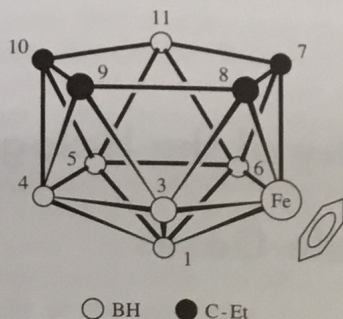


- 16.20** Phospham, $(\text{PN}_2\text{H})_n$, can be obtained by the reaction of red phosphorus with ammonia. Write a balanced equation for its production from these two reagents and draw a possible structure for this cross-linked polymer.
- 16.21** Monophosphazenes, $\text{R}_3\text{P}=\text{NR}'$, are well known and may be prepared from the reaction of R_3PCl_2 and $\text{R}'\text{NH}_2$. 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—N bonded, of $\text{S}_4(\text{NH})_{10}$.
- 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 (dimethylbenzene). How many isomers are there of dimethylborazine?
- 16.25** Complexes $(\text{OC})_4\text{Fe}(\text{P}_4\text{O}_6)$ and $(\text{OC})_3\text{Fe}(\text{P}_4\text{O}_6)_2$ form from the reaction of $\text{Fe}(\text{CO})_5$ and P_4O_6 . Suggest structures for these complexes. Would you expect similar reactions with P_4O_{10} ? (See Walker, M. L.; Mills, J. L. *Inorg. Chem.* **1977**, *16*, 3033.)
- 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 $\text{P}_4\text{O}_6\text{S}_4$, synthesized from P_4O_{10} and P_4S_{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 suggested¹⁷⁵ that Se_8^{2+} exists in the endo form rather than an exo "crown" form with Se(1) flipped down because of reduced lone-pair repulsions between Se(2), Se(3), Se(6) and Se(7). Sketch these two forms of 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, B_2H_7^- and B_3H_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:
- $[\text{PNCl}_2]_3 + \text{excess Me}_2\text{NH} \longrightarrow$
 - $\text{B}_2\text{H}_6 + 2\text{R}_3\text{P} \longrightarrow$
 - $\text{B}_2\text{H}_6 + 2\text{NH}_3 \longrightarrow$
 - $\text{P}_2\text{Cl}_4 + \text{excess Cl}_2 \longrightarrow$
- 16.33** Assuming that the external H—B—H angle in B_2H_6 accurately reflects the interorbital angle:
- Calculate the *s* and *p* character in these bonds.
 - Calculate the *s* and *p* character remaining for the bridging orbitals.
 - Compare the value from (b) with the experimental internal angles.
- 16.34** Use Wade's rules to predict the structures of the following:
- $\text{B}_5\text{H}_3(\text{CO})_2\text{Fe}(\text{CO})_3$
 - $\text{C}_2\text{B}_4\text{H}_6\text{Pt}(\text{PEt}_3)_2$
 - $\text{C}_2\text{B}_7\text{H}_7\text{Me}_2\text{Fe}(\text{CO})_3$
 - $\text{CB}_9\text{H}_{10}\text{AsCo}(\eta^5\text{-C}_5\text{H}_5)$

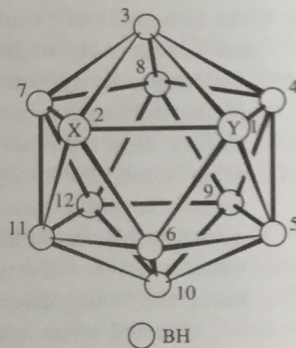
¹⁷⁵ Corbett, J. D. *Prog. Inorg. Chem.* **1976**, *21*, 129.

- 16.35 Use the polyhedral skeletal electron-counting rules and show that they are consistent with the *nido* 11-vertex structure shown below.¹⁷⁶



- 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 π donation from the p orbitals of oxygen increases?
- 16.38 The chloro groups in $[Re_2Cl_8]^{2-}$ are eclipsed, but the chloro groups in $[Os_2Cl_8]^{2-}$ are staggered. Offer an explanation. (See Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 4850.)
- 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 $Ni_3Cl_2S_2(PPh_3)_4$ is analogous to that of $(p\text{-cymene})_3Ru_3S_2^+$ (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.)

	X	Y
a.	Bi	S
b.	S	S
c.	P	CH
d.	P	Bi



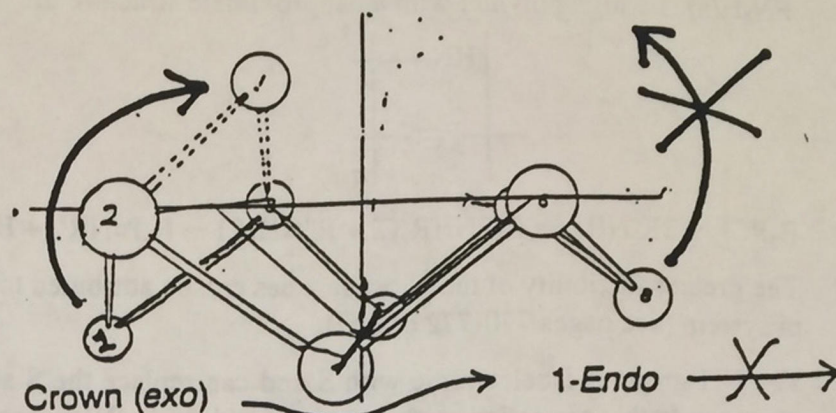
- 16.42 In addition to the phosphazenes discussed in this chapter, a large group of heterocyclic compounds known as phosphazanes has been characterized. These contain P—N single bonds and may contain phosphorus either in the +3 or +5 oxidation states. Draw structures of $[Cl_3PNMe]_2$ and $[Cl(O)PNMe]_2$. Phosphorus(III) tri- and tetraphosphazanes have been stabilized by placing *o*-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 *closo*- $Et_2C_2B_5H_5$. (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.

¹⁷⁷ Fenske, D.; Ohmer, J.; Hachgenei, H.; Merzweiler, K. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1277-1296.

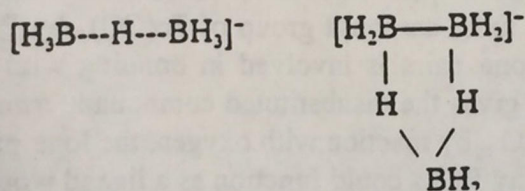
Handbook of Chemistry and Physics, 75th ed.; CRC: Boca Raton, FL, 1994; pp 5-6, 5-16, 5-24, 5-28.

- 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_8 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.

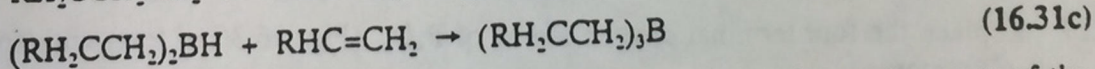
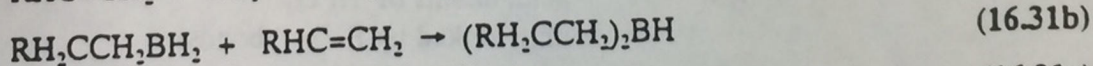
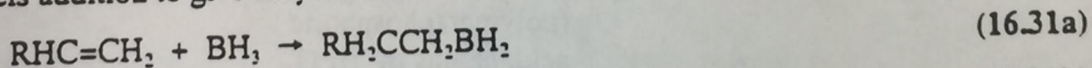


Sketch 16.1 The flip of S_1 from the crown conformation to the more stable 1-endo position. The second possible flip of S_8 does not occur.

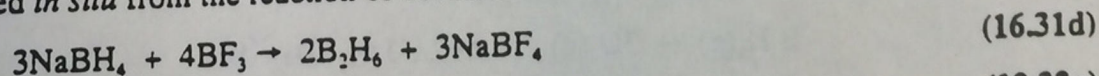
- 16.30 Both of these anions can be said to possess arachno structures.



- 16.31 Hydroboration provides a versatile synthesis of alcohols and ketones from alkenes or alkynes. They react with B_2H_6 or stabilized BH_3 ($\text{thf} \cdot \text{BH}_3$, $\text{Me}_2\text{S} \cdot \text{BH}_3$) by an anti-Markovnikov, cis addition to give alkylborons:



The extent to which this reaction proceeds depends upon the steric requirements of the alkene, more substituted ones giving R_2BH or RBH_2 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:

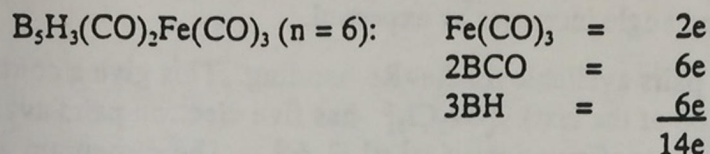


- 16.32 a. $[\text{PNCl}_2]_3 + \text{Me}_2\text{NH (excess)} \rightarrow \{\text{PN}(\text{N}(\text{Me})_2)_3\} + 6[\text{Me}_2\text{NH}_2]\text{Cl} \quad (12.32a)$
- b. $\text{B}_2\text{H}_6 + 2\text{R}_3\text{P} \rightarrow 2\text{R}_3\text{PBH}_3 \quad (16.32b)$
- c. $\text{B}_2\text{H}_6 + 2\text{NH}_3 \rightarrow [\text{H}_2\text{B}(\text{NH}_3)_2][\text{BH}_4] \quad (16.32c)$
- d. $\text{P}_2\text{Cl}_4 + \text{excess Cl}_2 \rightarrow 2\text{PCl}_3 \rightarrow 2\text{PCl}_5 \quad (16.32d)$

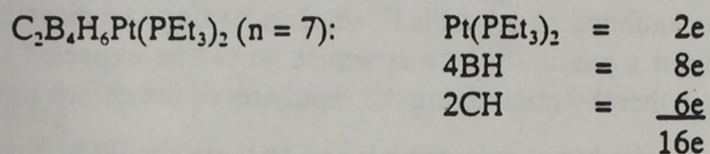
16.33 a. The external bond angle is 122° which yields $s = 34.6\%$ from Eq. 6.1.

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.

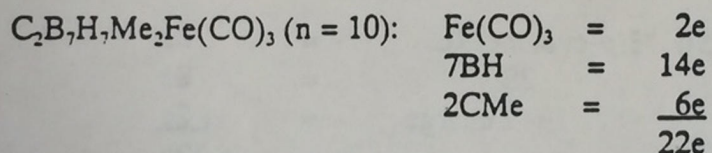
16.34 All are *closo* structures.



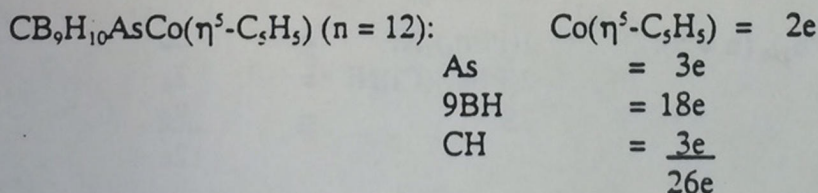
$$2n + 2 = 2 \times 6 + 2 = 14$$



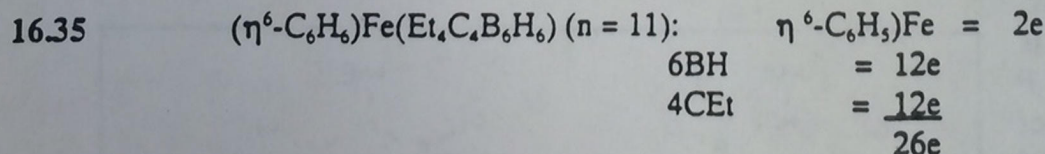
$$2n + 2 = 2 \times 7 + 2 = 16$$



$$2n + 2 = 2 \times 10 + 2 = 22$$



$$2n + 2 = 2 \times 12 + 2 = 26$$



$$2n + 2 = 2 \times 11 + 4 = 26$$

16.36 Neutral W_2 should be analogous to 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 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 $d_{x^2-y^2}$ and the d_{xy} orbitals of

each metal atom may overlap. One of the sigma bonds is mostly 5s in character and the other is mostly d_{z^2} 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 $[\text{Re}_2\text{Cl}_8]^{2-}$ has four electron pairs available for Re–Re bonding. This gives a configuration of $\sigma^2 \pi^4 \delta^2 \delta^*0$ (see Fig. 16.60 of the text). $[\text{Os}_2\text{Cl}_8]^{2-}$ has five electron pairs available for Os–Os bonding. This gives a configuration of $\sigma^2 \pi^4 \delta^2 \delta^*1$. The dirhenium anion can contain a delta bond only if the chloro groups are eclipsed. The diosmium anion cannot have a delta bond because the antibonding orbital is filled, thus leading to a diosmium triple bond. As delta bonding is not a possibility, the structure would be expected to have a staggered configuration (D_{4d}), 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.

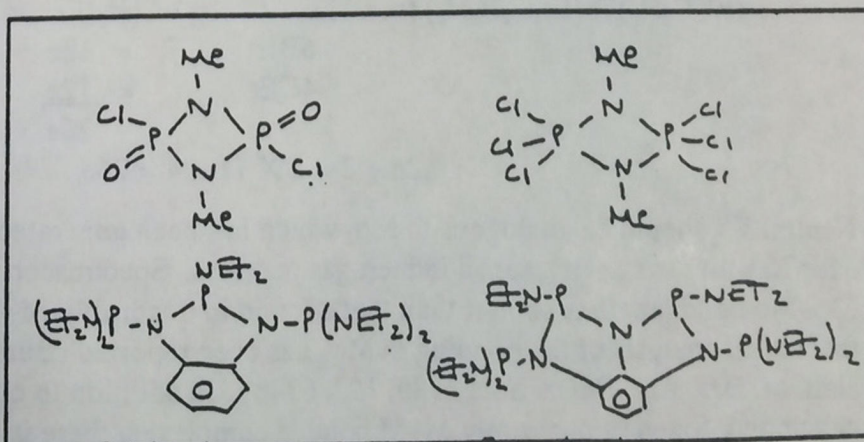
$$\begin{array}{rcl}
 \text{16.40 } [\text{Ru}_3(p\text{-cymene})_3\text{S}_2]^{2+} \text{ (n = 5):} & 3(p\text{-cymene})\text{Ru} & = 6e \\
 & 2\text{S} & = 8e \\
 & +2 \text{ charge} & = -2e \\
 & & \underline{12e}
 \end{array}$$

$2n + 2 = 2 \times 5 + 2 = 12$, so a *closo* structure is expected.

$$\begin{array}{rcl}
 \text{Ni}_3\text{Cl}_2\text{S}_2(\text{PPh}_3)_4 \text{ (n = 5):} & 1(\text{PPh}_3)_2\text{Ni} & = 2e \\
 & 2(\text{PPh}_3)(\text{Cl})\text{Ni} & = 2e \\
 & 2\text{S} & = \underline{8e} \\
 & & \underline{12e}
 \end{array}$$

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 Ph_3P molecules and each of the other two is bound to one Ph_3P molecule and one chloro group.

16.41 The compound, $1,2\text{-XYB}_{10}\text{H}_{10}$, has a *closo* structure and must obey the $2n + 2$ rule ($n = 12$). That means that there must

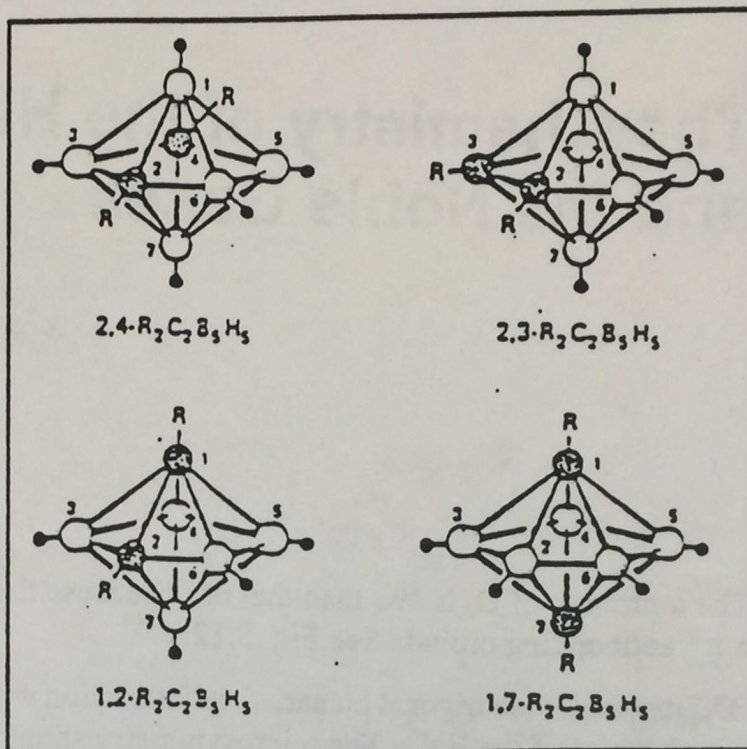


Sketch 16.2 From top to bottom, examples of diphosphazanes, a triphosphazane, and a tetraphosphazane.

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*- $\text{Et}_2\text{C}_2\text{B}_5\text{H}_5$, 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.



Sketch 16.3 The four isomers of *closo*-bis(C-ethyl)dicarba-pentaborane. [From Beck, J. S.; Sneddon, L. G. *Inorg. Chem.*, 1990, 29, 295-302. Reproduced with permission.