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 $Cl_3B_3N_3(CH_3)_3 + 3CH_3MgBr \rightarrow (CH_3)_3B_3N_3(CH_3)_3 + 3MgBrCl$

The structure of N, N', N''-trimethyl-B, B', B''-trimethylborazine is shown below:



- S12.4 How many skeletal electrons are present in B_5H_9 ? Five B-H units contribute $5 \times 2 = 10$ electrons, and the four additional H atoms contribute four additional electrons, for a total of 14 electrons or 7 pairs of electrons.
- S12.5 Use Wade's rules to determine the structure of B_4H_{10} ? Four B-H units contribute $4 \times 2 = 8$ electrons, and the six additional H atoms contribute six additional electrons, for a total of 14 electrons or 7 pairs of electrons. Boranes of formula B_nH_{n+6} have the *arachno* structure (see Figure 12.11), which is based on a *closo* structure with n + 1 vertices. In this case n = 4. The *closo* structure with 6 vertices is an octahedron, the nido structure with 5 vertices is a square pyramid. The butterfly-like arachno structure of B_4H_{10} contains 4 vertices and is tetrahedral; see Table 12.4.
- S12.6 A plausible product for the interaction of $Li[B_{10}H_{13}]$ with $Al_2(CH_3)_6$? By analogy with the reaction of $[B_{11}H_{13}]^{2^-}$ with $Al_2(CH_3)_6$, the plausible product would be $[B_{10}H_{11} (AlCH_3)]^-$, which would be formed as follows:

$$2[B_{10}H_{13}]^{-} + Al_2(CH_3)_6 \rightarrow 2[B_{10}H_{11}(AlCH_3)]^{-} + 4CH_4$$

S12.7 Propose a synthesis for 1,7-B_{10}C_2H_{10}(Si(CH_3)_2CI)_2? As in the example, you should consider attaching the Si(CH₃)₂Cl substituents to the carbon atoms of this carborane by using the dilithium derivative 1,7- $B_{10}H_{10}C_2L_{12}$. You can first prepare 1,2- $B_{10}C_2H_{12}$ from decaborane as in the example. Then, this compound is thermally converted to a mixture of the 1,7- and 1,12-isomers, which can be separated by chromatography:

$$1,2 - B_{10}C_2H_{12} \xrightarrow{\Delta} 1,7 - B_{10}C_2H_{12} (90\%) + 1,12 - B_{10}C_2H_{12} (10\%)$$

The pure 1,7-isomer is lithiated with RLi and then treated with Si(CH₃)₂Cl₂:

$$1,7-B_{10}C_2H_{10}Li_2 + 2Si(CH_3)_2Cl_2 \rightarrow 1,7-B_{10}C_2H_{10}(Si(CH_3)_2 + 2LiCl)$$

S12.8 Propose, with reasons, the chemical equation (or indicate no reaction) for reactions between (a) (CH₃)₂SAlCl₃ and GaBr₃? GaBr₃ is the stronger Lewis acid, so the reaction is (Me)₂SalCl₃ + GaBr₃ → Me₂SGaBr₃ + AlCl₃. (b) TICl and formaldehyde (HCHO) in acidic aqueous solution? Thallium trihalides are very unstable and are easily reduced, as shown below:

$$2 \text{TICl}_3 + \text{H}_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{TICl} + \text{CO}_2 + 4 \text{H}^+ + 4 \text{Cl}^-$$

12.1 Give a balanced equation and conditions for the recovery of boron? Boron is recovered from the mineral borax, Na₂B₄O₅(OH)₄·8H₂O, by formation of B₂O₃ followed by treatment with magnesium:

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO \quad \Delta H < 0$$

- 12.2 Describe the bonding in (a) BF_3 ? Covalent with a strong π component of the B-F bond (see Figure 12.2) (b) AlCl₃? In the solid state, AlCl₃ has a layered structure. At melting point, AlCl₃ converts to dimers with 2*c*, 2*e* bridging bonds. (c) B_2H_6 ? Structure 1 shows that B_2H_6 is an electron-deficient dimer with 3*c*, 2*e* bridging bonds.
- 12.3 Lewis acidity of group 13 and group 14 halides? Arrange in order of increasing Lewis acidity toward hard Lewis bases: BF₃, BCl₃, AlCl₃? For a given halogen, the order of acidity for group 13 halides toward hard Lewis bases like dimethylether or trimethylamine is BX₃ > AlX₃ > GaX₃, while the order toward soft Lewis bases such as dimethylsulfide or trimethylphosphine is BX₃ < AlX₃ < GaX₃. This fact establishes the order BCl₃ > AlCl₃ for the four Lewis acids in question. For boron halides, the order of acidity is BF₃ < BCl₃ < BBr₃, exactly opposite to the order expected from electronegativity trends. This is discussed in Section 12.4. While you can now predict with some confidence that both BF₃ and AlCl₃ are weaker Lewis acids than BCl₃

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toward hard Lewis bases, it is not possible to predict from the information given in the text whether BF₃ is stronger or weaker than AlCl₃. So the order of increasing Lewis acidity toward hard Lewis bases is $BF_3 \sim AlCl_3 < BCl_3$. **Predict the course of the following reactions?**

(a) $F_3B - N(CH_3)_3 + BCl_3 \rightarrow Cl_3B - N(CH_3)_3 + BF_3 (BCl_3 > BF_3)$

(b) $BH_3CO + BBr_3 \rightarrow NR$ (BH_3 is softer than BBr_3 ; CO is a soft base)

12.4 Deduce the formula of A and identify the cation and anion? For the product in the equation below, the cation is Na⁺ and the anion is TIBr₄⁻. Equal moles (2.5 mmol) of NaBr and TIBr₃ react to make Na[TIBr₄], which is the formula of A.

 $TlBr_3 + NaBr \rightarrow NaTlBr_4$

12.5 Identify compounds A, B, and C? (a) $4 BF_3 + 3 LiA H_4 \rightarrow 2 B_2 H_6 + 3 LiBF_4$; $A = B_2 H_6$ (b) $B_2 H_6 + 6 H_2 O \rightarrow 2 B(OH)_3$, $+ 6 H_2$; $B = B(OH)_3$ (c) $2 B(OH)_3 + heat \rightarrow B_2 O_3 + 3 H_2 O$; $C = B_2 O_3$ $B_2 O_3 + 3 CaF_2 \rightarrow 2 BF_3 + 3 CaO$

12.6 Does B_2H_6 survive in air? If not, write the equation for the reaction? No, B_2H_6 does not survive in air, instead it reacts spontaneously with the oxygen in air and forms the hydrated solid oxide, as shown below:

$$B_2H_6 + 3 O_2 \rightarrow B_2O_3 + 3 H_2O_2$$

12.7 Synthesis of $F_2BCH_2CH_2BF_2$? By analogy with the addition of B_2Cl_4 to ethene (ethylene) described in Section 12.4, one can prepare this compound by adding B_2F_4 to ethene. Starting with BCl₃, prepare B_2Cl_4 and then convert it to B_2F_4 with a double replacement reagent such as AgF or HgF₂, as follows:

$$2 \operatorname{BCl}_3 + \operatorname{Hg} \rightarrow \operatorname{B_2Cl}_4 + \operatorname{HgCl}_2$$
$$\operatorname{B_2Cl}_4 + 4 \operatorname{AgF} \rightarrow \operatorname{B_2F}_4 + 4 \operatorname{AgCl}$$

 $B_2F_4 + C_2H_4 \rightarrow F_2BCH_2CH_2BF_2$

- 12.8 Give formulas and conditions for the synthesis of (a) $B(C_2H_5)_3$? 2 NaBH₄ + 2 H₃PO₄ \rightarrow 2 NaHPO₄ + B₂H₆, B₂H₆ + THF \rightarrow 2 H₃BTHF, H₃BTHF + 2 C₂H₄ \rightarrow 3 BEt₃ + THF. (b) Et₃NBH₃? BH₃THF (from above) + Et₃N \rightarrow Et₃NBH + THF.
- 12.9 Draw the B_{12} unit and find a C_2 axis? See the structure of B_{12} unit (Figure 12.12). One of the many twofold rotation axes is a horizontal line in the plane of the paper, bisecting opposite pairs of B-B linkages.
- 12.10 Which is more stable, B_6H_{10} or B_6H_{12} ? Inspection of Table 12.4 shows that B_6H_{10} is an example of a *nido* borane, since it has the formula B_6H_{6+6} . The compound B_6H_{12} , which has the formula B_6H_{6+6} , is an *arachno* borane. In general, *arachno* boranes are much less stable than either *closo* or *nido* boranes. Therefore, B_6H_{10} would be expected to be more stable than B_6H_{12} .
- 12.11 The combustion of pentaborane(9)? (a) Balanced equation? The balanced equation for the reaction of B_5H_9 with O_2 is:

$$2 B_5 H_9(l) + 12 O_2(g) \rightarrow 5 B_2 O_3(s) + 9 H_2 O(g)$$

Note that the product water is listed as a gas rather than a liquid, since this combustion reaction will produce temperatures in excess of 100°C.

(b) Probable disadvantages? A serious drawback to using pentaborane, or any other borane for that matter, is that the boron-containing product of combustion is a solid, B_2O_3 . If an internal combustion engine is used, the solid will eventually coat the internal surfaces, increasing friction, and will clog the exhaust valves. A similar problem would arise if silanes, Si_xH_y , were used as a fuel, since the silicon-containing product, SiO_2 , is also a solid. Note that the carbon-containing product of hydrocarbon combustion, CO_2 , is a gas.

12.12 Classify $B_{10}H_{14}$ and discuss its structure and bonding with respect to Wade's rules? This compound is an example of a B_nH_{n+4} compound with n = 10, so it is a *nido* borane. According to Wade's rules, ten B-H

units contribute $10 \times 2 = 20$ electrons, and the four additional H atoms contribute four additional electrons (24) electrons = 12 pairs of skeletal electrons). The total number of valence electrons for $B_{10}H_{14}$ is $(10 \times 3) + (14 \times 10^{-5})$ 1) = 44. Since there are 10 (2c,2e) B-H bonds, which account for 20 of the valence electrons, the number of cluster valence electrons is the remainder, 44 - 20 = 24.

The synthesis of Fe(nido-B₉C₂H₁₁)₂? The starting material, B₁₀H₁₄, is converted to the closo carborane 1, 2-12.13 $B_{10}C_2H_{12}$ by treatment with acetylene in the presence of a Lewis base, usually diethylsulfide:

$$B_{10}H_{14} + C_2H_2 \rightarrow B_{10}C_2H_{12} + 2H_2$$

This compound is fragmented by the removal of a B atom as B(OEt)₃:

fragmented by the removal of a B atom as
$$B(OEt)_3$$
:
 $B_{10}C_2H_{12} + Na^+OEt^- + 2EtOH \rightarrow Na^+[B_9C_2H_{12}]^- + B(OEt)_3 + H_2$

The salt is deprotonated and treated with FeCl₂ to form the product:

$$Na^{+}[B_{9}C_{2}H_{12}]^{-} + NaH \rightarrow (Na^{+})_{2}[B_{9}C_{2}H_{11}]^{2-} + H_{2}$$

$$2 (Na^{+})_{2} [B_{9}C_{2}H_{11}]^{2-} + FeCl_{2} \rightarrow (Na^{+})_{2} [Fe(B_{9}C_{2}H_{11})_{2}]^{2-} + 2 NaCl_{2}$$

See Figure 12.14a for the structure of the product.

12.14 Compare BN and graphite? (a) Their structures? Both of these substances have layered structures. The planar sheets in boron nitride and in graphite consist of edge-shared hexagons such that each B or N atom in BN has three nearest neighbors that are the other type of atom and each C atom in graphite has three nearest neighbor C atoms. The structure of graphite is shown in Figure 13.2. The B-N and C-C distances within the sheets, 1.45 Å and 1.42 Å, respectively, are much shorter than the perpendicular interplanar spacing, 3.33 Å and 3.35 Å, respectively. In BN, the B_1N_3 hexagonal rings are stacked directly over one another so that B and N atoms from alternating planes are 3.33 Å apart, while in graphite the C_6 hexagons are staggered (see section 12.6) so that C atoms from alternating planes are either 3.35 Å or 3.64 Å apart (you should determine this yourself using trigonometry).

(b) Their reactivity with Na and Br₂? Graphite reacts with alkali metals and with halogens (see the answer to Self-test S13.1). In contrast, boron nitride is quite unreactive.

(c) Explain the differences? The large HOMO-LUMO gap in BN, which causes it to be an insulator. suggests an explanation for the lack of reactivity: since the HOMO of BN is a relatively low energy orbital, it is more difficult to remove an electron from it than from the HOMO of graphite, and since the LUMO of BN is a relatively high energy orbital, it is more difficult to add an electron to it than to the LUMO of graphite

12.15 Devise a synthesis for the following borazines? (a) $Ph_3N_3B_3Cl_3$? The reaction of a primary ammonium salt with boron trichloride yields N-substituted B-trichloroborazines:

$$3 \text{ PhNH}_3^+\text{Cl}^- + 3 \text{ BCl}_3 \rightarrow \text{ Ph}_3\text{N}_3\text{B}_3\text{Cl}_3 + 9 \text{ HCl}$$

(b) $Me_3N_3B_3H_3$? You first prepare $Me_3N_3B_3Cl_3$ using $MeNH_3^+Cl^-$ and the method described above, and then perform a Cl⁻/H⁻ metathesis reaction using LiH as the hydride source:

 $3 \text{ MeNH}_3^+\text{Cl}^- + 3 \text{ BCl}_3 \rightarrow \text{Me}_3\text{N}_3\text{B}_3\text{Cl}_3 + 9 \text{ HCl}$

$Me_3N_3B_3Cl_3 + 3 LiH \rightarrow Me_3N_3B_3H_3 + 3 LiCl$

The structures of Ph₃N₃B₃Cl₃ and Me₃N₃B₃H₃ are shown below: the product of the product of the second second