16.20 Phospham, \((\text{PN}_2\text{H})_n\), can be obtained by the reaction of red phosphorus with ammonia. Write a balanced equation for its production from these two reagents and draw a possible structure for this cross-linked polymer.

16.21 Monophosphazenes, \(R_3P=NR'\), are well known and may be prepared from the reaction of \(R_3\text{PCI}_2\) and \(R'\text{NH}_2\). Write a balanced equation for this reaction.

16.22 As discussed in the chapter, trimeric phosphazenes are usually planar but can be forced out of this geometry. In contrast, benzene derivatives are strictly planar. Discuss the reasons for the greater flexibility of the phosphazenes.

16.23 Draw all of the possible isomers, excluding those that are \(N=\text{N}\) bonded, of \(S_3\text{NH}_2\).

16.24 The classical argument concerning the equivalence of the positions on the benzene ring is based on the existence of three (ortho, meta, para) isomers of xylene (dimethylnaphthalene). How many isomers are there of dimethylboraazine?

16.25 Complexes \((\text{OC})_3\text{Fe}(\text{P}_2\text{O}_6)\) and \((\text{OC})_3\text{Fe}(\text{P}_2\text{O}_6)_2\) form from the reaction of \(\text{Fe}(	ext{CO})_5\) and \(\text{P}_2\text{O}_6\). Suggest structures for these complexes. Would you expect similar reactions with \(\text{P}_2\text{O}_{10}\)? (See Walker, M. L.; Mills, J. L. Inorg. Chem. 1977, 16, 303.)

16.26 Phosphorus pentoxide is an excellent dehydrating agent. For example, it can be used to remove water from nitric acid. Write a chemical equation for this reaction.

16.27 Suggest a structure for \(\text{P}_4\text{O}_{10}\), synthesized from \(\text{P}_4\text{O}_{10}\) and \(\text{P}_4\text{S}_{10}\).

16.28 Ethane reacts with oxygen to give carbon dioxide and water. Diborane reacts with oxygen to give boron(III) oxide and water. Write balanced equations for these two reactions. Look up heats of formation for the reactants and products of these reactions and calculate the heats of reactions. Considerable work was expended in evaluating boranes as high-energy fuels in the 1950s. Compare ethane and diborane as fuels.

16.29 It has been suggested\(^{175}\) that \(\text{Se}_8^{2+}\) exists in the endo form rather than an exo "crown" form with \(\text{Se}(1)\) flipped down because of reduced lone-pair repulsions between \(\text{Se}(3), \text{Se}(6)\) and \(\text{Se}(7)\). Sketch these two forms of \(\text{Se}_8^{2+}\). Add lone pairs to your drawing and indicate how stabilization occurs in the endo form.

16.30 What structures do you predict for the anions, \(\text{B}_2\text{H}_7^-\) and \(\text{B}_3\text{H}_8^-\)?

16.31 Diborane is widely used in organic chemistry (hydroboration) to convert alkenes into alcohols. Consult an organic book and show reactions for this conversion. What is the advantage of this method?

16.32 Complete the following equations:
   a. \([\text{PNCI}_2]_n + \text{excess Me}_2\text{NH} \rightarrow \)
   b. \(\text{B}_2\text{H}_6 + 2\text{R}_3\text{P} \rightarrow \)
   c. \(\text{B}_2\text{H}_6 + 2\text{NH}_3 \rightarrow \)
   d. \(\text{P}_2\text{Cl}_4 + \text{excess Cl}_2 \rightarrow \)

16.33 Assuming that the external \(\sigma\)–\(\sigma\) angle in \(\text{B}_2\text{H}_6\) accurately reflects the interorbital angle:
   a. Calculate the \(s\) and \(p\) character in these bonds.
   b. Calculate the \(s\) and \(p\) character remaining for the bridging orbitals.
   c. Compare the value from (b) with the experimental internal angles.

16.34 Use Wade’s rules to predict the structures of the following:
   a. \(\text{B}_4\text{H}_9(\text{CO})_2\text{Fe(CO)}_3\)
   b. \(\text{C}_2\text{B}_3\text{H}_6\text{Pt(PEt)}_2\)
   c. \(\text{C}_2\text{B}_3\text{H}_6\text{Me}_2\text{Fe(CO)}_3\)
   d. \(\text{CB}_9\text{H}_{10}\text{AsCo(η}^3-\text{C}_5\text{H}_4\))

16.35 Use the polyhedral skeletal electron-counting rules and show that they are consistent with the nido 11-vertex structure shown below.\(^{176}\)

\[\text{Diagram of a polyhedral structure} \]

16.36 What is the maximum bond order you would predict for neutral W\(_2\) (no ligands)?

16.37 What bond angle would you expect for M—O—R in an alkoxide complex? How might this bond angle change as \(\pi\) donation from the \(p\) orbitals of oxygen increases?


16.39 Note that the product of Eq. 16.125 contains Mo-Mo pairs that are doubly bridged by chlorine and Mo-Mo pairs that are not. If this molecule contains alternating single and triple bonds, which bonds are which?

16.40 The structure of \(\text{Ni}_3\text{Cl}_3\text{S}_2\)\((\text{PPh}_3)_4\) is analogous to that of \((\text{p-cymene})\text{Ru}_3\text{S}_2^{2+}\) (Fig. 16.55).\(^{177}\) Determine if Wade’s rules are satisfactory for this molecule.

16.41 Which of the following do you think would be most likely in view of isolobal considerations and Wade’s rules? (See Little, J. L.; Whitesell, M. A.; Kester, J. G.; Folting, K.; Todd, L. J. Inorg. Chem. 1990, 29, 804-808.)

\begin{align*}
X & \quad Y \\
\text{a. Bi} & \quad \text{S} \\
\text{b. S} & \quad \text{S} \\
\text{c. P} & \quad \text{CH} \\
\text{d. P} & \quad \text{Bi}
\end{align*}

16.42 In addition to the phosphazenes discussed in this chapter, a large group of heterocyclic compounds known as phosphazanes has been characterized. These contain \(P—N\) single bonds and may contain phosphorus either in the +3 or +5 oxidation states. Draw structures of \([\text{Cl}_3\text{PNMe}_2]\) and \([\text{Cl(CO)PNMe}_2]\). Phosphorus(III) tri- and tetraphosphazanes have been stabilized by placing \(\sigma\)-phenylene groups between adjacent nitrogen atoms. Give one example of each and draw its structure. (See Barendt, J. M.; Haltiwanger, R. C.; Squier, C. A.; Norman, A. D. Inorg. Chem. 1991, 30, 2342-2349.)

16.43 Draw structures for the four possible isomers of \(\text{closo-Et}_2\text{C}_3\text{B}_3\text{H}_4\). (See Beck, J. S.; Sneddon, L. G. Inorg. Chem. 1990, 29, 295-302).

\(^{176}\) Swisher, R. G.; Sinn, E.; Butcher, R.J.; Grimes, R. N. Organometallics 1985, 4, 882-890.

16.29 The flip of $S_1$ from its position in the crown conformation to the 1-endo conformation relieves LP-LP interactions with the adjacent sulfur atoms (see Sketch 16.1). A flip of $S_3$ to an endo position would also relieve some LP-LP interactions, but it would incur new ones with $S_1$. Thus only one sulfur atom at a time may occupy an endo position.

Sketch 16.1 The flip of $S_1$ from the crown conformation to the more stable 1-endo position. The second possible flip of $S_3$ does not occur.

16.30 Both of these anions can be said to possess arachno structures.

![Image](image_url)

\[ [H_3B-H-BH_3]^- \quad [H_2B-BH_2]^- \]


16.31 Hydroboration provides a versatile synthesis of alcohols and ketones from alkenes or alkynes. They react with $\text{B}_2\text{H}_6$ or stabilized $\text{BH}_3$ (thf$\cdot\text{BH}_3$, Me$_2\text{SeBH}_3$) by an anti-Markovnikov, cis addition to give alkylborons:

\[
\text{RHC}=\text{CH}_2 + \text{BH}_3 \rightarrow \text{RHCCH}_2\text{BH}_2 \quad (16.31a)
\]

\[
\text{RHC}=\text{CH}_2 + \text{RHC}=\text{CH}_2 \rightarrow \text{RHCCH}=\text{BH} \quad (16.31b)
\]

\[
(\text{RHCCH}_2)_2\text{BH} + \text{RHC}=\text{CH}_2 \rightarrow (\text{RHCCH}_2)_3\text{B} \quad (16.31c)
\]

The extent to which this reaction proceeds depends upon the steric requirements of the alkene, more substituted ones giving $\text{R}_2\text{BH}$ or $\text{RBH}_3$ as the final product. The trialkylborons are converted to hydrocarbons with acid, to alcohols with hydrogen peroxide, and to ketones with carbon monoxide followed by hydrogen peroxide. When diborane is used, it is generated in situ from the reaction of boron trifluoride and sodium borohydride:

\[
3\text{NaBH}_4 + 4\text{BF}_3 \rightarrow 2\text{B}_2\text{H}_6 + 3\text{NaBF}_4 \quad (16.31d)
\]

16.32 a. $[\text{PCl}_5]_2 + \text{Me}_2\text{NH} \text{(excess)} \rightarrow [\text{PN}(\text{N}(\text{Me})_2)_3 + 6[\text{Me}_2\text{NH}_2]\text{Cl}
\]

b. $\text{B}_2\text{H}_6 + 2\text{R}_3\text{P} \rightarrow 2\text{R}_3\text{PBH}_3$

(16.32b)

c. $\text{B}_2\text{H}_6 + 2\text{NH}_3 \rightarrow [\text{H}_2\text{B}(\text{NH}_3)_2][\text{BH}_4]$

(16.32c)

d. $\text{P}_2\text{Cl}_4 + \text{excess Cl}_2 \rightarrow 2\text{PCl}_3 \rightarrow 2\text{PCl}_5$

(16.32d)
16.33 a. The external bond angle is 122° which yields \( s = 34.6\% \) from Eq. 6.1.

b, c. The sum of s-character for the two terminal orbitals is 69.2%, leaving 30.8% for the two bridging orbitals, or 15.4% s-character in each orbital. This corresponds to a bond angle of 100.5°, larger than the observed bond angle of 97°. The bridging bonds are therefore slightly “bent” inwards, probably to increase the overlap somewhat.

16.34 All are closo structures.

\[
\begin{align*}
\text{B}_2\text{H}_3(\text{CO})_2\text{Fe}(\text{CO})_3 \quad (n = 6): & \quad \text{Fe}(\text{CO})_3 = 2e \\
& \quad 2\text{BCO} = 6e \\
& \quad 3\text{BH} = 6e \\
& \quad 14e \\
2n + 2 = 2 \times 6 + 2 = 14
\end{align*}
\]

\[
\begin{align*}
\text{C}_2\text{B}_2\text{H}_6\text{Pt}(\text{PEt}_3)_2 \quad (n = 7): & \quad \text{Pt}(\text{PEt}_3)_2 = 2e \\
& \quad 4\text{BH} = 8e \\
& \quad 2\text{CH} = 6e \\
& \quad 16e \\
2n + 2 = 2 \times 7 + 2 = 16
\end{align*}
\]

\[
\begin{align*}
\text{C}_2\text{B}_2\text{H}_6\text{Me}_2\text{Fe}(\text{CO})_3 \quad (n = 10): & \quad \text{Fe}(\text{CO})_3 = 2e \\
& \quad 7\text{BH} = 14e \\
& \quad 2\text{CMe} = 6e \\
& \quad 22e \\
2n + 2 = 2 \times 10 + 2 = 22
\end{align*}
\]

\[
\begin{align*}
\text{CB}_9\text{H}_{16}\text{AsCo}(&\eta^5-\text{C}_5\text{H}_5) \quad (n = 12): & \quad \text{Co}(\eta^5-\text{C}_5\text{H}_5) = 2e \\
& \quad \text{As} = 3e \\
& \quad 9\text{BH} = 18e \\
& \quad \text{CH} = 3e \\
& \quad 26e \\
2n + 2 = 2 \times 12 + 2 = 26
\end{align*}
\]

\[
\begin{align*}
(\eta^6-\text{C}_6\text{H}_6)\text{Fe}(\text{Et}_4\text{C}_2\text{B}_6\text{H}_6) \quad (n = 11): & \quad \eta^6-\text{C}_6\text{H}_6)\text{Fe} = 2e \\
& \quad 6\text{BH} = 12e \\
& \quad 4\text{CET} = 12e \\
& \quad 26e \\
2n + 2 = 2 \times 11 + 4 = 26
\end{align*}
\]

16.35 Neutral \( \text{W}_2 \) should be analogous to \( \text{Mo}_2 \) which has been generated from flash photolysis of \( \text{Mo}(\text{CO})_6 \) and has been trapped in inert gas matrices. Spectroscopic studies indicate that the Mo–Mo bond length is shorter than those found in quadruply M–M bonded complexes. A theoretical analysis of the bonding in \( \text{Mo}_2 \) has been reported (Bursten, B. E.; Cotton, F. A.; Hall, M. B. J. Am. Chem. Soc. 1980, 102, 6348). In addition to one sigma, two pi, and one delta bond, found in quadruply M–M bonded complexes, there is one additional sigma and one additional delta bond. All of this gives a \( \sigma^2 \pi^4 \delta^4 \sigma^2 \) configuration, i.e. a sextuple bond. The two additional bonds arise because the ligandless complex need not use any orbitals for metal–ligand bonding. Two delta bonds arise because both the \( d_{\pi\pi} \) and the \( d_{\sigma} \) orbitals of
each metal atom may overlap. One of the sigma bonds is mostly 5s in character and the
other is mostly 4d in character.

16.37 The M–OR multiple bond character varies in transition metal alkoxide complexes. If RO
functions as a one-electron donor, one would expect a M–O–R bond angle near 109.5°.
However, the two filled pi orbitals of oxygen have the right symmetry to donate to metal
centers. If a metal–oxygen double bond is present, an ideal M=O–R of 120° would be
expected. If two metal–oxygen pi bonds were present, a M=O=R bond angle of 180° might
be realized. Typically what is found are M=O–R bond angles between 130-165° suggesting
significant metal–oxygen pi character. The metal–oxygen bond distance is found to
decrease as the M–O–R bond angle increases as expected.

16.38 [Re₂Cl₆]³⁻ has four electron pairs available for Re–Re bonding. This gives a configuration
of σ² π⁴ δ² δ° (see Fig. 16.60 of the text). [Os₂Cl₆]²⁻ has five electron pairs available for
Os–Os bonding. This gives a configuration of σ² π⁴ δ⁰. The dirhenium anion can
contain a delta bond only if the chloro groups are eclipsed. The dioximium anion cannot
have a delta bond because the antibonding orbital is filled, thus leading to a dioximium triple
bond. As delta bonding is not a possibility, the structure would be expected to have a
staggered configuration (D₅h), thereby minimizing the repulsion of the chloro ligands.

16.39 The bridging chlorine atoms require Mo atomic orbitals and so there should be single bonds
beneath bridges and multiple bonds (Mo≡Mo) without.

16.40 [Ru₃(p-cymene)S₂]³⁺ (n = 5):

<table>
<thead>
<tr>
<th></th>
<th>3(p-cymene)Ru</th>
<th>2S</th>
<th>+2 charge</th>
<th>6e</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>8e</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-2e</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12e</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2n + 2 = 2 x 5 + 2 = 12, so a closo structure is expected.

Ni₃Cl₂S₂(PPh₃)₄ (n = 5):

<table>
<thead>
<tr>
<th></th>
<th>1(PPh₃)₂Ni</th>
<th>2(PPh₃)(Cl)Ni</th>
<th>2S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2e</td>
<td>2e</td>
<td>8e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12e</td>
</tr>
</tbody>
</table>

These two isostructural species are also isoelectronic and both obey Wade’s rules. Note that
in the nickel complex, one nickel atom is
bound to two Ph₃P
molecules and each of
the other two is bound
to one Ph₃P molecule
and one chloro group.

16.41 The compound,
1,2-XYB₁₀H₁₀, has a
closo structure and
must obey the 2n + 2
rule (n = 12). That
means that there must

Sketch 16.2 From top to bottom, examples of diphosphazanes, a
triphosphazane, and a tetraphosphazane.
be 26 framework electrons. The ten BH fragments give 20 framework electrons, leaving six electrons to be provided by elements X and Y. A Group 6 element (S) provides 4 framework electrons, while a Group 5 element provides 3 framework electrons (as does CH). Combinations Bi,S and S,S fail because the former provides 7 framework electrons, while the latter provides 8. Combinations P,CH and P,Bi are acceptable combinations because each provide 6 framework electrons.

16.42 Sketch 16.2 illustrates some examples of phosphazanes mentioned in the text.

16.43 There are four isomers of closo-Et₂C₂B₅H₁₁, assuming that the ethyl groups are substituted on the carbon atoms. (Note that if Et-B isomers are included, the number is increased greatly. The structures of these isomers are shown in Sketch 16.3.)