah, M. H.; Nixon, J. F. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley: New York, 1990; Chapter 9.

16 Note that since a phosphaalkyne (or any other triply bonded group) will be linear and "exposed" the protection afforded by [a] bulky group[s] is less than in the corresponding case of doubly bonded species.

One of the first challenges facing chemists attempting to prepare phosphorus analogues of nitrogen compounds was phosphabenzene. First the phosphorus analogue of pyridine was synthesized, and now all of the group VA (15) analogues of pyridine have been prepared.

However, these compounds must be considered the exception rather than the rule as far as the heavier elements are concerned.

The isolation of compounds containing simple C=P double bonds parallels the triple-bond work. The first stable acyclic phosphaalkene was synthesized several years ago.[17] Again, base-induced dehydrohalogenation and stabilization by bulky groups is important:

$$(10.20)$$
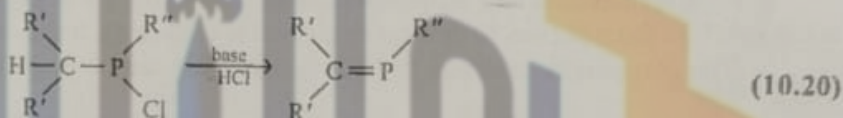
The steric hindrance is critical: If R = phenyl or 2-methylphenyl, the bulkiness is insufficient to stabilize the molecules, but the 2, 6-dimethylphenyl and 2, 4, 6-trimethylphenyl derivatives are stable.

Summary on the Occurrence of p_π-p_π Bonding in Heavier Nonmetals

For many years the occurrence of double and triple bonds such as discussed above for silicon and phosphorus was equally rare among other nonmetals, leading to the conclusion that only C=C, C=N, C=O, N≡N, etc. were stable multiple bonds. This, of course, was taken as challenge and much synthetic work was directed at the problem. None of the multiple bonds between heavier nonmetals is as strong as those between the $2p$ elements. Some typical estimates of the strength of the π bond (cf. to $H_2C=CH_2$ as a "standard" from organic chemistry) are (values in kJ mol^{-1}):

C=C	272				
C=Si	159	Si=Si	105		
C=Ge	130	Si=Ge	105	Ge=Ge	105
C=Sn	79				

It now appears that any X=Y double bond can be prepared, given an energetic enough research attack: Hundreds of these compounds have now been synthesized. The general method has been to involve bulky substituents. In this way the multiple bond chemistry of the heavier nonmetals has resembled attempts to make low-coordination-number complexes (Chapter 16).

The number of triple bonds of the heavier nonmetals that are known is considerably smaller—perhaps a dozen. It has already been noted above that protecting a triple bond sterically is considerably more difficult than for the case of a corresponding double bond. One very interesting aspect of the C≡S bond is that, in contrast to the C≡C in acetylenes, the triple bond does not ensure linearity at the carbon atom (Fig. 10.2). The reasons are not completely clear but may be related to the nonplanarity of $R_2Ge=GeR_2$ and $R_2Sn=SnR_2$.

[17] Becker, G. Z. Anorg. Chem. 1976, 423, 247. Cowley. A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L., Hunter, W. E.; Zhang, H.-M. J. Am. Chem Soc. 1984, 106, 7015-7020.
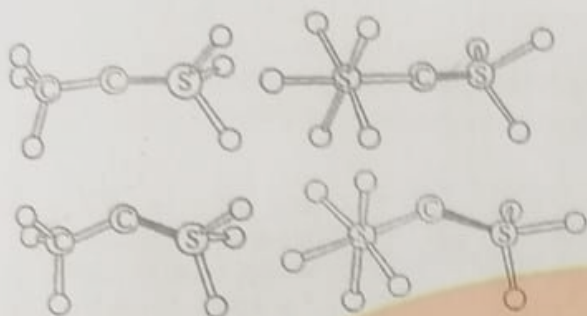
Fig. 10.2 Molecular structures of (a) $Cl_3C \equiv SF_3$ and (b) $SF_5C \equiv SF_3$. Crystal structures are above and gas structures below. Note strong bending in the gas phase. [From Seppelt, K. *Angew. Chem. Int. Ed. Engl.* 1991, *30*, 361–374. Reproduced with permission.]

"In spite of all of the remarkable success with the synthesis of such compounds, the fact remains that these double [and triple] bonds still form, in the final analysis, more unfavorable bonding systems than those of elements of the second period."[18]

The Use (or Not) of d Orbitals by Nonmetals

Theoretical Arguments against d Orbital Participation in Nonmetals

Several workers have objected to the inclusion of *d* orbitals in bonding in nonmetals. The principal objection is to the large promotion energy required to effect

$$s^2 p^n d^0 \longrightarrow s^1 p^n \, ^{m} p^{m+1} \qquad (10.21)$$

where $m = 0$ (P), 1 (S), or 2 (Cl), to achieve a maximum multiplicity and availability of electrons for bonding. A second factor which does not favor the utilization of *d* orbitals is the poor overlap that they make with the orbitals of neighboring atoms. The $3d$ orbitals of the free sulfur atoms, for example, are shielded completely by the lower-lying electrons and hence do not feel the nuclear charge as much as the $3s$ and $3p$ electrons. As a result they are extremely diffuse, having radial distribution maxima (Fig. 2.4) at a distance which is approximately *twice* a typical bond distance (Fig. 10.3).[19] This results in extremely poor overlap and weak bonding.[20]

Two alternatives have been suggested to account for the higher oxidation states of the nonmetals; both reduce the importance of high-energy *d* orbitals. Pauling has suggested that resonance of the following type could take place:

$$(10.22)$$

(I)   (II)

Four more forms like (II)
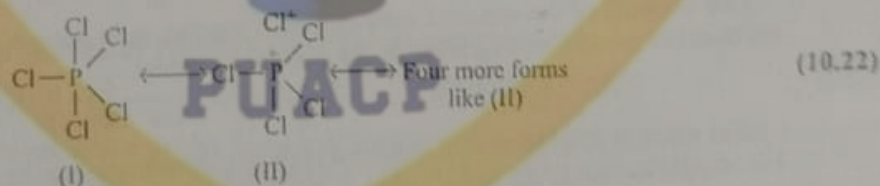
18 Seppelt, K. *Angew. Chem. Int. Ed. Engl.* 1991, *30*, 361–364. For recent reviews of some of these multiply bonded systems, see Niecke, E.; Gudat, D. *Angew. Chem. Int. Ed. Engl.* 1991, *30*, 217–237; Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Ibid.* 1991, *30*, 902–930; Barrau, J.; Escudie, J.; Satge. *J. Chem. Rev.* 1990, *90*, 283; and references to earlier work therein. See also Footnote 15.

19 For example, the radial distribution maxima of 3*d* orbital appear at 300–400 pm in the free sulfur atom, while the typical S—F bond length is 156 pm.

20 These same general arguments apply to all of the heavier nonmetals. The *d* and *f* orbitals are heavily shielded by the more penetrating *s* and *p* electrons.
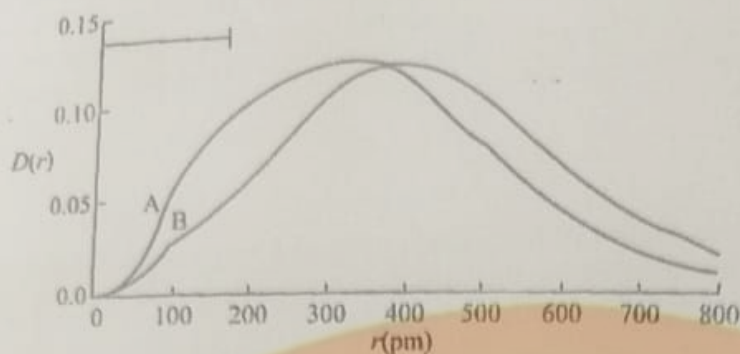
Fig. 10.3 The $3d$ orbital distribution functions in d^1 configurations (A) in the ^6D term of P ($s^1p^3d^1$); (B) in the ^5D term of S ($s^2p^3d^1$). Line represents a typical S—F bond length. [Modified from Mitchell K. A. R. *Chem. Rev.* 1969, 69, 157. Reproduced with permission.]

Only structure I involves d orbitals, and so the d character of the total hybrid is small. Each P—Cl bond has 20% ionic character and 80% covalent character from resonance structures such as II.

The second alternative is the three-center, four-electron bond developed by simple molecular orbital theory for the noble gas fluorides (see Chapter 12). Since this predicts that each bonding pair of electrons (each "bond") is spread over three nuclei, the bond between two of the nuclei is less than that of a normal two-center, two-electron bond. Furthermore, since the nonbonding pair of electrons is localized on the fluorine atoms, there is a separation of charge ("ionic character"). In both respects, then, this interpretation agrees with Pauling's approach and with the experimental facts.

Experimental Evidence for d_π–p_π Bonding; the Phosphorus–Oxygen Bond in Phosphoryl Compounds

In the case of d_π–p_π bonding we again find the old problem of detecting the existence of a bond. We can infer the presence of a σ bond when we find two atoms at distances considerably shorter than the sum of their van der Waals radii. The detection of a π bond depends on more subtle criteria: shortening or strengthening of a bond, stabilization of a charge distribution, etc., experimental data which may be equivocal.

One example of the apparent existence of π bonding is in phosphine oxides. Most tertiary phosphines are unstable relative to oxidation to the phosphine oxide:

$$2R_3P + O_2 \longrightarrow 2R_3PO \tag{10.23}$$

This reaction takes place so readily that aliphatic phosphines must be protected from atmospheric oxygen. The triarylphosphines are more stable in this regard but still can be oxidized readily:

$$Ph_3P \xrightarrow[KMnO_4]{HNO_3 \text{ or}} PH_3PO \tag{10.24}$$
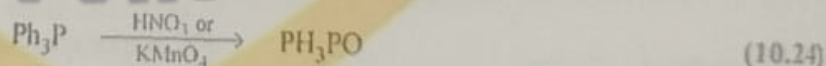
In contrast, aliphatic amines do not have to be protected from the atmosphere although they can be oxidized:

$$R_3N + HOOH \longrightarrow [R_3NOH]^+OH^- \xrightarrow{-H_2O} R_3NO \tag{10.25}$$
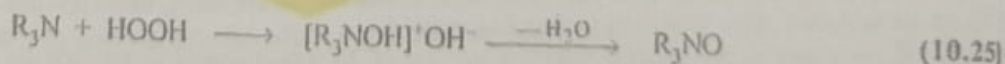
However, the amine oxides decompose upon heating:

$$Et_3NO \xrightarrow{heat} Et_2NOH + CH_2{=}CH_2 \tag{10.26}$$
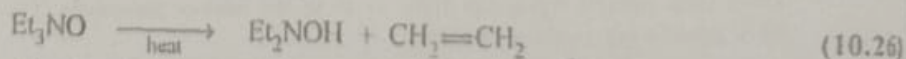
a reaction completely unknown for the phosphine oxides, which are thermally stable. In fact, the tertiary phosphine oxides form the most stable class of organophosphorus compounds. Those oxides with no β hydrogen atom are particularly stable: Trimethylphosphine oxide and triphenylphosphine oxide do not

decompose below 700 °C.[21] They are not reduced even by heating with metallic sodium. The tendency of phosphorus to form P→O or P=O linkages[22] is one of the driving forces of phosphorus chemistry and may be used to rationalize and predict reactions and structures. For example, the lower phosphorus acids exist in the four-coordinate structures even though they are prepared by the hydrolysis of three-coordinate halides:

$$X \overset{P}{\underset{X}{/|\backslash}} X \xrightarrow{H_2O} \left[HO \overset{P}{\underset{OH}{/|\backslash}} OH \right] \longrightarrow \overset{O}{\underset{HO\ OH}{\overset{\|}{P}-H}} \tag{10.27}$$

$$R \overset{P}{\underset{X}{/|\backslash}} X \xrightarrow{H_2O} \left[R \overset{P}{\underset{OH}{/|\backslash}} OH \right] \longrightarrow R \overset{O}{\underset{H}{\overset{\|}{/}}} P\ OH \tag{10.28}$$

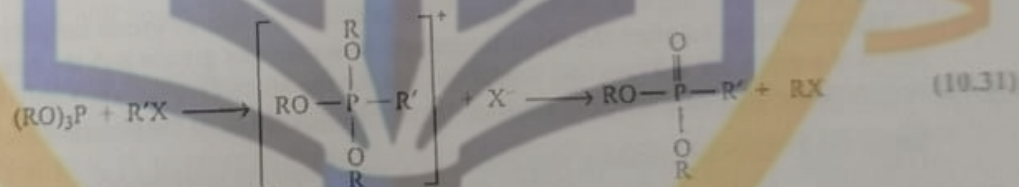$$X \overset{X}{\underset{X}{/}} P \overset{X}{\underset{P}{/}} X \xrightarrow{H_2O} \left[HO \overset{OH}{\underset{HO}{/}} P-P-OH \right] \longrightarrow H-\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{P}}-H \tag{10.29}$$
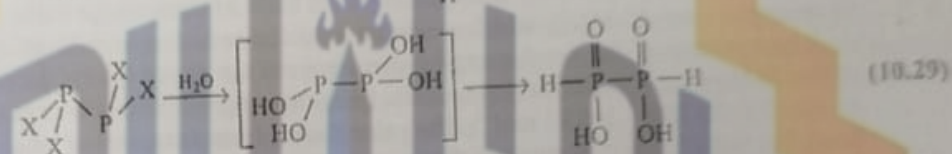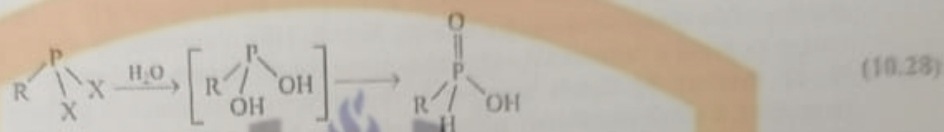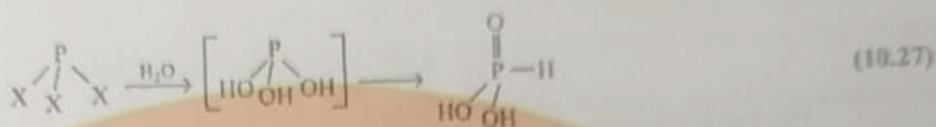
The tendency to form P=O bonds is responsible for the Arbusov reaction. The typical reaction is the rearrangement of a trialkyl phosphite to a phosphonate:

$$(RO)_3P \xrightarrow{RX} (RO)_2PR \tag{10.30}$$

If the catalytic amounts of RX in Eq. 10.30 are replaced by equimolar amounts of R'X, the role of the alkyl halide in the formation of an alkoxy phosphonium salt is revealed:

$$(RO)_3P + R'X \longrightarrow \left[RO-\overset{R}{\underset{R}{\overset{O}{|}}}P-R' \right]^+ + X^- \longrightarrow RO-\overset{O}{\overset{\|}{P}}-R' + RX \tag{10.31}$$

Oxidation of trialkyl phosphites by halogens illustrates the same principle:

$$(RO)_3P + Cl_2 \longrightarrow [(RO)_3PCl]^+Cl^- \longrightarrow (RO)_2P(O)Cl + RCl \tag{10.32}$$
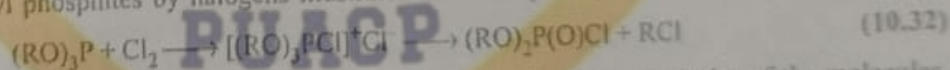
A final difference between amine oxides and phosphine oxides lies in the polarity of the molecules. The dipole moment of trimethylamine oxide is 16.7×10^{-30} C m (5.02 D) compared with 14.6×10^{-30} C m (4.37 D) for triethylphosphine oxide. A consequence of this polarity is the tendency of the amine oxides to form hydrates, $R_3NO \cdot H_2O$, and their greater basicity relative to the phosphine oxides.

The difference between the behavior of the amine oxides and phosphine oxides can be rationalized in terms of the possibility of back bonding in the latter. Whereas amine oxides are restricted to a single structure

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[21] Corbridge, D. E. C. *Phosphorus*, 4th ed.; Elsevier: Amsterdam, 1990; p 320.
[22] Whether the P—O bond is essentially a single, σ, dative bond, P→O, or has at least some d_π–p_π double-bond character is, of course, the argument here, and to portray the following structures with either P→O or P=O tends to anticipate the question unintentionally: See the resonance forms in Eq. 10.33.

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containing a dative N—O bond, $R_3N{\rightarrow}O$, the phosphine oxides can have contributions from $d_\pi - p_\pi$ bonding between the phosphorus and oxygen atoms:

$$R_3P^+ \longrightarrow O^- \longleftrightarrow R_3P = 0 \qquad (10.33)$$

(I)   (II)
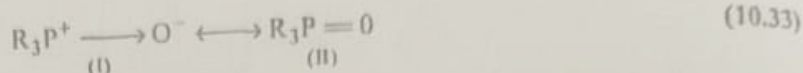
The double bond character introduced by the latter strengthens the bond and accounts for the extraordinary stability of the phosphorus oxygen linkage. Note that this extra stability cannot be attributed to ionic resonance energy (a priori a reasonable suggestion since the difference in electronegativity is greater in P—O than N—O) because the dipole moment of the nitrogen compound is greater than that of the phosphorus compound, a result completely unexpected on the basis of electronegativities, unless consideration is taken of canonical form 10.33(II), which would be expected to lead to a reduced moment.

A comparison of the bond energies also supports the above interpretation. The dissociation energies of P=O bonds in a variety of compounds lie in the range of 500–600 kJ mol⁻¹ compared with values for N→O of about 200 – 300 kJ mol⁻¹. The value for the latter is typical of what we might expect for a single bond, but 600 kJ mol⁻¹ is stronger than any known single bond. A closer examination of the strengths of various P=O bonds in terms of infrared stretching frequencies shows some interesting trends. For a series of similar molecules, such as the phosphine oxides, the stretching frequency provides an indication of the strength of the bond (Table 10.2)[23]. The highest stretching frequency among the phosphoryl compounds is that of F_3PO, and the lowest of the halides is that of Br_3PO (the iodo compound is unknown). When the stretching frequencies are plotted as a function of the sum of the electronegativities of the substituents, a straight line is obtained:

$$\nu_{PO} = 930 + 40\Sigma_\chi \qquad (10.34)$$

where χ is the Pauling electronegativity of a substituent atom or group on phosphorus.

The correlation between the electronegativity of substituent groups and the strength of the P=O bond provides support for a π-bonding model but not for the alternative dative σ only model. A σ bond might be expected to be destabilized as electron density is removed from the phosphorus, requiring it to withdraw

Table 10.2 Infrared stretching frequencies of some phosphoryl compounds[a]

Compound	ν_{PO} (cm⁻¹)	S_c
F_3PO	1404	11.70
F_2ClPO	1358	10.75
Cl_3PO	1295	8.85
Cl_2BrPO	1285	8.52
$ClBr_2PO$	1275	8.19
Br_3PO	1261	7.86
Ph_3PO	1190	(7.2)
Me_3PO	1176	(6.0)

[a] χ = substituent electronegativity

[23] Note that the *dissociation energy*, $R_3PO \rightarrow R_3PO \rightarrow R_3P + O$ is not a sensitive measure of the P=O *bond energy* because the remaining three bonds may be strengthened or weakened in the dissociation process. The IR stretching frequency is a function of the force constant, k, and the reduced mass, μ, of the vibrating groups. If the molecule is assumed to be a light oxygen atom vibrating on a "fixed" larger mass of the R_3P group, the reduced mass is constant, and so changes in frequency will reflect corresponding changes in the force constant. For similar molecules the force constant will be related to the total bond energy.

electrons from the P→O bond, weakening it. In contrast, if the oxygen can back bond to the phosphorus through a $d-p\,\pi$ bond, the induced charge on the phosphorus can be diminished and the P=O bond strengthened.

The bond lengths in phosphoryl compounds are in accord with the concept of double-bond character. In the simplest case, that of P_4O_{10}, there are two P—O bond lengths. There are twelve relatively long ones (158 pm) within the cage framework proper and four shorter ones (141 pm) between the phosphorus atoms and the oxygen atoms external to the cage. It is interesting to note that the ratio of these two bond lengths (0.89) is about the same as C=C to C—C or C=O to C—O.

Isoelectronic with the phosphine oxides are the phosphorus ylids, R_3PCH_2. As for the oxides, two resonance forms

$$R_3 \overset{+}{P}—\overset{-}{C}H_2 \longleftrightarrow R_3P = CH_2 \qquad\qquad (10.35)$$

$$(I) \qquad\qquad\qquad (II)$$
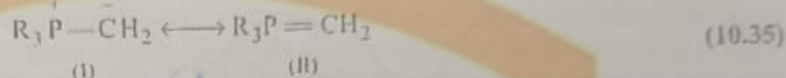
contribute to the stability of the phosphorus ylids but not the corresponding ammonium ylids, $R_3N^+—\overset{-}{C}H_2$. This difference is reflected in the reactivity. The ammonium ylids are generally quite basic and quite reactive; the phosphorus ylids are much less so, many not being sufficiently basic to abstract a proton from water and, in fact, not dissolving in water unless strong acids are present.

A Comparison of Pi Bonding in Phosphine Complexes and Oxides

The controversy over the nature of the P=O bond is reminiscent of that over the nature of phosphorus–metal bonds in coordination compounds. In both, interpretations have long ranged from a σ only to a highly synergistic σ–π model. The σ^* orbitals have also been invoked in more recent phosphorus π bonding arguments, inasmuch as d–σ^* hybrids may be involved.[24] So the question turns out not to be simply σ vs. π but the relative contributions of d and σ^* orbitals to the latter. As with so many questions in inorganic chemistry, the answer is neither black nor white, but gray. If the symmetries and energies of orbitals are compatible, bonding will occur. The appropriate question is one of relative importance.

Evidence from Bond Angles

The trimethylamine molecule has a pyramidal structure much like that of ammonia with a CH_3—N—CH_3 bond angle of $107.80 \pm 1°$. In contrast, the trisilylamine molecule is planar. Although steric effects of the larger silyl groups might be expected to open up the bond angles, it seems hardly possible that they could force the lone pair out of a fourth "tetrahedral" orbital and make the molecule perfectly planar (even Ph_3N has bond angles of 116°). It seems more likely that the lone pair adopts a pure p orbital on the nitrogen atom because orbitals on the three silicon atoms can overlap with it and delocalize the lone pair over the entire system (Fig. 10.4).

Rather similar results are obtained by comparing the bond angles in the silyl and methyl ethers (Fig. 10.5) and isothiocyanates (Fig. 10.6). In dimethyl ether the oxygen is hybridized approximately sp^3 with two lone pairs on the oxygen atom as compared to an approximate sp^2 hybrid in disiloxane with π bonding. In the same way the methyl isothiocyanate molecule, CH_3N=C=S has a lone pair localized on the nitrogen atom, hence is bent (N – sp^2), but the delocalization of this lone pair into a π orbital on the silicon atom of H_3SiN=C=S leads to a linear structure for this molecule.

The hypothesized delocalization of lone pair electrons in the above silicon compounds is supported by the lowered basicity of the silyl compounds as compared to the corresponding carbon compounds. This

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24 Orpen. A. G.; Connelly. N. G. *J Chem. Soc., Chem. Commun.* 1985, 1310–1311. Pacchioni. G.; Bagus, P. S. *Inorg. Chem.* 1992, *31*, 4391–4398.

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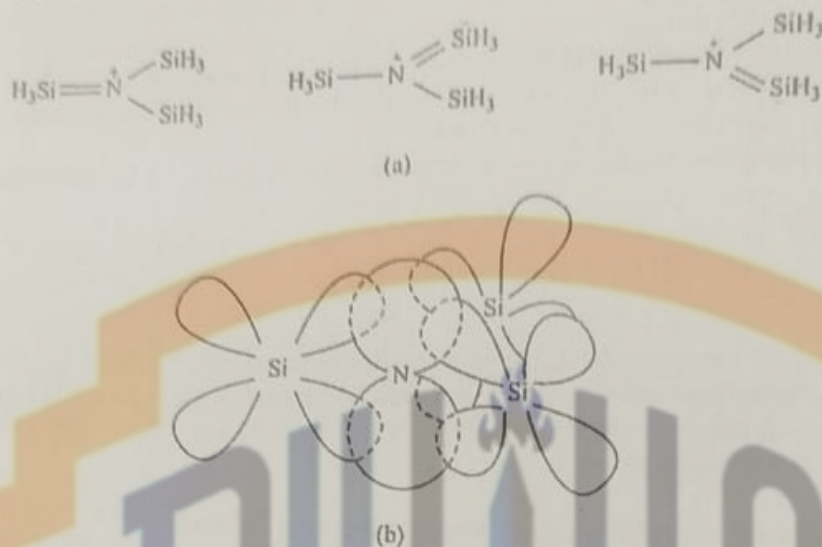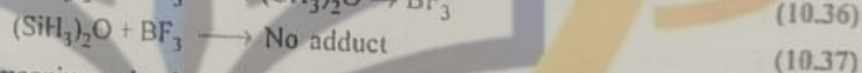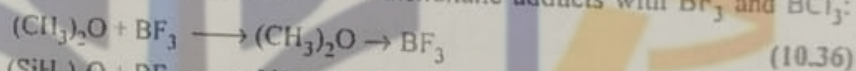

(a)

(b)

Fig. 10.4 Delocalization of the lone pair in trisilyl amine. (a) Resonance structures. (b) Overlap of d_{Si} and p_N orbitals.

reduced basicity is contrary to that expected on the basis of electronegativity effects operating through the σ system since silicon is less electronegative than carbon. It is consistent with an "internal Lewis acid-base" interaction between the nitrogen and oxygen lone pairs and empty acceptor d orbitals on the silicon. Experimentally this reduced basicity is shown by the absence of disiloxane adducts with BF_3 and BCl_3:

$$(CH_3)_2O + BF_3 \longrightarrow (CH_3)_2O \rightarrow BF_3$$

$$(SiH_3)_2O + BF_3 \longrightarrow \text{No adduct}$$

(10.36)

(10.37)

and by the absence of trisilylammaonium salts. Instead of onium salt formation trisilylamine is cleaved by hydrogen chloride:

$$(SiH_3)_3N + 4HCl \longrightarrow NH_4Cl + 3SiH_3Cl$$

(10.38)
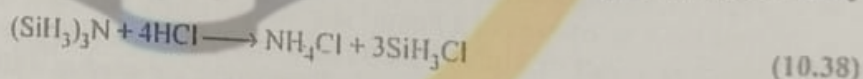
Pi Bonding in the Heavier Congeners

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,

Fig. 10.5 Comparison of the molecular structures of dimethyl ether and disiloxane.

Fig. 10.6 Comparison of the molecular structures of methyl isothiocyanate and silyl isothiocyanate.

13

antimony. selenium, tellurium. etc. In general it is thought that the problems faced in phosphorus and sulfur chemistry concerning 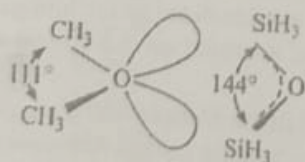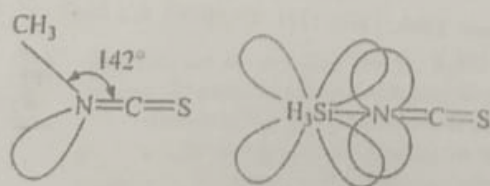promotion energies and diffuse character may be even larger in the heavier congeners. In the latter regard it is interesting to note the apparent effectiveness of π bonding in metal complexes. To the extent that softness in a ligand can be equated with the ability to accept electrons from soft metal ions in $d_\pi - d_\pi$ "back bonds," information can be obtained from the tendency to complex with (b) metal ions (see Chapter 8): P > As > Sb. This order would indicate that the smaller phosphorus atom can more effectively π bond with the metal atom.

Theoretical Arguments in Favor of d Orbital Participation

In contrast to the arguments presented against participation by d orbitals in the bonding of nonmetals, several workers have pointed out that the large promotion energies and diffuse character described above are *properties of an isolated sulfur or phosphorus atom.* What we need to know are the *properties of a sulfur atom in a molecule,* such as SF_6 or PF_5. This is an exceedingly difficult problem and cannot be dealt with in detail here. However, we have seen how it is possible to calculate such properties as electronegativity on isolated atoms as charge is added or withdrawn (see Chapter 5) and how this *might approximate* such properties in a molecular environment.

It is apparent from the preceding discussions that participation of d orbitals, if it occurs at all, is found only in the nonmetals when in high oxidation states with electronegative substituents. The partial charge induced on the central P or S atom will be large merely from the electronegativity of the fluorine (as in PF_5, SF_6) or oxygen (as in OPX_3, O_2SX_2) irrespective of any bonding model (such as Pauling's or the three-center bond) invoked.

We have seen in Chapter 2 that increasing effective nuclear charge makes the energy levels of an atom approach more closely the degenerate levels of the hydrogen atom. We might expect, in general, that increasing the effective nuclear charge on the central atom as a result of inductive effects would result in the lowering of the d orbitals more than the corresponding s and p orbitals since the former are initially shielded more and hence will be more sensitive to changes in electron density. The promotion energy would thus be lowered. A second effect of large partial charges on the central atom will be a shrinking of the large, diffuse d orbitals into smaller, more compact orbitals that will be more effective in overlapping neighboring atomic orbitals. For example, sample calculations indicate that in SF_6 the d orbitals have been contracted to an extent that the radius of maximum probability is only 130 pm compared with the large values of 300–400 pm in the free sulfur atom.

Experimental Evidence for d Orbital Contraction and Participation

One of the most remarkable molecules is thiazyl trifluoride, NSF_3 (Fig. 10.7). This compound is very stable. It does not react with ammonia at room temperature, with hydrogen chloride even when heated, or with metallic sodium at temperatures below 400 °C. The S—N bond, 141.6 pm, is the shortest known between these two elements. The FSF bond angles of 94° are compatible with approximate sp^3 bonding and the presence of an sp^3 hybrid σ bond and two p-d π bonds between the sulfur and the nitrogen. The contraction of the d orbitals by the inductive effect of the fluorine atoms presumably permits effective overlap and π-bond formation. The alternative explanation would require a double dative bond from the sulfur atom, extremely unlikely in view of the positive character of the sulfur atom.
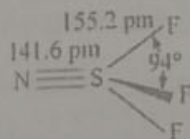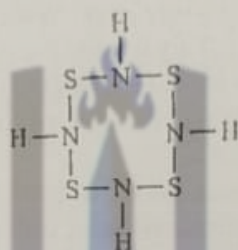
155.2 pm F
141.6 pm 94°
N≡S F
F

Fig. 10.7 Molecular structure of thiazyl trifluoride. NSF_3.

The bond length is consistent with a triple bond. Bond lengths of 174 pm for single S—N bonds (in NH_2SO_3H) and 154 pm for double S=N bonds (in $N_4S_4F_4$) are consistent with a bond order of 2.7 in thiazyl trifluoride. This value is also in agreement with an estimate based upon the force constant. The relative bond lengths of S—N, S=N and S≡N bonds are thus 1.00:0.88:0.81 compared with similar shortenings of 1.00:0.87:0.78 for corresponding C—N, C=N, and C≡N bonds.

Two other molecules indicating the influence of fluorine substitution on d orbital participation are $S_4N_4H_4$ and $N_4S_4F_4$ (see Chapter 11). Tetrasulfur tetraimide is isoelectronic with the S_8, molecule and so the structure

$$
\begin{array}{ccccc}
 & & H & & \\
 & & | & & \\
 & S & —N— & S & \\
 & | & & | & \\
H—N & & & & N—H \\
 & | & & | & \\
 & S & —N— & S & \\
 & & | & & \\
 & & H & &
\end{array}
$$

and corresponding crown conformation appear quite reasonable. The fluoride, however, has an isomeric structure with substitution on the sulfur atoms:

$$
\begin{array}{ccccc}
F—S=N—S—F \\
| \quad\quad || \\
N \quad\quad N \\
|| \quad\quad | \\
F—S—N=S—F
\end{array}
$$
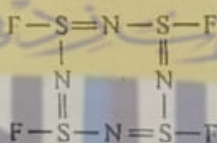
Double bonding in this molecule is clearly shown by the alternation in S—N bond lengths in the ring (see Fig. 11.18b). Now both the above electronic structure for $S_4N_4F_4$ and that for $S_4N_4H_4$ are reasonable but raise the question: Why doesn't tetrasulfur tetraimide isomerize from the N-substituted form to the S-substituted form isoelectronic with the fluoride:

$$
\begin{array}{ccccc}
H—S=N—S—H \\
| \quad\quad || \\
N \quad\quad N \\
|| \quad\quad | \\
H—S—N=S—H
\end{array}
$$
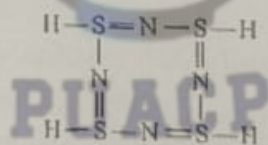
retaining the same number of σ bonds and gaining four π bonds? Apparently the reason the isomerism does not take place is that although π bonding is feasible in the presence of the electronegative fluorine atoms, it is so weak with electropositive hydrogen substituents that it cannot compensate for the weakening of the σ bonding as the hydrogen atom shifts from the more electronegative nitrogen atom to the less electronegative sulfur atom.

Presumably substitution by halogens in the phosphazene series results in contracted d orbitals and more efficient π bonding in the ring (see Chapter 11). Unsymmetrical substitution may allow the normally planar ring to bend. A good example of this is found in 1, 1-diphenyl-3,3,5,5-tetrafluorotriphosphatriazene:

$$
\begin{array}{ccccc}
 & Ph \quad Ph & \\
 & \diagdown \; \diagup & \\
 & P & \\
 & \diagup \quad \diagdown & \\
 N & & N \\
 || & & | \\
F—P & & P—F \\
 \diagup \quad \diagdown & & \diagup \\
F & N & F
\end{array}
$$
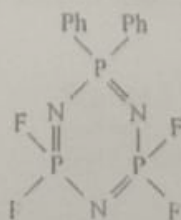
The three nitrogen atoms and the fluoro-substituted phosphorus atoms are coplanar (within 2.5 pm), but the phenyl-substituted phosphorus atom lies 20.5 pm above this plane. The explanation offered is that the more electropositive phenyl groups cause an expansion of the phosphorus d orbitals, less efficient overlap with the p orbitals of the nitrogen atom, and a weakening of the π system at that point. This allows[25] the ring to deform and the Ph_2P moiety to bend out of the plane.

Further examples of the jeopardy involved in casually dismissing d orbitals participation are the findings of Haddon and coworkers[26] that d-orbital participation is especially important in S_4F_4, which is nonplanar, and also that it accounts for about one-half of the delocalization energy in the one-dimensional conductor $(SN)_x$. In the latter case, the low electronegativity of the d orbitals (see Chapter 5) increases the ionicity of the S—N bond and stabilizes the structure.
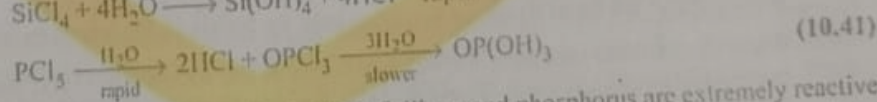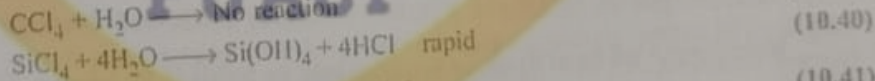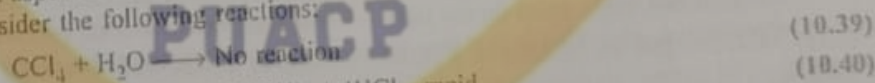
Finally, it will be recalled that the existence of strong P=O bonds in OPF_3 is consistent with enhanced back donation of electron density from the oxygen atom to the phosphorus atom bearing a positive partial charge from the four σ bonds to electronegative atoms. In light of the above discussion of the contraction of phosphorus and sulfur d orbitals when bearing a positive charge, better overlap may be added to the previous discussion as a second factor stabilizing this molecule.

The question of d orbital participation in nonmetals is still an open controversy. In the case of σ-bonded species such as SF_6 the question is not of too much importance since all of the models predict an octahedral molecule with very polar bonds. Participation in π bonding is of considerably more interest, however. Inorganic chemists of a more theoretical bent tend to be somewhat skeptical, feeling that the arguments regarding promotion energies and poor overlap have not been adequately solved. On the other hand, chemists interested in synthesis and characterization tend to favor the use of d orbitals in describing these compounds, pointing to the great heuristic value that has been provided by such descriptions in the past and arguing that until rigorous and complete calculations on these molecules show the absence of significant d orbital participation it is too soon to abandon a useful model.

Reactivity and d Orbital Participation

It has been pointed out 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 relationship 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.

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

$$CCl_4 + H_2O \longrightarrow \text{No reaction} \tag{10.39}$$

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl \quad \text{rapid} \tag{10.40}$$

$$PCl_5 \xrightarrow[\text{rapid}]{H_2O} 2HCl + OPCl_3 \xrightarrow[\text{slower}]{3H_2O} OP(OH)_3 \tag{10.41}$$

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 which readily react with water:

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25 Note that this explanation does not state that the presence of the weakening of the π bonding causes the ring bending but *allows* it, perhaps resulting from crystal packing forces.
26 Haddon, R. C.; Wasserman, S. R.; Wudl F.; Williams, G. R. J. J. Am. Chem. Soc. 1980, 102, 6687 6693.

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$$RCCl + H_2O \longrightarrow R-\overset{\overset{O}{\parallel}}{\underset{\underset{\underset{H}{\diagup}\quad\overset{}{\diagdown}H}{O^+}}{C}}-Cl \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-OH + HCl \tag{10.42}$$
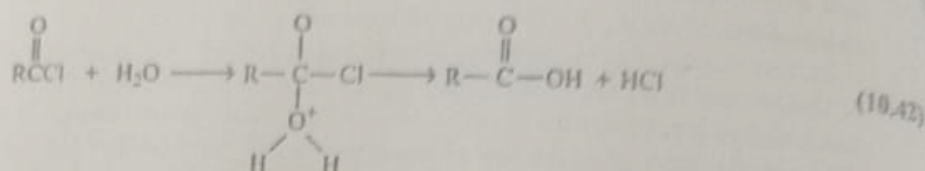
The unsaturation of the carbonyl group provides the possibility of the carbon expanding its coordination shell from 3 to 4, thereby lowering the activation energy. Carbon tetrahalide cannot follow a similar path, but the halides of silicon and phosphorus can employ $3d$ orbitals to expand their octets:

$$\text{(structure)} + H_2O \longrightarrow \text{(structure)} \longrightarrow OPCl_3 + 2HCl, \text{ etc.} \tag{10.43}$$
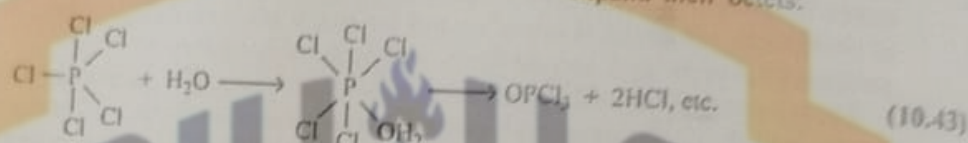
This enhanced reactivity of compounds of silicon and phosphorus is typical of all of the heavier nonmetals in contrast to the elements of the second row.

The simplest reaction path for nucleophilic displacement may be illustrated by the solvolysis of a chlorodialkylphosphine oxide:

$$CH_3O^- + \text{(structure)} \longrightarrow \left[\text{(structure)} \right] \longrightarrow CH_3O-CH_3O-\text{(structure)}-R' + Cl^- \tag{10.44}$$

In contrast to equation 10.42, the increased stability of the five-coordinate intermediate in Equation 10.44 may be attributed to the presence of d-orbitals in the heavier elements.
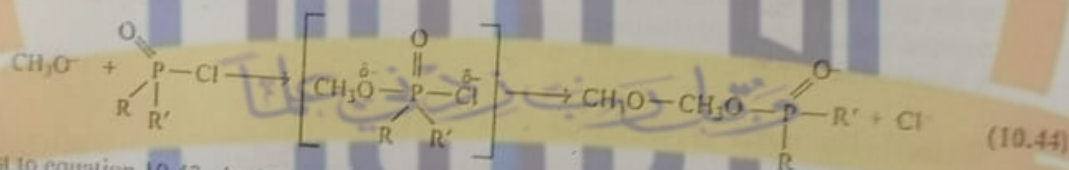
Periodic Anomalies of the Nonmetals and Posttransition Metals

It is generally assumed that the properties of the various families of the periodic chart change smoothly from less metallic (or more electronegative) at the top of the family to more metallic (or less electronegative) at the bottom of the family. Certainly for the extremes of the chart—the alkali metals on the left and the halogens and noble gases on the right—this is true; the ionization potentials, for example, vary in a rather monotonous way. This is not true for certain central parts of the chart, however.

Reluctance of Fourth-Row Nonmetals to Exhibit Maximum Valence

There is a definite tendency for the nonmetals of the fourth row—As, Se, and Br—to be unstable in their maximum oxidation state. For example, the synthesis of arsenic pentachloride eluded chemists until comparatively recently,[27] although both PCl_5 and $SbCl_5$ are stable. The only stable arsenic pentahalide is AsF_5; $AsCl_5$ decomposes at $-50\,°C$, and $AsBr_5$ and $AsCl_5$ are still unknown.

In Group VIA (16) the same phenomenon is encountered. Selenium trioxide is thermodynamically unstable relative to sulfur trioxide and tellurium trioxide. The enthalpies of formation of SF_6, SeF_6, and TeF_6 are -1210, -1117, and -1320 kJ mol^{-1}, respectively. This indicates comparable bond energies for S—F and Te—F bonds (317 and 330 kJ mol^{-1}, respectively), which are more stable than Se—F bonds (285 kJ mol^{-1})

The best known exceptions to the general reluctance of bromine to accept a +7 oxidation state are perbromic acid and the perbromate ion, which were unknown prior to 1968 (see Chapter 12). Their subsequent synthesis

[27] Seppelt, K. Z. Anorg. Chem. 1977, 434, 5.

has made their "nonexistence" somewhat less crucial as a topic of immediate concern to inorganic chemists, but bromine certainly continues the trend started by arsenic and selenium. Thus the perbromate ion is a stronger oxidizing agent than either perchlorate or periodate.
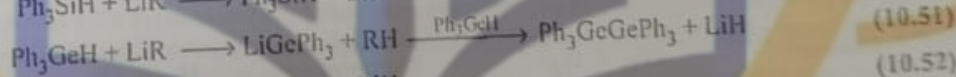
Anomalies of Groups IIIA (13) and IVA (14)

Before seeking an explanation of the reluctance of As, Se, and Br to exhibit maximum oxidation states, a related phenomenon will be explored. This involves a tendency for germanium to resemble carbon more than silicon. Some examples are:

1. *Reduction of halides (X) with zinc and hydrochloric acid.* Germanium resembles carbon and tin resembles silicon:

$$\ce{>C-X ->[Zn][HCl] >C-H} \tag{10.45}$$

$$\ce{>Si-X ->[Zn][HCl] No >Si-H} \tag{10.46}$$

$$\ce{>Ge-X ->[Zn][HCl] >Ge-H} \tag{10.47}$$

$$\ce{>Sn-X ->[Zn][HCl] No >Sn-H} \tag{10.48}$$

2. *Hydrolysis of the tetrahydrides.* Silane hydrolyzes in the presence of catalytic amounts of hydroxide. In contrast, methane, germane, and stannane do not hydrolyze even in the presence of large amounts of hydroxide ion.

3. *Reaction of organolithium compounds with* $(C_6H_5)_3MH$. Triphenylmethane and triphenylgermane differ in their reaction with organolithium compounds from triphenylsilane and triphenylstannane:

$$Ph_3CH + LiR \longrightarrow LiCPh_3 + RH \tag{10.49}$$

$$Ph_3SiH + LiR \longrightarrow Ph_3SiR + LiH \tag{10.50}$$

$$Ph_3GeH + LiR \longrightarrow LiGePh_3 + RH \xrightarrow{Ph_3GeH} Ph_3GeGePh_3 + LiH \tag{10.51}$$

$$Ph_3SnH + LiR \longrightarrow Ph_3SnR + LiH \tag{10.52}$$

4. *Alternation in enthalpies of formation.* There is a tendency for the enthalpies of formation of compounds of the Group IVA (14) elements to alternate from C–Si–Ge–Sn–Pb. Although closely related to the previous phenomena, this variation is also related to the "inert pair effect" and will be discussed further below.

The elements of Group IIIA (13) show similar properties, although, in general, the differences are not so striking as for Group IVA (14). It may be noted that the covalent radius of gallium appears to be slightly smaller than that of aluminum in contrast to what might have been expected. The first ionization energies of the two elements are surprisingly close (578 and 579 kJ mol^{-1}), and if the sum of the first three ionization energies is taken, there is an alternation in the series: B – 6887, Al – 5139, Ga – 5521, In – 5084, Tl – 5438 kJ mol^{-1}.

The "Inert Pair Effect"

Among the heavier posttransition metals there is a definite reluctance to exhibit the highest possible oxidation state. Thus in Group IVA (14), tin has a stable +2 oxidation state in addition to +4, and for lead the +2 oxidation state is far more important. Other examples are stable Tl$^+$ (Group IIIA, 13) and Bi^{3+} (Group VA, 15).

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These oxidation states correspond to the loss of the np electrons and the retention of the ns electrons as an "inert pair".[28]

It can readily be shown that there is no exceptional stability (in an absolute sense) of the s electrons in the heavier elements. Table 10.3 lists the ionization energies of the valence shell s electrons of the elements of Groups IIIA (13) and IVA (14). Although the 6s electrons are stabilized to the extent of 300 kJ mol^{-1} (3 eV) relative to the 5s electrons, this cannot be the only source of the inert pair effect since the 4s electrons of Ga and Ge have even greater ionization energies and these elements do not show the effect—the lower valence Ga(I) and Ge(II) compounds are obtained only with difficulty.

The pragmatic criterion of the presence or absence of an inert pair effect can be taken as the tendency (or lack thereof) for the following reaction to proceed to the right:

$$MX_n \longrightarrow MX_{n-2} + X_2 \qquad (10.53)$$
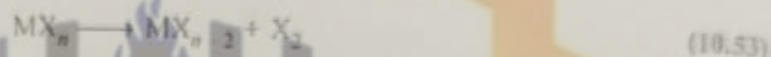
We might then inquire as to the systematic variation in thermodynamic stability of the higher and lower halides of these elements. There seem to be two general effects operating. The combination of the two effects gives irregular changes in covalent bond energies (see Table 10.4). The simplest is the tendency for weaker covalent bond formation by larger atoms (see Chapter 8). The second is the "anomalous" properties of those elements that follow the first filling of a given type of orbital $(s, p, d, f . . .)$.[29] All of these elements exhibit a lower tendency to form stable compounds than do their lighter and heavier congeners. Both sodium and magnesium form less stable compounds than would be expected, when compared to lithium and beryllium, or potassium and calcium.[30] These elements are those that follow immediately after the first filling of a set of p orbitals (Ne), and the same effects of incomplete shielding (though less pronounced to be sure) presumably are operating here as well as in the postlanthanide and postscandide elements. This principle has also been used to predict some of the chemical properties of the superheavy transactinide elements.

Table 10.3   Ionization energies of s electrons in kJ mol^{-1} (eV)

Element	$IE_2 + IE_3$	Element	$IE_3 + IE_4$
B	6,087 (63.1)	C	10,843 (112.4)
Al	4,561 (47.3)	Si	7,587 (78.6)
Ga	4,942 (51.2)	Ge	7,712 (79.9)
In	4,526 (46.9)	Sn	6,873 (71.2)
Tl	4,849 (50.3)	Pb	6,165 (63.9)

Table 10.4   Bond energies of some group IVA (14) halides in kJ mol^{-1} (k cal mol^{-1})

Element	MF_2	MF_4	MCl_2	MCl_4	MBr_2	MBr_4	MI_2	MI_4
Si	—	565 (135)	—	381 (91)	—	310 (74)	—	234 (55.9)
Ge	481 (115)	452 (108)	385 (92.0)	349 (83.4)	326 (77.8)	276 (66.0)	264 (63.1)	212 (50.6)
Sn	481 (115)	414 (98.9)	386 (92.3)	323 (77.2)	329 (78.7)	273 (65.2)	262 (62.5)	205 (49.0)
Pb	394 (94.2)	33 (79.1)	304 (72.6)	243 (58.1)	260 (62.2)	201 (48.0)	205 (49.0)	142 (33.9)

---

[28] This is also related to the fact that "$R_2Sn=SnR_2$" compounds may exist as R_2Sn units in solution. Closely related, but not identical, is the fact that an unoxidized s electron pair may or may not be stereochemically active. See discussions in Chapters 6 and 12.
[29] Huheey, J. E.; Huheey, C. L. J. Chem. Educ. 1972, 49, 227.
[30] Evans, R. S.; Huheey, J. E. J. Inorg. Nucl. Chem. 1970, 32, 777.

For the lighter elements these effects can readily be formulated in terms of ordinary shielding effects as discussed in Chapter 2. For heavier elements, however, the theory of relativity must be invoked.

Relativistic Effects

Normally the theoretical basis of chemistry is the nonrelativistic Schrödinger equation. To this are added the postulate of electron spin and ideas related to it such as the Pauli exclusion principle. Although the latter are thus seemingly ad hoc "add ons" to make the theory work, most of the theoretical chemistry has been done on this basis. The corresponding relativistic approach yields the Dirac equation.[31] This gives four quantum numbers directly, although only the principal quantum number n is the same in both treatments. The relativistic treatment results in a number of novel effects, both descriptive,[32] and theoretical[33] most of which can usually be neglected with little loss of accuracy and a great gain in convenience. There are two exceptions to this generalization however. One is spin–orbit, or jj, coupling (see Chapter 14 and Appendix C). The second is that neglect of relativistic effects becomes increasingly serious as the atomic number increases. The s (and to a slightly lesser extent, p) electrons will accelerate greatly as they approach the nucleus, and their speed relative to the fixed speed of light cannot be ignored. It has been estimated that for mercury (Z = 80) the speed of a $1s$ electron is over half that of light.[34] This results in an approximately 20% increase in electronic mass and an approximately 20% decrease in orbital size.[35] In the simplest case we can say that s and p orbitals will contract, and that d and f orbitals will expand somewhat. The seeming paradox that the d and f orbitals *expand* instead of contract is an *indirect effect*. Direct relativistic effects on d and f orbitals are small because these orbitals do not have electron density near the nucleus. However, the *increased shielding* of d and f orbitals by relativistically contracted s and p orbitals tends to cancel the effect of increased Z.[36] So the s and p electrons are moved closer to the nucleus, their energy is lowered (made more negative), and they are stabilized. The d and f orbitals are raised in energy (destabilized) and expand. Since the outermost orbitals are the ns and np rather than the $(n-1)d$ or $(n-2)f$, each atom as a whole contracts.[37]

The relativistic effect goes approximately as Z^2, and this is the reason for its importance in the heavier elements. In terms of energy and size, it starts to become important in the vicinity of Z = 60–70, contributing perhaps an additional 10% to the nonrelativistic lanthanide contraction (see Chapter 13).[38] As we have seen, this results in an almost exact cancellation of the expected increase in size with increase in n from zirconium to hafnium.

While the contraction resulting from the poor shielding of $4f$ electrons ceases at hafnium, the relativistic effect continues across the sixth row of the periodic table. It is largely responsible for the stabilization of

31 Dirac, P. A. M. *Proc. R. Soc. London, Ser. A.* 1928, *A117*, 610, 1928. *A118*, 351.

32 Some of these, such as the facts that gold metal has its familiar color and that mercury metal is a liquid, fall outside the scope of this text. See Pyykkö, P., Desclaux, J.-P. *Acc. Chem. Res.* 1979, *12*, 276–281. Others will be discussed below.

33 Some of these are: Although the quantum number l still determines orbital type (s, p, d, f ...), it no longer determines orbital shape. All orbitals of given value of n and l no longer have the same energies. Orbital shape is determined by the angular momentum quantum numbers j and the magnetic quantum number m. The shapes of orbitals are not the familiar ones given by the Schrodinge equation, but seemingly "misshapen" nodeless analogues. See McKelvey, D. R. *J. Chem. Educ.* 1983, *60*, 112–116; Powell, R. H. *Ibid.* 1968, *45*, 558.

34 The relativistic mass of an electron (m) increases with its velocity (u) according to the relation, $m = m_o [1 - (u/c)^2]^{-1/2}$; where m_o is the rest mass and c is the speed of light.

35 This is most readily seen from the inverse relationship between Bohr radius and mass ($a_o = 4\pi\epsilon h^2/mZe^2$).

36 Pitzer, K. S. *Acc. Chem. Res.* 1979, *72*, 271–276. See also Footnote 34.

37 Note from Figure 2.4 how the maximum electron density for a $3d$ orbital lies well under those of the $3s$ and $3p$ and, by extension, even more so those of the $4s$ and $4p$ orbitals.

38 For smaller effects in the lighter elements, see Pyykko, P. *Chem. Rev.* 1988, *88*, 563–594.

the 6s orbital and the inert s pair effect shown by the elements Hg–Bi. It also stabilizes one[39] of the 6p orbitals of bismuth allowing the unusual +1 oxidation state in addition to +3 and +5.[40]

"Anomalous" Ionization Energies and Electron Affinities

Many introductory chemistry books give simple rules for remembering the periodic changes of ionization energies and electron affinities. The rules usually follow some modification of "Ionization energies and electron affinities increase as one moves to the right in the periodic chart; they decrease as one moves from the top to bottom." These generalizations, as well as the shielding rules that account for the atomic behavior, were discussed in Chapter 2, along with some of the exceptions. Unfortunately for simplicity, the exceptions are somewhat more numerous than is generally realized. Many of the problems discussed in the preceding sections result from these "exceptions."

The horizontal behavior of atoms follows the general rule with good regularity as might be expected from adding a single proton at a time with expected monotonic changes in properties. We have already seen the exception of the inversion of the ionization potentials of the VA (15) and VIA (16) groups related to the stability associated with half-filled subshells. A similar inversion of electron affinities takes place, for the same reason, between groups IVA (14) and VA (15).

The vertical exceptions to the generalizations are much more widespread: If we count every time that a heavier element has a higher ionization potential or higher electron affinity than its next lighter congener, we find that about one-third of the elements show "electron affinity anomalies"[41] and a somewhat higher fraction of the elements show "ionization energy anomalies." With such a high fraction of exceptions, one wonders why the rules were formulated as they were originally. The answer seems to lie in the lack of data available until recently; most of the good data were for familiar elements, such as the alkali metals and the halogens. For these main-group elements, with the exception of the lower electron affinity of fluorine resulting from electron–electron repulsion (and paralleled by oxygen and nitrogen), the rules work fairly well; however, the poorer shielding d and f electrons upset the simple picture. For the transition metals, higher ionization energies with increasing atomic number in a group are the *rule*, not the exception. As we have seen in the preceding discussion, this carries over somewhat into the posttransition elements, causing some of the problems associated with families IIIA (13) and IVA (14).

The increased ionization energies of the heavier transition metals should not be unexpected by anyone who has had a modicum of laboratory experience with any of these elements. Although none of the coinage metals is very reactive, gold has a well-deserved reputation for being less reactive than copper or silver;[42] iron, cobalt, and nickel rust and corrode, but osmium, iridium, and platinum are noble and unreactive and therefore are used in jewelry; platinum wires are the material of choice for flame tests without contamination; and one generates hydrogen with zinc and simple acids, not with mercury.

Although the increased electron affinity associated with the heavier elements usually manifests itself only indirectly (via electronegativity, etc.), it is directly responsible for the fact that cesium auride, Cs⁺Au⁻, is an

[39] Recall that one of the differences of relativistic orbitals from the nonrelativistic ones that we are accustomed to handling is that the orbitals of a given value of l are not degenerate: The $6p_{1/2}$ orbital lies below the $6p_{3/2}$.

[40] Jorgensen, C. K. *Z. Anorg. Allg. Chem.* 1986, 540/541, 91–105.

[41] The experimental values of atomic electron affinities have been reviewed and plotted as periodic functions. Chen, E. C. M.; Wentworth, W. E. *J. Chem Educ.* 1975, 52, 486.

[42] The legend of *aqua* seems to persist even in the absence of student contact with this powerful elixir. However, admiration for its chemical reactivity is usually misplaced. Thermodynamically, it can be no stronger an oxidizing agent that nitric acid itself. It is the *complexing* ability of the soft chloride ions on the soft Au³⁺ ion that allows Au → AuCl₄⁻ to be effected at $E^0 = -1.00$ V. Rather more astonishing is the fact that similar interaction of very *soft* I ions causes the relatively innocuous tincture of iodine (found in many medicine cabinets) to dissolve metallic gold readily (Nakao, Y. *J. Chem. Soc., Chem. Commun.* 1992, 426–427).

5

ionic salt rather than an alloy. Both the increased ionization energy and increased electron affinity in these elements result from relativistic effects.

Gold exhibits other interesting anomalies. For example some Au(I) compounds with an expected coordination number of two (Chapter 16) and a filled core of $5d^{10}$ electrons, nevertheless show additional Au–Au interactions.[43] In addition to the Au(I)–Au(I) bonds, there are similar interactions between atoms that are (a) congeners of [e.g., Ag(I)][44], (b) isoelectronic with [e.g. Hg(II)][45], or (c) isoelectronic plus an inert pair with [e.g., Tl(I), Pb(II)][46] the gold(I) atom. Some examples are listed in Table 10.5. The number of these bonds is limited, but the subject is still a very new one.

The general tendency for atoms (including other gold atoms) to exhibit greater than expected valences toward gold atoms is often termed *aurophilicity*. This is a useful descriptive name for a bonding behavior that is not completely understood. It appears to result from relativistic effects and the fact that the gold $5d^{10}$ electrons do not act as "good" core electrons but mix with low lying excited states.[47] To rationalize, if not truly explain, one can consider promotion of electrons from the $5d^{10}$ configuration and their involvement in the bonding.
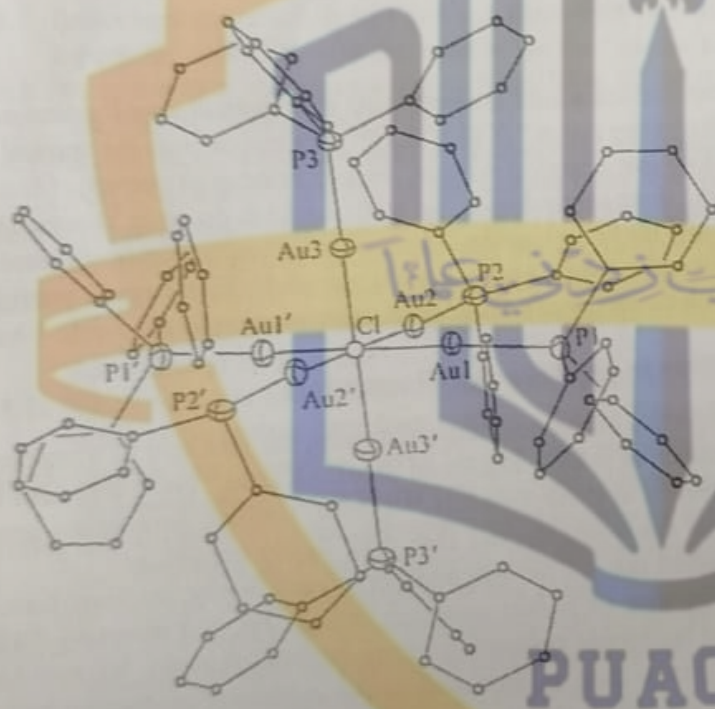

Fig. 10.8   Structure of the "hedgehog" dication, $[(Ph_3PAu)_6C]^{2+}$. The inferred Au—Au bonds are not shown. [From Scherbaum, F.; Grohmann, A.; Huber, B.; Kruger, C.; Schmidbaur, H. *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 1544–1546. Reproduced with permission.]

43 (a) Khan, N.I.; Wang, S.; Fackler, J. P., Jr. *Inorg Chem* 1989, 28, 3579–3588. (b) Schmidbaur, H.; Graf, W.; Muller, G. *Angew. Chem. Int. Ed. Engl.* 1988, 27, 417–419. (c) Balch, A.L.; Fung, E.Y.; Olmstead, M.M. *J. Am. Chem. Soc.* 1990, 112, 5181–5186. (d) Schmidbaur, H.; Weidenhiller, G.; Steigelmann, O.; Muller, G. *Chem. Ber.* 1990, 123, 285–287.
44 Wang, S.; Fackler, J.P., Jr.; Carlson, T.F. *Organometallics* 1990, 9, 1973–1975.
45 Wang, S.; Fackler, J.P., Jr. *Organometallics*, 1990, 9, 111–115; *Acta Crystallogr.* 1990, C46, 225–2255.
46 Wang, S.; Garzon, G.; King, C.; Wang, J-C.; Fackler, J. P., Jr. *Inorg. Chem.* 1989, 28, 4623–4629.
47 Jansen, M. *Angew Chem. Int. Ed. Engl.* 1987, 26, 1098–1110; Rosch, N.; Gorling, A.; Ellis, D. E.; Schmidbaur, H. *Ibid* 1989, 28, 1357–1359 Pyykko, P.; Zhao, Y. *Ibid* 1991, 30, 604–605.
48 Scherbaum, F.; Grohmann, A.; Huber, B.; Kruger C.; Schmidbaur, H. *Ibid* 1989, 28, 463–465. Steigelmann, O.; Bissinger, P.; Schmidbaur, H. *Angew Chem Int. Ed. Engl.* 1988, 27, 1544–1546. Scherbaum, F.; Grohmann, A.; Muller, G.; Schmidbaur, H. *Ibid* 1990, 29, 1399–1400.

Table 10.5 Some further examples of Group IB (11) metal-metal interactions.

Compound	M_1, M_2	M_1—M_2 (pm)
$[AgCH_2P(S)Ph_2]_2$	Ag^I, Ag^I	299.0^a
$Au[CH_2P(S)Ph_2]_2Hg$	Au^I, Hg^{II}	308.5^b
$[ClAuP(S)Ph_2CH_3]_2Hg$	Au^I, Hg^{II}	$331.0, 336.1^{b, c}$
$Au[CH_2P(S)PH_2]_2Tl$	Au^I, Tl^{II}	295.9^d
$[Au(CH_2P(S)Ph_2)_2]_2Pb$	Au^I, Pb^{II}	$289.6, 296.3^{c, d}$

^{a} See footnote 44.
^{b} See footnote 45.
^{c} There are two Au—M_2 interactions per molecule.
^{d} See footnote 46.

Schmidbaur's groups[48] has synthesized some gold(I) compounds with unusual coordination numbers for small nonmetals. For example, the "hedgehog cation," $[C(AuPR_3)_6]^{2+}$, has carbon with the unusual covalency of six (Fig. 10.8). While carbon has no low energy d orbitals, there is nothing to prevent it from forming $a_{1g}(2s)$ and $t_{1u}(2p)$ MOs and forming three-center bonds. So why should it do so in this compound and never in "organic chemistry"? Ordinarily the better overlap of hybridized sp^n carbon orbitals ensures carbon's tetracovalency. Perhaps the possibility of a dozen Au(I) — Au(I) aurophilic bonds could provide another $300 - 400$ kJ mol^{-1}, commensurate with the energy of a C—C bond, compensating for weaker C—Au bonding.

Alternation of Electronegativities In the Heavier Nonmetals

We have seen above the unusual properties of the nonmetals following the first row of transition metals. This is usually described as "a reluctance to exhibit maximum oxidation state," but it may also be stated in terms of an *increased electronegativity* in these elements.[49] Indeed, gallium, germanium, arsenic and perhaps selenium seem to have higher electronegativities than their lighter congeners.

In the same way, it has been suggested that the heavier member of each family, thallium, lead, perhaps bismuth, has a greater electronegativity than its lighter congener, indium, tin, and antimony. 'When first proposed the explanation rested on the lanthanide contraction acting on these elements. We now know that relativistic effects for these elements are at least as important as the lanthanide contraction and perhaps a better way of staling the premise is that all of the elements from about platinum on (there is no sharp demarcation, of course) are more electronegative than would otherwise be expected.

Conclusion

The periodic chart is the inorganic chemist's single most powerful weapon when faced with the problem of relating the physical and chemical properties of over 100 elements. In addition to knowing the general trends painted in broad brush strokes by the simple rules, the adept chemist should know something of the "fine structure" that is at the heart of making inorganic chemistry diverse and fascinating.

Problems

10.1 Carbon tetrachloride is inert towards water but boron trichloride hydrolyzes in moist air. Suggest a reason.

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[49] Indeed, in many ways, these statements are equivalent.

10.2 Below are some conclusions that an average general chemistry student (certainly not you!) might have after reading about the periodic table in a general chemistry textbook written by average authors (not us!). Please rewrite each statement to clarify possible misconceptions (if any).

a. Electron affinities increase toward the upper right of the periodic table.

b. Ionization energies decrease toward the bottom of the table.

c. Atomic radii increase toward the bottom of the table.

d. Atomic radii decrease toward the right of the table.

e. Electronegativity decreases toward the left and toward the bottom of the table.

10.3 Gallium dichloride, $GaCl_2$, is a diamagnetic compound that conducts electricity when fused. Suggest a structure.

10.4 The small F—S—F bond angles in $F_3S \equiv N$ can be rationalized by

a. Bent's rule

b. Gillespie-type VSEPR rules

c. Bent bonds

Discuss each and explain their usefulness (or lack thereof) in the present case.

10.5 Either look up the article by Chen and Wentworth[a1] or plot the electron affinities from Table 2.5 onto a periodic chart. Discuss the reasons for the "exceptions" that you observe.

10.6 Write the first ionization energies from Table 2.3 on a period chart. Discuss the reasons for the "exceptions" that you observe.

10.7 "R_2Ge, R_2Sn, and R_2Pb exist as diamagnetic monomers in solution." What experiments must an inorganic chemist perform to substantiate these statements.[53]

10.8 The compound R_2Sn_2 shown on page 272 is diamagnetic. Draw out the most reasonable electronic structure for it, and compare it with the geometric structure. Discuss.

10.9 Lithium carbonate is often administered orally in the treatment of mania or depression both. From what you have learned of the diagonal relationships in the periodic chart predictone possible unpleasant side effect of lithium therapy.

10.10 Zinc is a much more reactive metal than cadmium, (as expected from the discussion on) yet both are used to protect iron from rusting. How is this possible?

10.11 Sodium hypophosphite, NaH_2PO_2, has been suggested as a replacement of sodium nitrite, $NaNO_2$, as a meat preservative to prevent botulism. Draw the structure of each anion.

10.12 The simplest relationship between electronegativity and dipole moments is a linear one: The greater the difference in electronegativity, the greater the dipole. How can you reconcile this with the N—O and P—O dipoles cited in this chapter?

10.13 The P_4 molecule in white phosphorus has extremely strained bonds: The bond angles in the T_d molecule are only 60°. Therefore the bonds are weak, only 201 kJ mol^{-1} for each one. The total bond energy of two moles of P_2 (962 kJ, Appendix E) is 244 kJ less than that of one mole of P_4 (1206 kJ, Appendix E). In contrast, the total bond energy of two moles of N_2 has been calculated[50] to be 777 kJ greater than that of one mole of N_4 (a hypothetical tetrahedral molecule isostructural with P_4).

a. Explain the disparity of bond energies of these isoelectronic and isostructural molecules.

b. If you could manufacture N_4 and keep it as a metastable material, can you think of any uses for it?

10.14 Footnote 49 suggests that a reluctance to exhibit maximum oxidation state may be equivalent to an increased electronegativity in the posttransition elements. Discuss.

10.15 How many parallels can you find between $[Fe_6(CO)_{16}C]^{2-}$ (Fig. 18.21b) and $[(AuPPh_3)_6C]^{2-}$ (Figs. 18.21c and 10.8) that contribute to the unusual hexacoordinate carbon atom?

[50] Lee, T. J.; Rice. J. E. J. Chem. Phys. 1991, 94, 1215–1221.