CONVENTION ALERT

In looking at Figure 3.71, don't forget the curved **arrow formalism** (p. 91). Those double barbed arrows track the movements of pairs of electrons. The color-coding should help. Notice also the red and green equilibrium arrows. The different lengths reflect the exothermicity or endothermicity of each step. The first step is endothermic, and the second is exothermic.

Let's look at the intermediate carbocation in Figure 3.71. In Chapter 2 (p. 60), we described the methyl cation ($^+CH_3$). The cation formed by protonation of 2,3-dimethyl-2-butene is related to the methyl cation, but the three hydrogens of $^+CH_3$ have been replaced with three alkyl groups: two methyls and an isopropyl (Fig. 3.72).

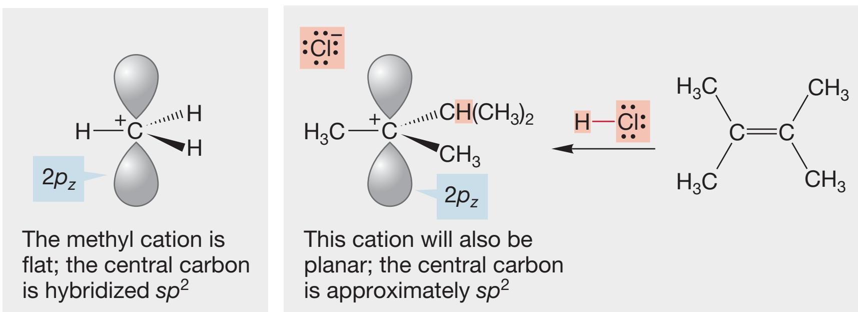

FIGURE 3.72 Protonation of 2,3-dimethyl-2-butene gives a planar carbocation, closely related to the methyl cation. The central carbon of each species is hybridized sp^2.

No great structural differences appear, however. The trigonal (attached to three groups) carbon is hybridized sp^2 and the C—C—C angles will be roughly 120°. The empty carbon $2p_z$ orbital extends above and below the plane of the central carbon and the three carbons attached to it (Fig. 3.72). Let's even verify that the carbon is positively charged (Fig. 3.73).

In a neutral carbon atom, the six positive nuclear charges are balanced by six electrons. The central carbon in this cation has a pair of 1*s* electrons and a half-share in the electrons in the three covalent bonds to the alkyl groups, for a total of five. The six positive charges in the nucleus are balanced by only five electrons, and so the carbon atom is positively charged.

Polar reactions such as these are best understood in terms of **H**ighest **O**ccupied **M**olecular **O**rbital–Lowest **U**noccupied **M**olecular **O**rbital (**HOMO–LUMO**) orbital interactions. As we have already seen (Section 1.7, p. 39), when a filled occupied orbital overlaps an empty orbital, the two electrons are stabilized in the new, lower energy molecular orbital. The words "Lewis bases react with Lewis acids" are essentially equivalent to saying, "The interaction of a filled and empty orbital is stabilizing." Indeed, this notion is one of the central unifying themes of organic reactivity, as essentially all polar reactions can be understood this way.

We will revisit this reaction in detail in Chapter 9, but see right now if you can identify the HOMOs and LUMOs in the two steps of this reaction, that is, do Problems 3.27 and 3.28.

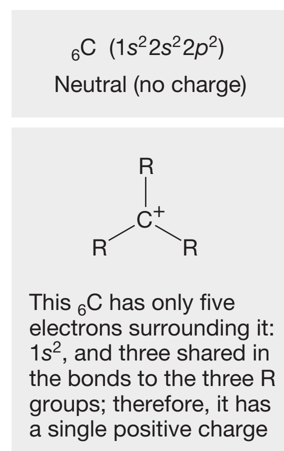

FIGURE 3.73 The determination of the charge on carbon in a carbocation.

WORKED PROBLEM 3.27 Identify the HOMO and LUMO for the second step of the reaction in Figure 3.68.