1

INTRODUCTION: GENERAL ASPECTS

1.1. AIMS AND OBJECTIVES

This book is concerned with an important area of organic (i.e., carbon) chemistry that has developed enormously over the past half-century, yet is still neglected in many organic textbooks. This is the chemistry of compounds in which carbon atoms are covalently bonded to more neighboring atoms than can be explained in terms of classical two-center, electron-pair bonds. Such carbon atoms are referred to as *hypercarbon atoms*[1] (short for *hypercoordinated carbon atoms*) because when first discovered, their *coordination numbers* seemed *unexpectedly high*.

Carbon contains four atomic orbitals (AOs) in its valence shell (the $2s$, $2p_x$, $2p_y$, and $2p_z$ AOs) and thus can accommodate at most four electron pairs (the "octet rule").[2] Commonly, these electron pairs are used to form four single bonds (as in alkanes), two single bonds and one double bond (as in alkenes), one single bond and one triple bond (as in alkynes), or two double bonds (as in cumulenes). With only four bond pairs, carbon atoms cannot bond simultaneously to more than four neighboring atoms using only two-center electron-pair bonds. If attached to more than four neighboring atoms, they must resort to some form of *multicenter σ bonding*, in which the bonding power of a pair of electrons is spread over more than two atoms. All carbon atoms with coordination numbers greater than four are therefore necessarily hypercoordinated, and compounds containing such atoms (of which there are

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now a very large number) will be the main concern of this book. However, there are circumstances in which carbon atoms with only three or four neighbors may participate in multicenter σ bonding to two or even three of these neighbors, and we shall include them in our discussion where appropriate.

We have four main objectives:

1. *To illustrate the wide and developing scope of hypercarbon chemistry* by illustrating the variety of compounds now known to contain hypercarbon atoms (carbocations,[3–6] organometallics,[7–9] carboranes,[10] metal–carbon cluster compounds,[11,12] and metal carbides[13]). They include bridged metal alkyls such as alkyl-lithium reagents $(LiR)_n$[14–17] in which the hypercoordinated nature of the metal-attached carbon atoms, and the roles that the metal atoms play in their chemistry, are often overlooked.
2. *To discuss the ways in which the bonding in such systems can be described*, notably using three-center–two-electron (3*c*–2*e*) bonds as well as classical two-center–two-electron (2*c*–2*e*) bonds, but also by simple molecular orbital (MO) treatments that shed useful light on the more symmetrical systems.
3. *To show how hypercarbon compounds are closely related to many classically bonded systems and aromatic systems*, and are not exotic species remote from mainstream organic chemistry.
4. *To show how the study of hypercarbon compounds helps us to understand the mechanisms of many organic reactions*, reactions in which carbon atoms become temporarily hypercoordinated in intermediates or transition states even though the reagents and products contain only normally coordinated carbon atoms.

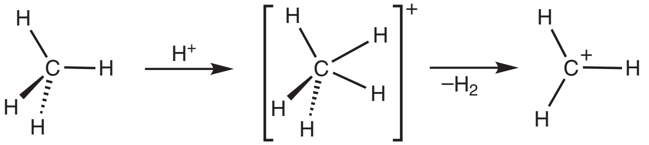
In introducing the subject in Section 1.2, we define some of the terms we shall be using. In Section 1.3, we illustrate the various types of hypercarbon compounds now known. Since we shall rely heavily on the *3c–2e bond concept* in their bonding, and since its usefulness is perhaps less widely appreciated in organic chemistry than in inorganic or organometallic chemistry, we devote Section 1.4 of this introductory chapter to discussion of that concept and illustrate its value for selected systems. We also demonstrate the relevance and value of some simple MO arguments applied to hypercarbon systems (Sections 1.4 and 1.5), and conclude this introductory chapter by indicating the types of reactions thought to involve hypercarbon systems. More detailed discussion of particular categories of hypercarbon compounds, including structural, bonding, thermochemical, and reactivity aspects, follow in subsequent chapters.

1.2. SOME DEFINITIONS

Throughout this book, we shall be concerned with the twin issues of coordination and bonding. The terminology by which chemists refer to these issues varies considerably from area to area. It is important, therefore, to define and to illustrate the sense in which certain terms will be used here.

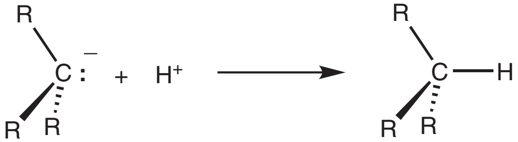
We define the *coordination number* of an atom as the *number of neighboring atoms* by which that atom is directly surrounded, to each of which it is attached by the direct sharing of electronic charge. The coordinating atoms may not all be at the same distance (some may be bonded more strongly than others, and so may be closer to the atom under consideration), but all will be located in directions and at distances that indicate sharing of electronic charge with the central atom, rather than linkage to the central atom via a second neighboring atom.

On occasions, the term "valence" is used as if it were synonymous with "coordination number." We shall not use it in that sense here. We define *the valence of an atom as the number of bonding electron pairs used by that atom*. Normally, carbon is *tetravalent* (i.e., the octet rule is obeyed), and hypercarbon compounds are no exception. (See also discussions about hypervalency by Akiba[18] and the octet rule and hypervalency by Gillespie and Silvi.[19]) A hypercarbon atom uses four electron pairs to bond to whatever number of atoms there are in its coordination sphere. The carbon atom in methane is tetravalent and four coordinate, forming four 2*c*–2*e* bonds to its neighboring hydrogen atoms. It remains tetravalent but becomes pentacoordinate when methane is protonated to form the methonium ion (CH_5^+), an energetic, highly reactive species[20–22] with a structure in which three hydrogen atoms remain at a normal, single-bond distance while the other two are at a greater distance.[20,23–26] However, the methyl cation CH_3^+ into which CH_5^+ decomposes contains a triply coordinated *trivalent* carbon atom [Eq. (1.1): The lines from carbon in that equation represent links to the coordinating hydrogen atoms, not necessarily bonds in the classical electron-pair sense].

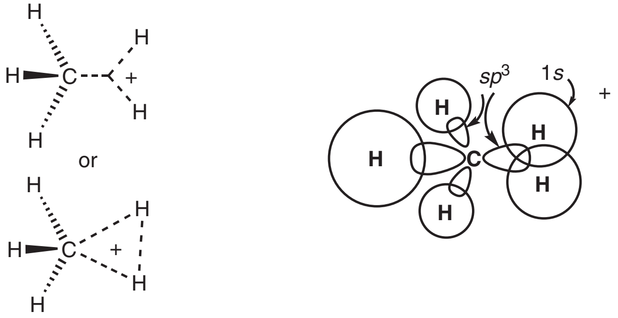


(1.1)

The carbon atom in CH_3^+ is said to be *coordinatively unsaturated*, a term we shall use in connection with any atom that can readily expand its coordination number, either (as in the case of the carbon atom of CH_3^+) by bonding to another *ligand (a coordinating atom or group)*, which supplies electrons for the purpose (e.g., $CH_3^+ + X^- \rightarrow CH_3X$), or by using electrons that were previously *nonbonding*, for example, as occurs when coordinatively unsaturated carbon atoms in carbanions R_3C^- are protonated, that is, when *nonbonding lone-pair electrons* are converted into bond pairs [Eq. (1.2)]:



(1.2)



Scheme 1.1

When discussing bonding, we shall find it convenient to retain wherever practicable the concept of single, double, and triple bonds, that is, links between pairs of atoms that involve the sharing between those atoms of two, four, or six electrons, respectively. We shall refer to them as 2*c*–2*e*, two-center–four-electron (2*c*–4*e*), and two-center–six-electron (2*c*–6*e*) bonds. However, as already indicated, we shall find it necessary, in discussing hypercarbon compounds, to use the concept of *multicenter σ bonds*, bonds in which the bonding power of a pair of electrons is considered to extend over three or occasionally four atoms. In CH_5^+, for example, a *3c–2e bond* can account for the bonding between the carbon atom and the two hydrogen atoms furthest from the carbon atom, represented as in Scheme 1.1.

Such a 3*c*–2*e* bond is envisaged as resulting from the mutual overlap of a suitable AO from each of the atoms involved, a 1*s* AO from each hydrogen atom, and an sp^3 hybrid AO from carbon. The 3*c*–2*e* bond can be represented by broken lines from the atoms that meet at the center of that triangle, where the AOs of the three atoms will overlap (Scheme 1.1). It must be remembered, however, that there is no atom at the point at which the broken lines meet.

It should be stressed that although such a 3*c*–2*e* bond shares the bonding pair of electrons between three atoms instead of two as in classical bonds, and therefore is sometimes referred to as *delocalized*, the description of the bonding in CH_5^+ by three 2*c*–2*e* bonds and one 3*c*–2*e* bond is nevertheless a description in terms of *localized bonds*. It is a valence bond description of this cation that attempts to account for the distribution of the atoms and the internuclear distances by allocating pairs of electrons to localized regions between pairs of atoms or within triangular arrays of three atoms. A *delocalized* description of the bonding in this cation would allocate the four pairs of electrons to four MOs embracing all six atoms, each or most making some contribution to all of the pairwise interactions, bonded or nonbonded, in CH_5^+, but generating overall much the same electron density in particular regions as the localized bond model. Thus, electron density corresponding to essentially one pair of electrons would be found in each of the "normal" C–H bonds, but the electron density associated with each long C–H bond, and also in the H---H link between the two anomalous (hypercoordinated) hydrogen atoms, would approximate to two-thirds of an electron apiece (for electron bookkeeping purposes, the sharing of a pair of electrons between the three atoms linked by a 3*c*–2*e* bond corresponds to the allocation of two-thirds of an electron to each edge of the triangle defined by those three atoms.).

An additional term we may find occasionally useful, though we shall restrict its use to avoid ambiguity, is *electron deficient*. This term has at least three different senses in which it has found use in connection with organic systems. It is often applied as meaning "center for nucleophilic attack" to refer to carbon atoms bearing electron-withdrawing substituents. Second, it is also used in referring to compounds with coordinatively unsaturated carbon atoms like those of carbenium ions, R_3C^+, which can accommodate an extra pair of electrons. The third usage,[27,28] is as a label for molecules, or sections thereof, that contain too few electrons to allow their bonding to be described exclusively in terms of two-center, electron-pair bonds. In this book we prefer to restrict our discussion to compounds wherein molecules or sets of atoms are held together by *multicenter bonding* (i.e., by electron-deficient bonding). Similarly, *electron precise*[28] is a term that can be used as a label for systems in which there are *exactly the right number of electrons to give each pair a two-center-bonding role*, as in CH_4. *Electron-rich* systems are *those containing nonbonding (lone-pair) electrons*, as in CH_3^-, NH_3, or H_2O.

A molecule or polyatomic ion containing *n* atoms can often be identified as electron deficient from its formula, if it contains fewer than $(n - 1)$ valence shell electron pairs. This is because *at least* $(n - 1)$ two-center covalent links will be needed to hold *n* atoms together, whatever the structure may be. Thus, the methonium ion, CH_5^+, with six atoms held together by only four valence shell electron pairs, is clearly electron deficient in this sense. The dication CH_6^{2+},[29] with seven atoms, is even more so.

1.3. STRUCTURES OF SOME TYPICAL HYPERCARBON SYSTEMS

Before exploring the various bonding situations that occur in hypercarbon systems, we illustrate the structures of some representative examples, grouped according to type in Figures 1.1–1.6.

Figure 1.1 shows the structures, determined in pioneering X-ray crystallographic studies, of some *bridged metal alkyls*, *aryls*, *alkenyls*, *and alkynyls*.[9,14–17,27,30–36] Compounds of these types first showed how the carbon atoms of typical monovalent organic groups could participate in *multicenter σ bonding*. Note that the hypercarbon atoms in all of these compounds bond to either two or three metal atoms, and that, although the coordination numbers of the bridging carbon atoms in $(AlPh_3)_2$[34] (isoBu$_2$AlCH=CH*tert*-Bu)$_2$,[35] and (Me BeC≡CMeNMe$_3$)$_2$[36] are not unusual (4, 4, and 3, respectively) the $(MC)_2$ rings in these compounds (M represents the metal atom), like those in $(AlMe_3)_2$[30]

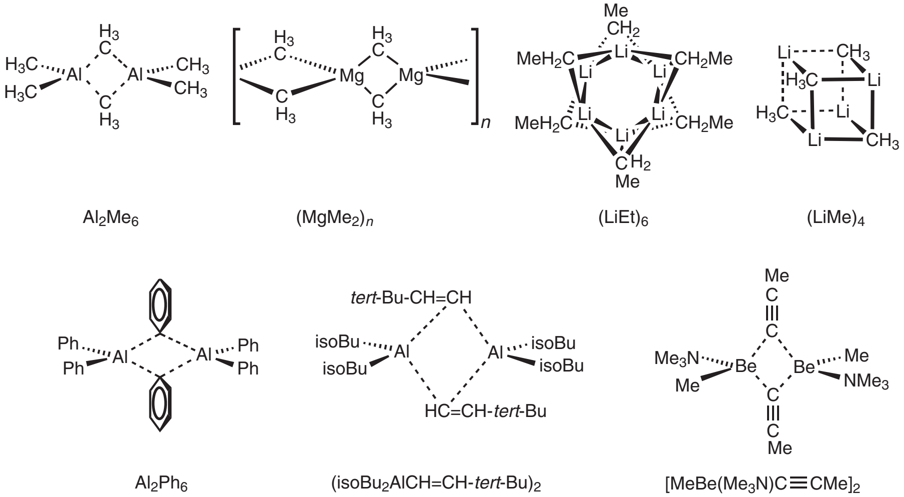


Figure 1.1. Representative bridged metal alkyls, aryls, alkenyls, and alkynyls.

and $(MgMe_2)_n$[31] are held together by fewer electron pairs than two-center M–C links.

Figure 1.2 shows the structures of various types of *carbocations,* $C_xH_y^{n+}$, including the highly reactive, unstable methonium cation (CH_5^+),[20,23] the hydrogen-bridged 1,6-dimethylcyclodecyl cation (1,6-$Me_2C_{10}H_{17}^+$),[37] the pyramidal ions (1,2-$Me_2C_5H_3^+$)[38,39] and ($Me_6C_6^{2+}$),[40] the homoaromatic cation ($C_6H_9^+$),[41] and the 2-norbornyl cation ($C_7H_{11}^+$)[42–44] the structures of all of which were once the subjects of much debate. Although none of these structures has been determined by X-ray diffraction, good evidence for them was obtained from spectroscopic studies in solutions,[45,46] and the structures have subsequently been supported by reliable calculations.[47–49] (See further discussion in Chapter 5, Sections 5.4, 5.5, and 5.6) There was never any doubt about the structures of the two *metalla-carbocations* also shown in Figure 1.2, $[C(AuPPh_3)_5]^+$ [50,51] and $[C(AuPPh_3)_6]^{2+}$,[51,52] which may be regarded as permetallated derivatives of the elusive cations CH_5^+ and CH_6^{2+}, in which the hydrogen atoms have been replaced by $AuPPh_3$ units. Also shown in Figure 1.2(b) are the structures of the *carbocationic transition states* through which the classically bonded carbocations isoPrCMe_2^+ and *tert*-BuCMe_2^+ can undergo degenerate rearrangement, that is, rearrangement in which migration of an atom or group from one atom to another generates a product equivalent but not identical to the original.

Figure 1.3 shows the structures of some deltahedral (i.e., triangular-faced polyhedral) *carboranes*,[8–10,53–61] *mixed hydride clusters of boron and carbon* with BBB, BBC, or BCC faces. Each carbon atom in these cluster compounds has a hydrogen atom attached to it by a bond pointing away from the center of the cluster, but otherwise uses its three remaining valences to bond to the

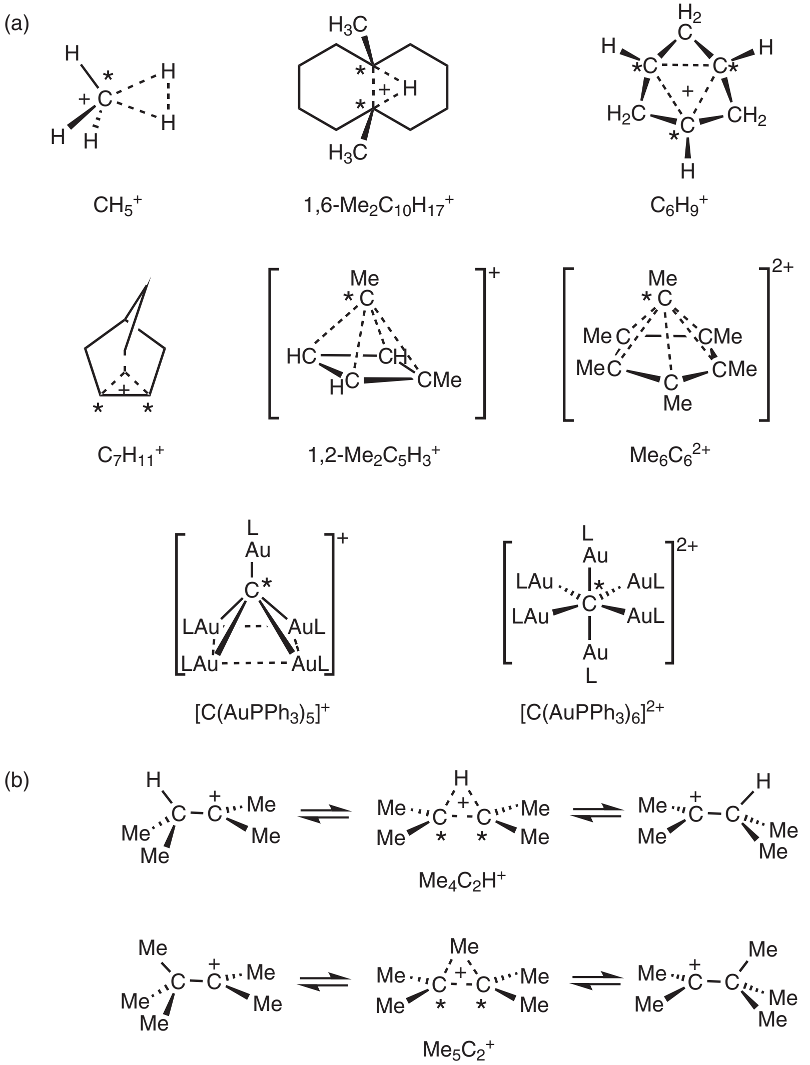
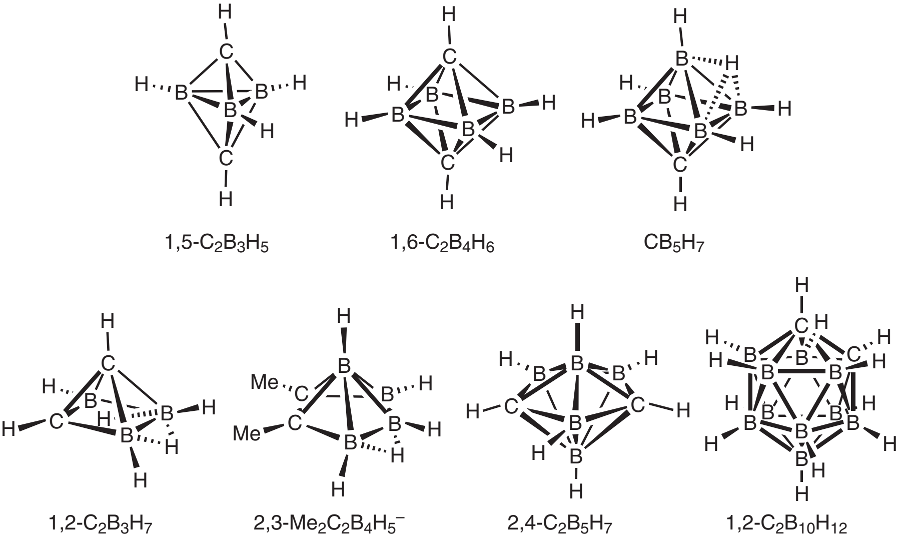


Figure 1.2. Carbocations containing hypercarbon atoms. (a) Carbocations; (b) carbocationic intermediates or transition states (*denotes hypercarbons).

four or five neighboring boron or carbon atoms. The examples chosen include some with five- or six-coordinate carbon atoms ($C_2B_4H_6$, $C_2B_5H_7$, $C_2B_{10}H_{12}$) and others ($C_2B_3H_5$, $C_2B_5H_7$) where the environment (and bonding) of the carbon atoms is similar, although they are only four coordinate. Despite the generally high coordination numbers of their carbon atoms, many carboranes are now known that are highly thermally and oxidatively stable substances, with a vast derivative chemistry and potential for a variety of applications in pure and applied chemistry and in materials and biological sciences.



1,5-$C_2B_3H_5$ 1,6-$C_2B_4H_6$ CB_5H_7

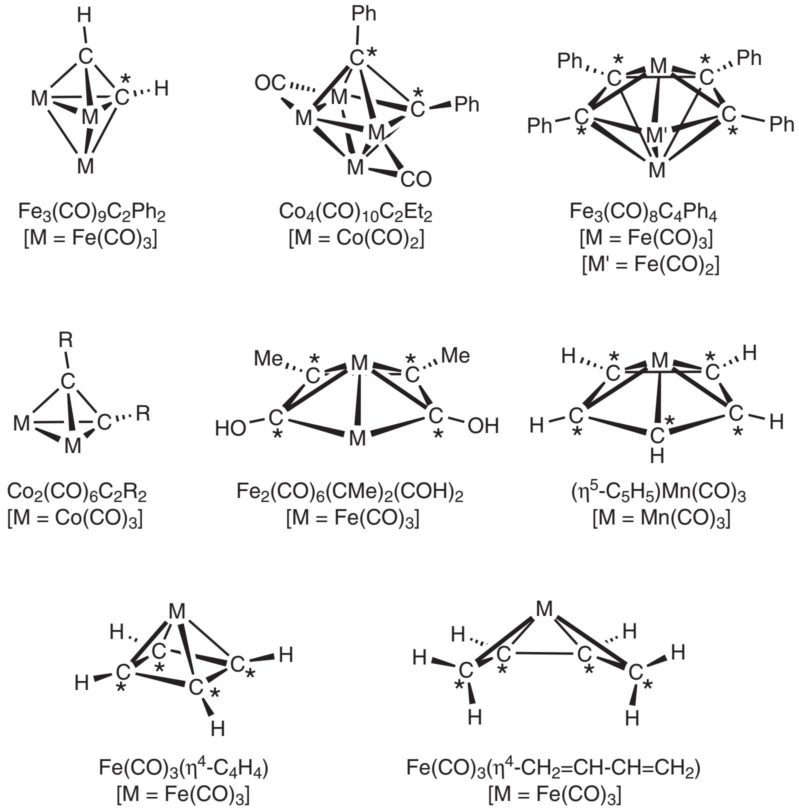
1,2-$C_2B_3H_7$ 2,3-$Me_2C_2B_4H_5^-$ 2,4-$C_2B_5H_7$ 1,2-$C_2B_{10}H_{12}$

Figure 1.3. Some carboranes.

Figure 1.4 shows the structures of some *mixed metal–carbon clusters*.[8,9,11,12,14,27] Their shapes closely resemble those of the carboranes just mentioned, a resemblance we shall find of considerable significance. It is also apparent that the polyhedral (generally deltahedral) examples chosen [$Fe_3(CO)_9C_2Ph_2$,[62] $Co_4(CO)_{10}C_2Et_2$,[63] and $Fe_3(CO)_8C_4Ph_4$ [64]] have many features in common with the cyclopentadienyl-, cyclobutadiene-, and butadiene-metal complexes $(C_5H_5)Mn(CO)_3$, $(C_4H_4)Fe(CO)_3$, and $(C_4H_6)Fe(CO)_3$ also shown. The family relationship that extends from carboranes through mixed metal–carbon clusters to metal complexes of aromatic ring systems like the cyclopentadienide anion ($C_5H_5^-$) also extends to aromatic ring systems themselves.[10,65]

In Figure 1.5, we show the structures of some *metal carbide clusters*,[11,12] compounds in which hypercarbon atoms are embedded in polyhedra (such as square pyramids,[66] octahedra,[67] trigonal prisms,[68] or square antiprisms[69]) of metal atoms. Although these carbon clusters may appear to be remote from typical organic systems, they illustrate clearly the capacity of carbon atoms to bond simultaneously to five, six, or, even eight neighboring atoms, and provide useful models for what may be the key species in Fischer–Tropsch and related chemistry at metal surfaces. The carbon atoms of carbon monoxide may undergo conversion at metal surfaces into carbide environments such as these, through which loss of carbon to the bulk metal or ultimate conversion into hydrocarbons may take place.

The carbon atoms of most binary metal carbides M_xC_y have hypercoordinated environments like those shown in Figure 1.5. In particular, octahedral carbon coordination is common in the interstitial carbides formed by many transition metals, materials of variable composition in which carbon atoms



$Fe_3(CO)_9C_2Ph_2$
[M = $Fe(CO)_3$]

$Co_4(CO)_{10}C_2Et_2$
[M = $Co(CO)_2$]

$Fe_3(CO)_8C_4Ph_4$
[M = $Fe(CO)_3$]
[M' = $Fe(CO)_2$]

$Co_2(CO)_6C_2R_2$
[M = $Co(CO)_3$]

$Fe_2(CO)_6(CMe)_2(COH)_2$
[M = $Fe(CO)_3$]

$(\eta^5\text{-}C_5H_5)Mn(CO)_3$
[M = $Mn(CO)_3$]

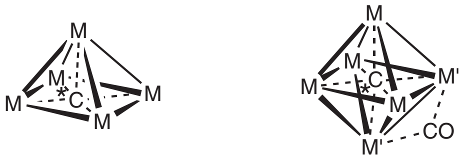
$Fe(CO)_3(\eta^4\text{-}C_4H_4)$
[M = $Fe(CO)_3$]

$Fe(CO)_3(\eta^4\text{-}CH_2{=}CH\text{-}CH{=}CH_2)$
[M = $Fe(CO)_3$]

Figure 1.4. Mixed metal–carbon cluster compounds (metal–hydrocarbon π complexes) (* denotes hypercarbons).

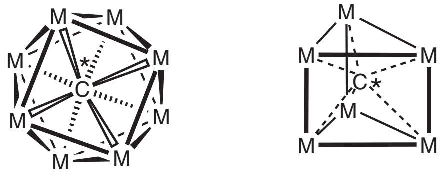
occupy interstices in the metal lattice that may suffer little distortion, even though the carbon valence shell electrons enter the metal valence band and so modify (and commonly strengthen) the metallic bonding.[13] Both octahedral and distorted trigonal prismatic arrangements of iron atoms about carbon atoms are believed to feature in the various iron carbide phases that are so important in iron and steel production. Mankind has been exploiting the beneficial aspects of carbon hypercoordination, albeit unrecognized as such, since the dawn of the Iron Age.

To conclude this brief survey of the various types of compound known to contain hypercarbon atoms, Figure 1.6 shows examples of compounds in which *coordinatively unsaturated metal atoms* (metal atoms with fewer electrons in the valence shell than can be accommodated in a low-energy vacant AO) form strong *agostic* bonding interactions with neighboring C–H groups, effectively forming 3*c*–2*e* CHM bonds (where M is the metal). The term "agostic" was adopted for these systems (from the Greek "to hold or clasp to oneself, as of



$Fe_5(CO)_{15}C$
$[M = Fe(CO)_3]$

$Ru_6(CO)_{17}C$
$[M = Ru(CO)_3]$
$[M' = Ru(CO)_2]$



$Co_8(CO)_{18}C^{2-}$
(metal carbide core only)

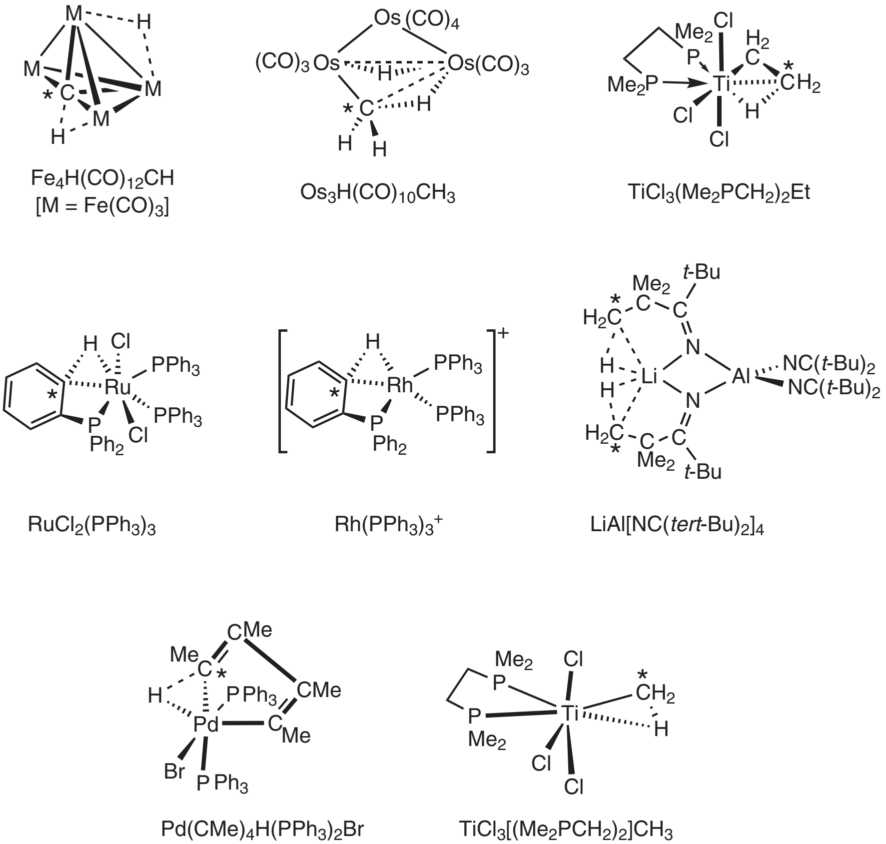
$Rh_6(CO)_{15}C^{2-}$
[M = RhCO]
(all edges CO bridged)

Figure 1.5. Metal carbides (* denotes hypercarbons).

a shield")[70] because the metal atoms distort the coordination spheres of the carbon atoms involved, drawing their CH units toward the metal, converting normal classically bonded carbon atoms into hypercarbon atoms. Such agostic systems attracted much interest because they showed how coordinatively unsaturated metal atoms could activate C–H bonds, not only in ligands already attached to the metal atom by another bond (generally a metal–carbon bond) but indeed by *coordination to the σ-bonding electrons* of otherwise uncoordinated alkanes. There is now a growing literature on what are referred to as *σ complexes*, complexes in which an H–E bond, where E = H, C, B, or Si, acts as a two-electron donor to a metal center. Such complexes are increasingly being seen as facilitating a variety of metathetical reactions at metal centers, as in *σ-complex-assisted metathesis (sigma-CAM) reactions*,[71] without the significant changes in metal oxidation states that accompany more traditional explanations invoking successive oxidative addition and reductive elimination reactions.

1.4. THE THREE-CENTER BOND CONCEPT: TYPES OF THREE-CENTER BONDS

In Section 1.2 we noted that the bonding in CH_5^+ could be described in terms of three 2*c*–2*e* C–H bonds and one 3*c*–2*e* C---H---H bond. In Section 1.3 we noted that 3*c*–2*e* C---H---M bonds could account for agostic interactions between coordinatively unsaturated metal atoms and substituent alkyl groups, and indeed for metal–alkane σ complexes. Similarly, 3*c*–2*e* M---C---M bonds



$Fe_4H(CO)_{12}CH$ [M = $Fe(CO)_3$]

$Os_3H(CO)_{10}CH_3$

$TiCl_3(Me_2PCH_2)_2Et$

$RuCl_2(PPh_3)_3$

$Rh(PPh_3)_3^+$

LiAl[NC(*tert*-Bu)$_2$]$_4$

$Pd(CMe)_4H(PPh_3)_2Br$

$TiCl_3[(Me_2PCH_2)_2]CH_3$

Figure 1.6. Agostic systems containing carbon–hydrogen–metal 3*c*–2*e* bonds (* denotes hypercarbons).

can be used to account for the bridged structures of metal alkyls, alkenyls, and aryls (Fig. 1.1). The hydrogen bridge across the middle of the cyclodecyl ring in 1,6-$Me_2C_{10}H_{17}^+$ (Fig. 1.2)[37] can be explained by a 3*c*–2*e* C–H–C bond.

Such bond schemes, illustrated in Figure 1.7, show that 3*c*–2*e* C---C---C, C---C---B, or C---B---B bonds may help us describe the bonding in pyramidal carbocations or carboranes, though resonance between several canonical forms (delocalization) may need to be invoked for the more symmetrical species. That section of the molecule over which delocalization of two- and three-center bonds occurs is represented by broken lines in Figure 1.7. Details of such bonding schemes are discussed in later chapters dealing with specific categories of compound. Here, however, it is appropriate to attempt to put such systems in perspective by noting their relationship to other examples of 3*c*–2*e* bonding, and by noting the characteristic features of such systems.

The simplest known example of a 3*c*–2*e* bond is that in the trihydrogen cation (H_3^+), the existence of which, in the gas phase, was first demonstrated

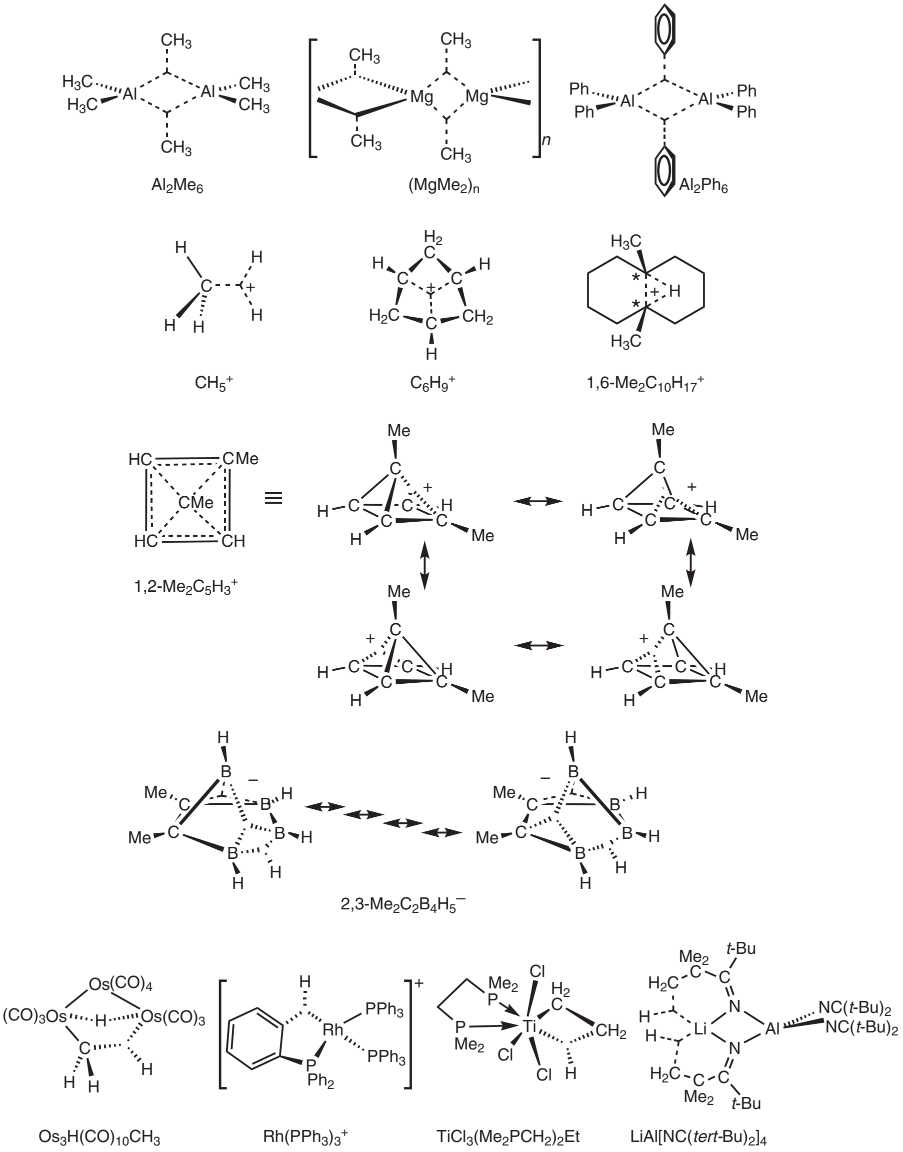


Figure 1.7. Two- and three-center–two-electron bonding schemes for representative compounds from Figures 1.1 to 1.6.

by J. J. Thompson[72] in 1911 (even before G. N. Lewis formulated his electron-pair theory[73] of chemical bonding). Later, much additional evidence was obtained for H_3^+ [74] even in solution chemistry (superacids).[75] The H_3^+ cation is the most abundant ion present when hydrogen gas is subjected to an electrical discharge. Its formation by the reaction $H_2 + H_2^+ \rightarrow H_3^+ + H$ is some

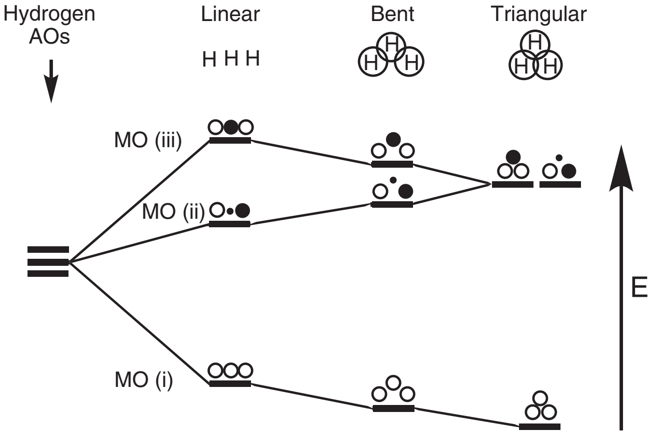


Figure 1.8. The H_3^+ cation; possible geometries and MO energies.

40 kcal mol^{-1} (170 kJ mol^{-1}) exothermic,[76] and this illustrates the power of two electrons to hold together three atomic nuclei at the corners of an equilateral triangle calculated to have an edge length of 0.87 Å,[76,77] some 0.12 Å longer than the single, 2*c*–2*e* bond length (0.75 Å) in the dihydrogen molecule, H_2. The 2*c*–1*e* bond in H_2^+ is 1.08 Å in length.[78] These lengths reflect the lower electron density in the H---H linkages in H_2^+ and H_3^+ compared with H_2. In three-center bonded systems in general, interatomic distances typically exceed those in related 2*c*–2*e*-bonded systems by about 0.15–0.25 Å.[27]

The three hydrogen nuclei in H_3^+ are effectively held together by the electronic charge that accumulates when the three hydrogen 1*s* AOs mutually overlap (Fig. 1.8). A linear arrangement of the three nuclei would allow less effective overlap of the AOs involved, as the MO correlation diagram in Figure 1.8 indicates. Note how the energy of the occupied bonding MO (that which corresponds to the 3*c*–2*e* bond) decreases as the shape changes from linear to bent to equilateral triangular, strengthening the bonding interaction between what were originally the terminal hydrogen atoms. Vibrational spectroscopic and calculational studies have substantiated the equilateral triangular structure.[74]

Similar orbital correlation diagrams can be constructed for other sets of three atoms contributing comparable AOs, in particular for XHX systems where the atom X, a carbon, boron, or metal atom, for example, contributes a *p* or *sp* hybrid AO (Fig. 1.9), although the antibonding orbitals MO (ii) and MO (iii) would not then become equal in energy for the triangular structure. Provided that the triatomic system needs to accommodate only one pair of electrons, a triangular arrangement is again preferred because this strengthens the 3*c*–2*e* X---H---X bond [stabilizing orbital MO (i)] by increasing X---X bonding at no expense to X---H bonding interactions. However, if two electron pairs have to be accommodated, as in the case of classical hydrogen bonds[79,80]

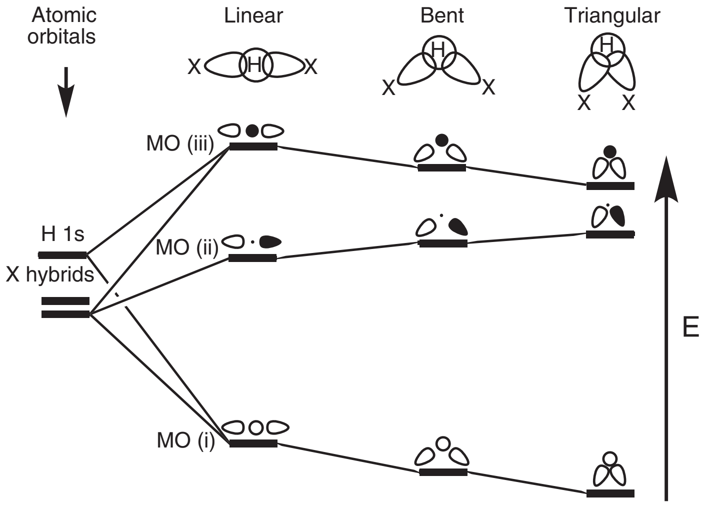
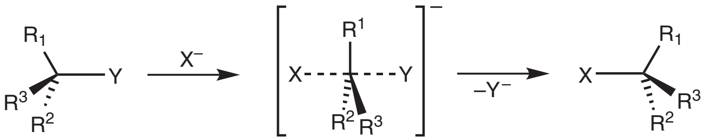


Figure 1.9. Triatomic XHX systems in which X uses a hybrid AO; possible geometries and MO energies.

with N–H---N, O–H---O, F–H---F, or similar units, then both MO (i) and MO (ii) will be occupied, and there is no incentive for the XHX system to bend, since any stabilization of MO (i) is offset by a greater destabilization of MO (ii), which is exclusively X---X antibonding. In *classical hydrogen-bonded systems*, where four electrons are involved, the unit X---H---X is linear, in contrast to the triangular shape preferred by the 3*c*–2*e* systems. (Many further examples of the way electron numbers influence molecular shape will be found in later chapters of this book, notably Chapters 3 and 4).

A different triatomic system with which it is instructive to contrast these systems is the XCY linear triatomic unit that features in the transition state in an S_N2 reaction [Eq. (1.3)]:



(1.3)

The carbon atom in the transition state is five-coordinate, and might at first sight appear to be pentavalent by apparently accommodating five pairs of electrons in its valence shell. However, this is not the case. First-row elements like carbon have no suitable low-energy AOs available to allow a total of 10 valence shell electrons.[81,82] In the transition state, the carbon atom can be assumed to use three sp^2 hybrid AOs to form classical 2*c*–2*e* bonds to the substituents R^1, R^2, and R^3, and we can treat it as a carbenium ion, $R^1R^2R^3C^+$, sandwiched between the incoming nucleophile, X^-, and the leaving group, Y^-,

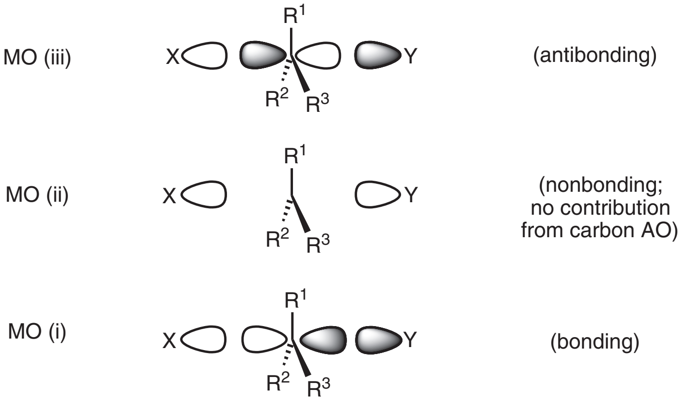
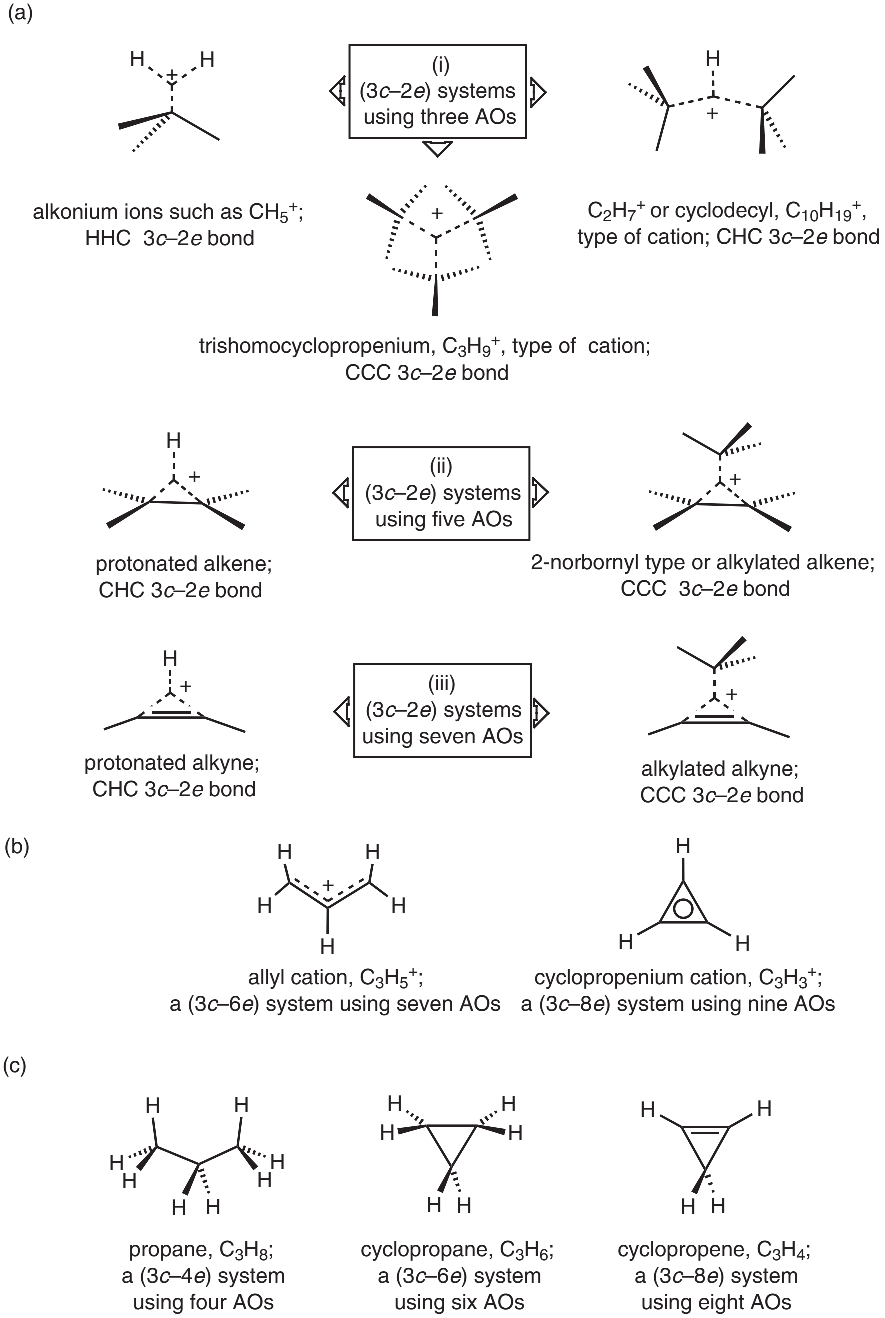


Figure 1.10. MOs involving the five-coordinate carbon atom in the transition state in an S_N2 reaction.

with which it can interact using its vacant 2*p* AO. The MO diagram for this system is shown in Figure 1.10. Once again, there is one strongly bonding MO, MO (i), formed from the carbon 2*p* AO and an out-of-phase combination of X^- and Y^- AOs, corresponding to a linear 3*c*–2*e* bond. The next MO, MO (ii), has no contribution from the carbon 2*p* AO, because it consists of an in-phase combination of the orbitals on X and Y, a combination of the wrong symmetry to combine with the carbon *p* AO. It is this MO, sharing a pair of electrons between X and Y but *not* involving the carbon atom, that accommodates the second pair of electrons in the triatomic system (X^- and Y^- contribute a pair apiece). These electrons therefore do *not* add to the four pairs already associated with the carbon atom's valence shell.

The $(XCR^1R^2R^3Y)^-$ system just discussed, and the classical hydrogen bonds mentioned earlier, are examples of triatomic systems that have to accommodate two pairs of electrons, each atom contributing one AO (see also Reference 83). There are many other systems in which two pairs of electrons fulfill a bonding role between three atomic nuclei, but in which one or more of the atoms contributes more than one AO with which to bond to its two neighbors. The various possibilities for hydrocarbon systems are shown in Figure 1.11, together with some classically bonded systems. The numbers of electrons and AOs listed are those available to link the three atoms concerned, the other AOs being used for σ bonds to hydrogen or carbon atoms.

From Figure 1.11(a), (i)–(iii), it is evident that 3*c*–2*e* σ bonding can occur between three carbon atoms, or between two carbon atoms and a hydrogen atom, in circumstances where (1) there is no other bonding between the three atoms concerned, (2) two of the atoms are linked by a single (2*c*–2*e*) bond as well, or (3) two of the atoms are linked by a double (2*c*–4*e*) bond as well. *The requirements for 3c–2e bonding are thus: Either all three atoms concerned contribute one AO apiece, or one of the atoms concerned contributes only one AO,*



alkonium ions such as CH_5^+;
HHC 3*c*–2*e* bond

$C_2H_7^+$ or cyclodecyl, $C_{10}H_{19}^+$,
type of cation; CHC 3*c*–2*e* bond

trishomocyclopropenium, $C_3H_9^+$, type of cation;
CCC 3*c*–2*e* bond

protonated alkene;
CHC 3*c*–2*e* bond

2-norbornyl type or alkylated alkene;
CCC 3*c*–2*e* bond

protonated alkyne;
CHC 3*c*–2*e* bond

alkylated alkyne;
CCC 3*c*–2*e* bond

allyl cation, $C_3H_5^+$;
a (3*c*–6*e*) system using seven AOs

cyclopropenium cation, $C_3H_3^+$;
a (3*c*–8*e*) system using nine AOs

propane, C_3H_8;
a (3*c*–4*e*) system
using four AOs

cyclopropane, C_3H_6;
a (3*c*–6*e*) system
using six AOs

cyclopropene, C_3H_4;
a (3*c*–8*e*) system
using eight AOs

Figure 1.11. Three-center bonding possibilities for some cationic and neutral hydrocarbon systems. (a) Some σ delocalized systems; (b) some π delocalized systems; (c) some related electron-precise hydrocarbons.

and the total number of electrons available for bonding between the three atoms is one fewer than the number of AOs available.

If each of the three atoms involved uses more than one AO, and if the number of electrons available is one fewer than the number of AOs, then $3c$–$2e$ π bonding can occur, as shown by the examples of the allyl and cyclopropenium cations [Fig. 1.11(b)]. The difference arises because the establishment of a framework of $2c$–$2e$ σ bonds between two or all three of the carbon atoms limits the three-center bonding to that arising from p AOs oriented perpendicular to the plane in which the carbon atoms lie.

Also shown in Figure 1.11(c), for purposes of comparison, are three neutral classically bonded hydrocarbons, propane, cyclopropane, and cyclopropene. For these systems, and for electron-precise systems in general, the number of electrons available for bonding (n) is equal to the number of AOs available (and so precisely the right number to fill the $n/2$ bonding MOs).

Note that the systems in Figure 1.11 that have $3c$–$2e$ bonds, whether σ [Fig. 1.11(a)] or π [Fig. 1.11(b)], are *cationic*, as is necessary if the number of AOs is to exceed the numbers of electrons available. Noting this allows us to envisage carbocations and their neutral hydrocarbon precursors or products of their possible decomposition (Fig. 1.12), points that will prove relevant to a consideration of the mechanisms of reactions involving hypercarbon intermediates or transition states. Thus, protonation of a $2c$–$2e$ C–H bond can be envisaged as a means of generating a $3c$–$2e$ CHH bond, while protonation of a $2c$–$2e$ C–C bond can in principle lead to a $3c$–$2e$ CHC bond. Similar protonation of a carbon–carbon multiple bond, whether double or triple, converts a pair of carbon–carbon π-bonding electrons into a pair of $3c$–$2e$ C---H---C σ-bonding electrons. Figure 1.12 also serves as a reminder that carbocationic species requiring a $3c$–$2e$ C---H---C or C---C---C bond may revert to, or indeed be less stable than, a classically bonded carbenium ion structure in which one of the available AOs remains unused (as a $2p$ AO on the carbocationic center, oriented perpendicular to the plane of the σ bonds to that center).

Before turning from a consideration of three-center bond systems to ones in which the bonding is more delocalized, it is worth noting briefly what other types of systems exhibit $3c$–$2e$ σ bonding, to set these carbon systems in a more general context. We have already noted that bridged metal alkyls and aryls exhibit $3c$–$2e$ M---C---M bonding (where M is an electropositive metal atom, Figure 1.1) and that coordinatively unsaturated metal atoms can convert $2c$–$2e$ C–H bonds into $3c$–$2e$ C---H---M bonds (Fig. 1.6). These and the various other three-center bonding possibilities open to organometallic systems are summarized in Figure 1.13, which shows the relationship between the systems already mentioned and metal–alkene or metal–alkyne complexes, and protonated metal–carbenes and metal–carbynes. It should be mentioned, however, that although the metal–alkene and metal–alkyne interactions shown in Figure 1.13 indicate the type of weak bonding that the coordinatively unsaturated metal atoms of monomeric aluminum trialkyls AlR_3 can participate in with alkenes or alkynes, they show only part of the metal–carbon bonding that

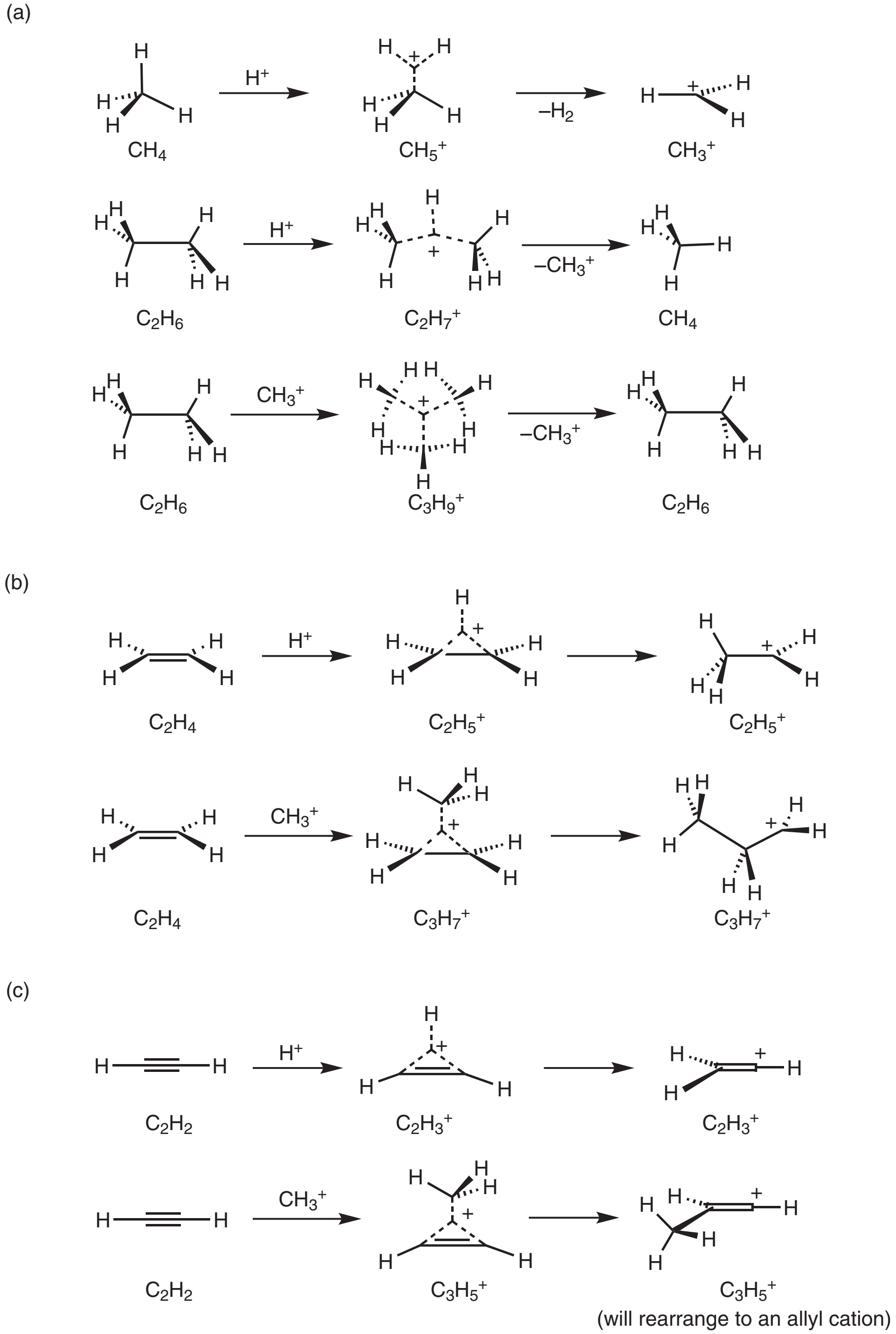


Figure 1.12. Different types of hypercoordinated carbocations; formation from hydrocarbon precursors by protonation or alkylation and cleavage products. (a) Three-center–two electron (3*c*–2*e*) systems; (b) three-center–four electron (3*c*–4*e*) systems; (c) three-center–six electron (3*c*–6*e*) systems.

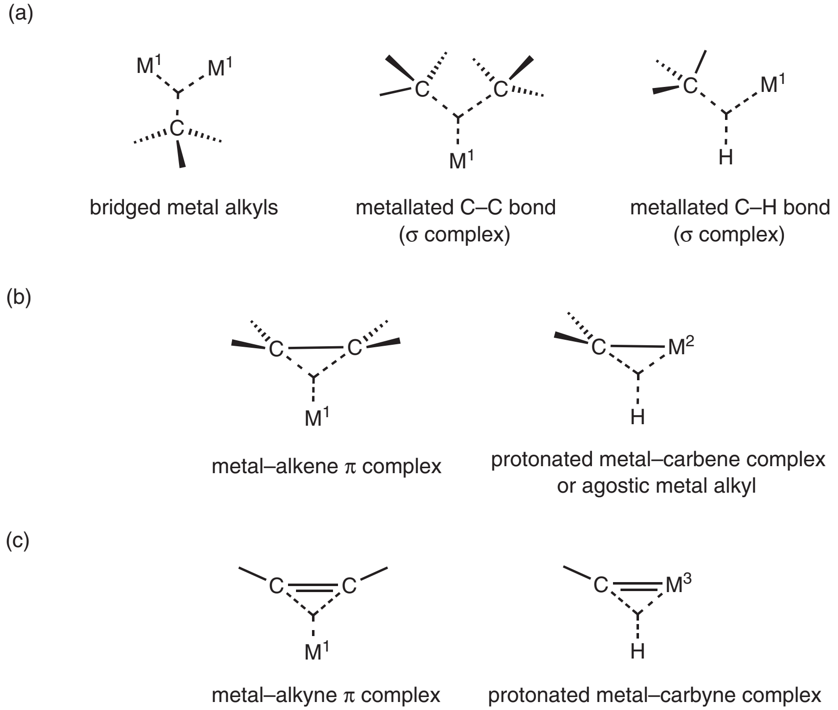


Figure 1.13. Three-center bonding possibilities for organometallic systems. M^n represents a metal-containing unit where the superscript number n indicates the number of metal AOs that unit contributes to bond to the other two atoms. (a) Three-center–two electron (3*c*–2*e*) systems; (b) three-center–four electron (3*c*–4*e*) systems; (c) three-center–six electron (3*c*–6*e*) systems.

occurs in the relatively stable complexes of alkenes and alkynes with transition metals, such as the earliest reported such complex, Zeise's salt, $KPtCl_3(C_2H_4)H_2O$.[84,85]

Very stable alkene complexes of this type are formed by metal atoms that can contribute not only the vacant AO into which to draw electronic charge from the filled carbon–carbon π-bonding MO [Fig. 1.14(a), (i)], but also a filled *pd* hybrid AO that can transfer electronic charge back into the alkene's empty π-antibonding MO [Fig. 1.14(a), (ii)].[86] The net result is to convert the MCC triatomic system from a four-electron, five-AO system in the case of a metal like aluminum [Fig. 14(b), (i)] into a six-electron, six-AO system for a metal like platinum, for which an electron-precise bonding description is possible [Fig. 1.14(b), (ii)].

To place these 3*c*–2*e* carbon systems in a wider context, it should be noted that 3*c*–2*e* bonding is widespread in inorganic chemistry, principally in the chemistry of elements to the left of carbon in the periodic table, which is in the chemistry of boron and the metallic elements in general.[7,10–12,14–17,78] This is

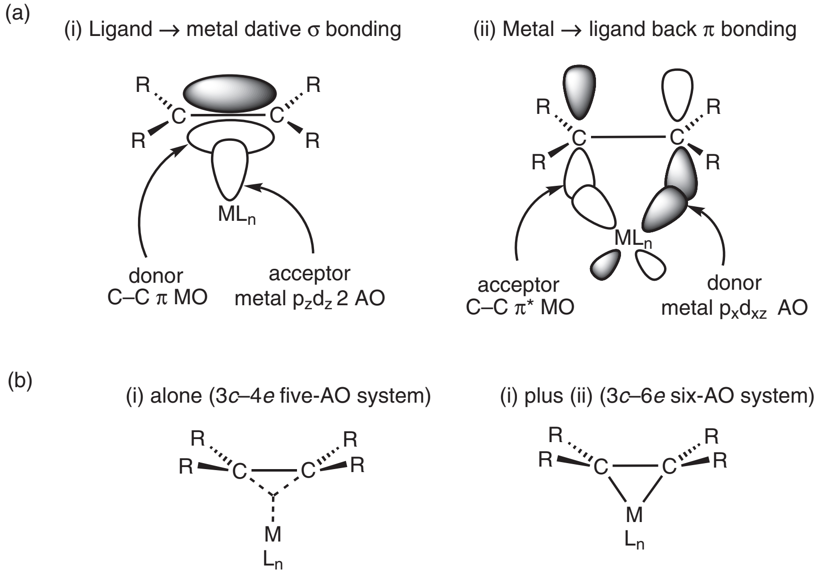


Figure 1.14. Bonding in transition metal–alkene complexes. (a) Orbitals involved; (b) valence bond representations.

because such elements generally have more valence shell AOs than electrons, and so need to spread the bonding power of these electrons over a larger number of centers than elements like carbon, with equal numbers of valence shell electrons and AOs, or elements to the right of carbon (in Groups 15–18) that have more valence shell electrons than AOs. Indeed, the concept of three-center, two-electron bonding, which had been suggested tentatively earlier, really only first made a significant impact in the 1940s and 1950s, when it proved invaluable, in the work of pioneers like H. C. Longuet-Higgins[87] and W. N. Lipscomb,[88] in explaining the intricate networks of atoms revealed by structural studies on boron hydrides such as B_2H_6, B_4H_{10}, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$, where localized 3*c*–2*e* B---H---B and B---B---B bonds, used together with 2*c*–2*e* B–H and B–B bonds, neatly accounted for structures that defied description solely in terms of 2*c*–2*e* bonds.

Because analogies between hypercarbon systems and their isoelectronic polyborane counterparts will provide a recurrent theme in this book, we show in Figure 1.15 the structures and bond networks of some boron hydrides alongside their organic counterparts, generated by replacing BH units in the borane by carbon atoms in the hydrocarbon. Note that where 3*c*–2*e* B---H---B bonds are needed to describe the bonding in the borane, 2*c*–2*e* C–C bonds are needed to describe the carbon–carbon bonding in the hydrocarbon, and where 3*c*–2*e* B---B---B bonds are needed to describe the bonding in the borane, 3*c*–2*e* C---C---C bonds are needed in the hydrocarbon. The ^{11}B and ^{13}C chemical shifts of isoelectronic boranes and carbocations showed how similar their

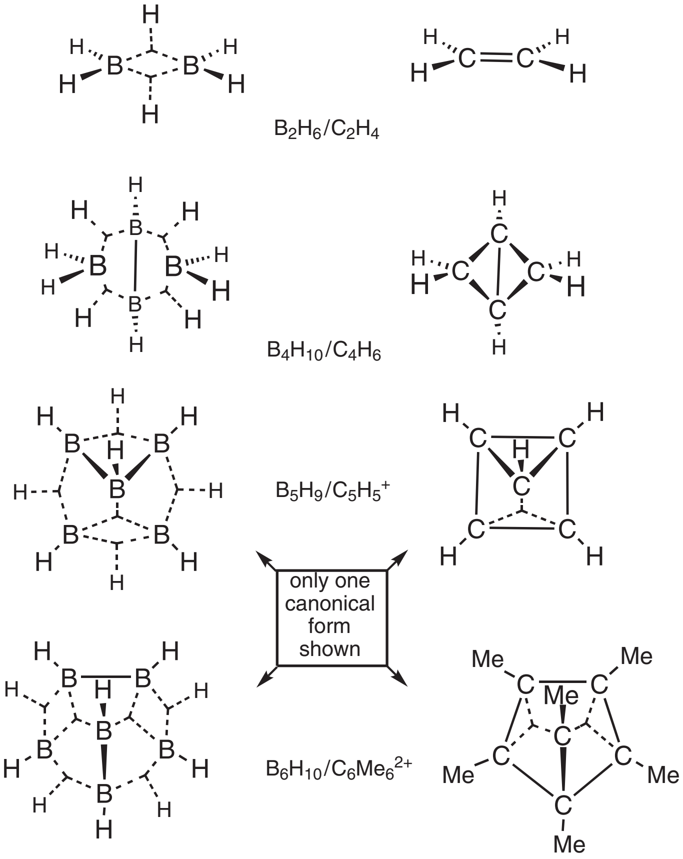


Figure 1.15. Two- and three-center bond networks in some boron hydrides and their hydrocarbon counterparts.

structures must be before these were unambiguously confirmed (see Chapter 5, Section 5.8). We shall explore these points further, and the utility of other types of 3*c*–2*e* bonds between carbon and hydrogen, boron and/or metal atoms, in later chapters of this book. Figure 1.16 lays out in diagrammatic form the various types of trinuclear systems held together by 3*c*–2*e* bonds that we shall be concerned with in later chapters. X-ray evidence is available for examples of most of these, and spectroscopic and ab initio calculational support is available for the remainder (the species involved are short-lived).

1.5. THE BONDING IN MORE HIGHLY DELOCALIZED SYSTEMS

Thus far, our discussion of the bonding in hypercarbon systems has focused on various types of three-center bonding situations, noting the importance of

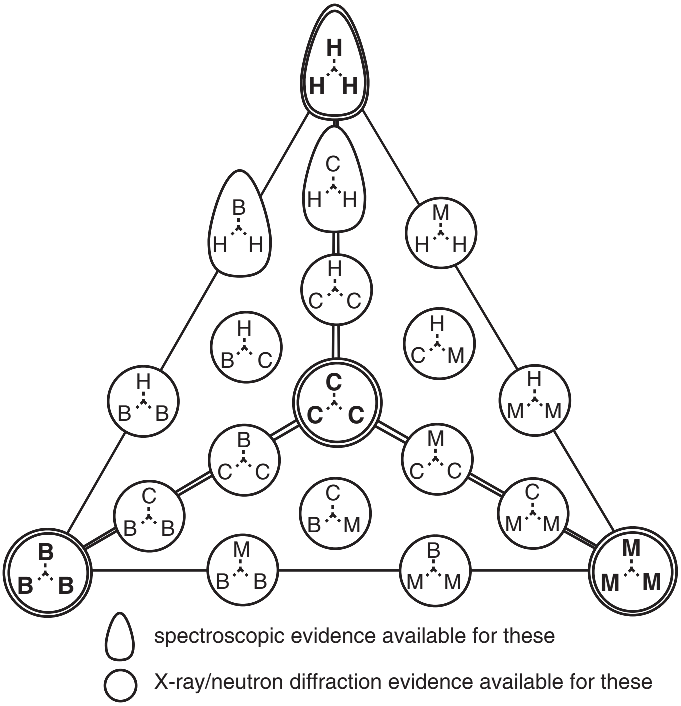


Figure 1.16. The various triatomic arrangements of carbon, hydrogen, metal, and/or boron atoms that can be linked by 3*c*–2*e* σ bonds.

the spatial arrangement of the three atoms (linear, bent, or triangular) and the numbers of electrons and AOs available to hold those atoms together. Such three-center bonding descriptions can be applied to a wide range of hypercarbon systems, notably to bridged metal alkyls, many carbocations, agostic systems, and σ complexes in which otherwise coordinatively unsaturated metal atoms interact with suitably located C–H groups in ligands, or with C–H, B–H, Si–H or other 2*c*–2*e* bonds in substituents or reagent molecules. However, when hypercarbon atoms participate in highly symmetrical systems such as the pyramidal carbocations $C_5H_5^+$ or $C_6Me_6^{2+}$, description of the bonding in terms of specific networks of two- and three-center electron-pair bonds is less satisfactory; resonance between all possible ways of arranging these bonds needs to be invoked, blurring the bonding picture created. *Resonance delocalization* of the two- and three-center bonds over a whole section of a molecule or ion contributes to the stability of such systems, and must be taken into account in considering the distribution of electron density over the network of atoms involved.

For example, for the square pyramidal cation $C_5H_5^+$ and derivatives thereof (Figs. 1.7 and 1.15), there are four ways of assigning the 3*c*–2*e* C---C---C bond and two 2*c*–2*e* C–C bonds that, in localized bonding terms, link the apical carbon atom to the four basal atoms. To assess how many electrons on average are available for each two-center link between the apical carbon atom and the four basal carbon atoms or between basal atoms, we can regard a 2*c*–2*e* C–C bond as assigning one electron pair to the link concerned, whereas a 3*c*–2*e* C---C---C bond effectively contributes one-third of an electron pair to each of the three CC edges of the triangle in which it lies. Hence, on average, each of the four 2-center links holding the apical to the basal carbon atoms in $C_5H_5{}^+$ is associated with two-thirds of an electron pair, and so can be regarded as a two-center link of fractional bond order 0.67.

Each of the basal CC links, already having had a pair of electrons assigned to it because of the 2*c*–2*e* σ bond along that basal edge, also gains on average one-twelfth of an electron pair as its share of the 3*c*–2*e* C---C---C bond pair, giving it an overall bond order of 13/12 (1.08; Fig. 1.17).

Similar arguments applied to the pentagonal pyramidal dication $(C_6Me_6)^{2+}$ (Fig. 1.17) in which one 2*c*–2*e* C–C bond and two 3*c*–2*e* C---C---C bonds link the apical carbon atom to the five basal carbon atoms, lead to the following C–C bond orders in the C_6 pyramid: apical–basal links, 7/15, which is 0.47; and basal–basal links, 17/15, which is 1.13.

The use of localized two- and three-center bond schemes gets progressively more complicated and less helpful as the symmetry of the system increases.

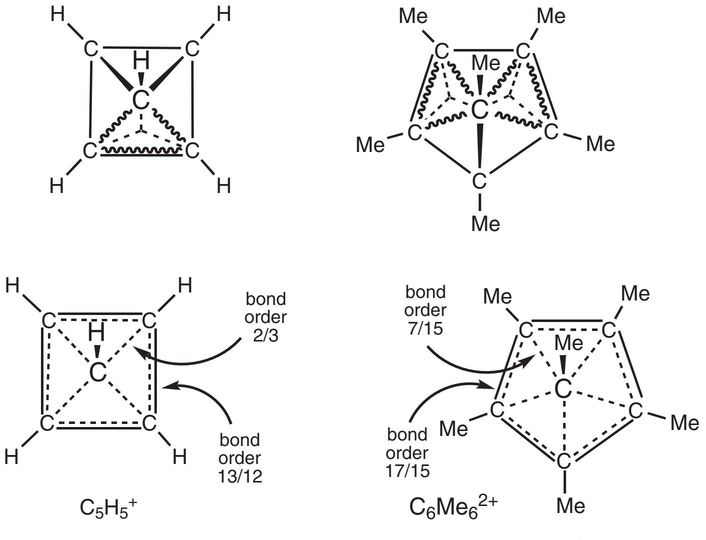


Figure 1.17. Bond orders in pyramidal cations $C_5H_5{}^+$ and $C_6Me_6{}^{2+}$ indicated by two- and three-center electron-pair networks. Top: each full line linking two C atoms in these canonical forms represents one electron pair; each wavy line linking two C atoms represents one-third of an electron pair. Bottom: allowing for resonance between the four ($C_5H_5{}^+$) or five ($C_6Me_6{}^{2+}$) ways of allocating such bond networks to these pyramidal species generates the following two-center bond orders (numbers of electron pairs per C–C link).

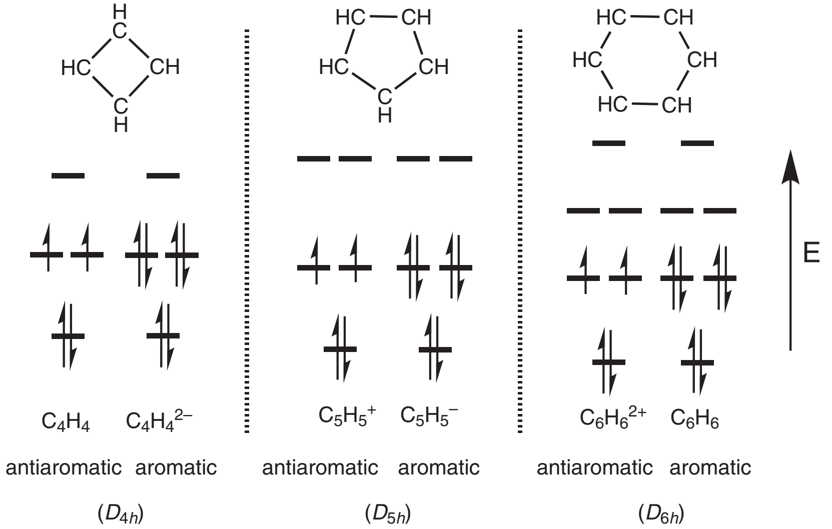


Figure 1.18. MO diagrams showing how neutral C_4H_4 and cationic $C_5H_5^+$ and $C_6Me_6^{2+}$ would be antiaromatic if polygonal.

MO treatments are preferred in such cases. The manner in which these same cations, $(C_5H_5)^+$ and $(C_6Me_6)^{2+}$, can be treated in MO terms is worth illustrating here for the purpose of comparison with the localized bond schemes just discussed, and also to underline the relationship between these pyramidal systems and normal aromatic ring systems.

The cations $C_5H_5^+$ and $C_6Me_6^{2+}$ are examples of species that would be described as *antiaromatic* if they had two-dimensional regular polygonal structures. With only four electrons to assign to the π system in each case, they would have triplet ground-state electronic configurations, with one electron in each of the doubly degenerate highest occupied molecular orbitals (HOMOs). (The neutral cyclobutadiene, C_4H_4, would be a member of the same series if it had a D_{4h} square planar structure.) The preferred pyramidal structures offer two main advantages: They generate closed-shell electronic configurations and provide a more strongly bonding role for the electrons in the HOMOs.

These points are illustrated in Figure 1.18, which shows how the doubly degenerate nature of the HOMO of the π system leads to triplet electronic configurations for D_{4h} (C_4H_4), D_{5h} $(C_5H_5)^+$, and D_{6h} ($C_6H_6^{2+}$ or $C_6Me_6^{2+}$) ring systems. In Figure 1.19, we show how the framework MOs of square pyramidal (C_{4v}) $C_5H_5^+$ can, in principle, be constructed by bringing the apical CH^+ unit down along the fourfold axis of a basal square planar C_4H_4 residue. The apical CH^+ unit supplies a pair of electrons that can be considered, in the isolated unit, to occupy an *sp* hybrid AO pointing away from the C–H bond. This AO has the right symmetry to combine with the fully symmetric combination of *p* orbitals on the C_4H_4 species (the lowest energy π-bonding MO) to form a nondegenerate framework-bonding MO. The pair of AOs of the CH^+ unit

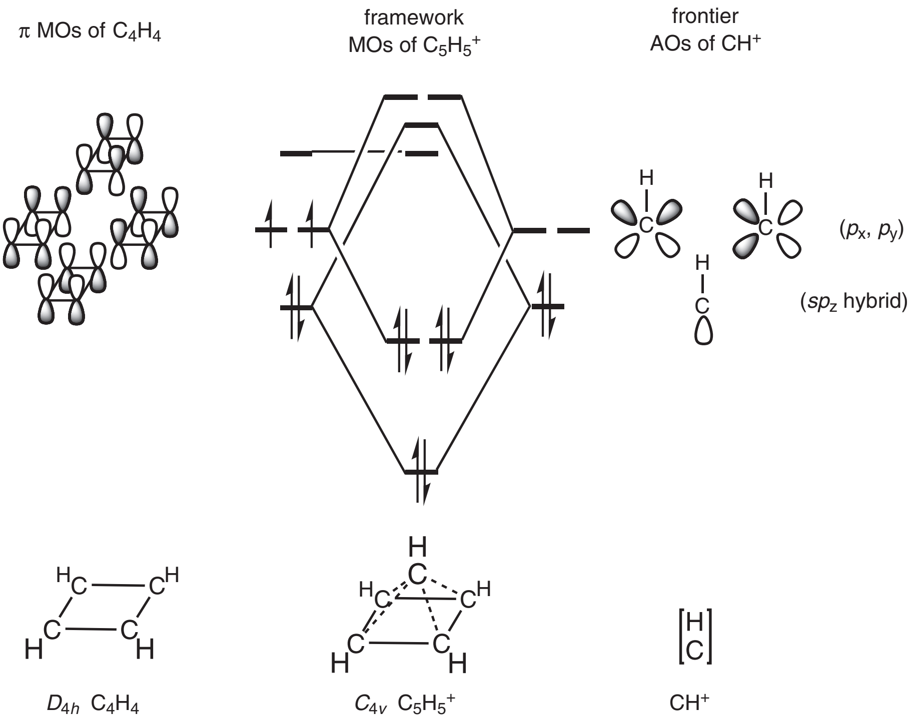


Figure 1.19. Framework MOs of pyramidal C_{4v} $C_5H_5^+$ generated from the π MOs of planar D_{4h} C_4H_4 and the frontier AOs of a CH^+ unit.

perpendicular to the C–H bond interacts with the half-filled degenerate HOMOs of C_4H_4 to convert them from the carbon–carbon nonbonding role they would play in D_{4h} C_4H_4 into a degenerate pair of bonding MOs that considerably strengthen the bonding between the apical and basal atoms. The four electrons in the HOMOs of the basal C_4H_4 unit, together with the pair in the *sp* hybrid AO of the apical CH^+ unit, provide the three pairs needed for a closed-shell electronic configuration.

A similar treatment of $C_6Me_6^{2+}$, considered to be generated by bringing an apical CMe^+ unit down along the fivefold axis to a pentagonal $C_5Me_5^+$ species, is illustrated in Figure 1.20. Again, electrons that at best play a weakly bonding role in the case of the planar ring system $C_5Me_5^+$ acquire a strongly bonding role in the pyramidal cationic product.

These MO treatments of the bonding in pyramidal cations, exploring the interaction between the π MOs of the basal C_nH_n ring with the AOs of the capping CH^+ unit, closely parallel the usual treatment of the metal–carbon bonding in metal complexes of C_nH_n ring systems.[11,16,89] The bonding in $C_5H_5^+$ thus closely resembles that in the iron carbonyl-cyclobutadiene complex $(C_4H_4)Fe(CO)_3$ (Fig. 1.4), while that in $C_6Me_6^{2+}$ resembles that in the pentamethylcyclopentadienyl-manganescarbonyl complex $(C_5Me_5)Mn(CO)_3$

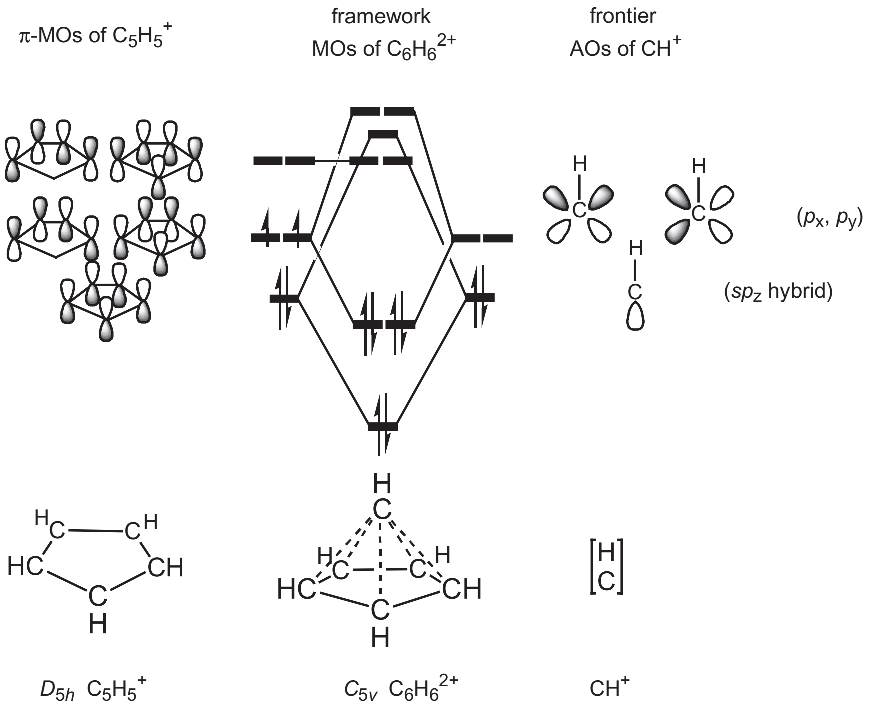


Figure 1.20. Framework MOs of pyramidal C_{5v} $C_6H_6^{2+}$ generated from the π MOs of planar D_{5h} $C_5H_5^+$ and the frontier AOs of a CH^+ unit.

(Fig. 1.4), or indeed in ferrocene, $Fe(C_5H_5)_2$. This is because such units as CH^+ and $Fe(CO)_3$ or $[Mn(CO)_3]^-$ have very similar frontier orbital characteristics with which to bond to other units.[89] Though not isoelectronic, they are *isolobal.*[90,91] *Their frontier orbitals have similar energies, extensions in space, and lobal characteristics*, which enables them to participate in the same types of bonding (Fig. 1.21).

The development of the concept of isolobality, as a means of recognizing the common bonding characteristics of what might seem to be quite disparate entities, owes much to the experimental studies of organometallic and metallacarborane systems containing hypercarbon atoms that showed what types of metal-containing residues might replace CH or BH units of C_nH_n rings or carboranes, as will be discussed in Chapter 3.

1.6. REACTIONS INVOLVING HYPERCARBON INTERMEDIATES

For most of the systems discussed so far, hypercoordinated carbon atoms have featured in the most stable forms of the compounds in question. For example, the bridged metal alkyl structures found by X-ray studies on crystalline samples of such substances as $(AlMe_3)_2$[30] or $(LiMe)_4$[32] persist in solutions of

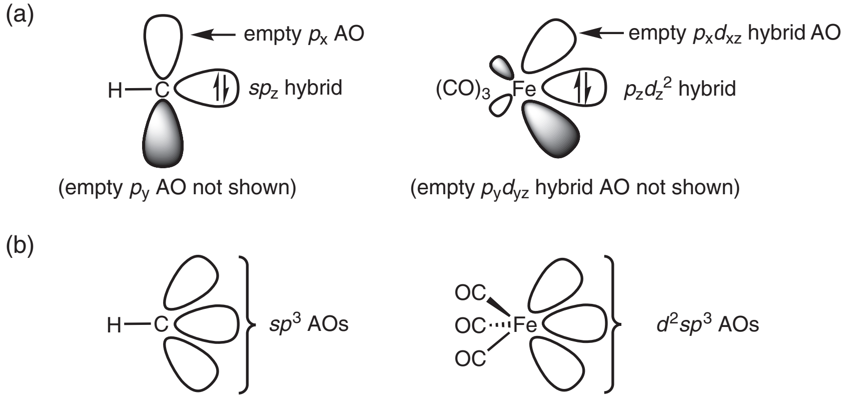
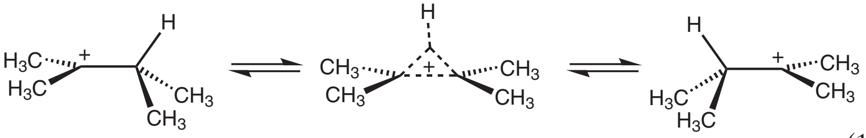


Figure 1.21. The isolobal relationship between a CH^+ unit and an $Fe(CO)_3$ unit. (a) Furnishing one radially oriented AO and two tangentially oriented AOs; (b) furnishing three trigonally oriented AOs.

these compounds in inert (hydrocarbon) solvents, and the shapes of the pyramidal cations $C_5Me_2H_3^+$ [38,39] and $C_6Me_6^{2+}$ [40] were originally deduced from ^{13}C and ^1H nuclear magnetic resonance (NMR) studies on solutions in acid media. For other systems, however, structures explicable solely in terms of classical 2*c*–2*e* bonds may be more stable than alternative structures involving hypercarbon atoms, which provide low-energy transition states through which rearrangement may occur, as in the case of the degenerate rearrangement of the tetramethylethyl cation ($Me_2CCMe_2H^+$), a process for which the activation enthalpy $\Delta H^{\ddagger}$ is $<3\,\text{kcal}\,\text{mol}^{-1}$ [Eq. (1.4)]:[92]

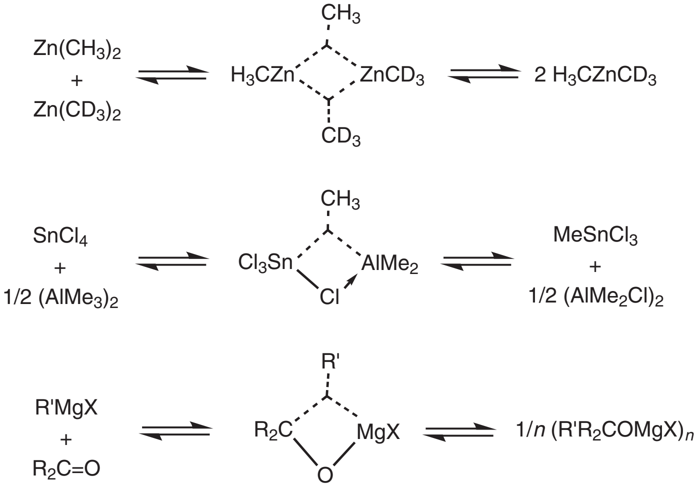


(1.4)

In Chapter 6, we shall draw attention to the wide range of reactions now seen to involve hypercarbon intermediates. We give a few examples here to illustrate their scope.

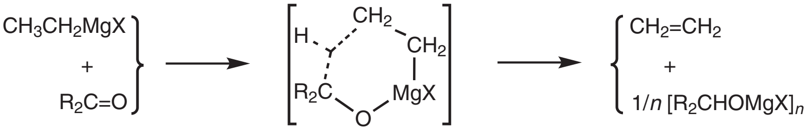
Although the bridged structures of metal alkyls[7–9] such as $(AlMe_3)_2$ and $(MgMe_2)_n$ are not mimicked by their congeners $GaMe_3$ and $ZnMe_2$, which are monomeric, those bridged structures show how alkyl groups may readily be transferred from one metal atom to another, or from a metal atom to a carbon atom, via hypercarbon intermediates or transition states (Scheme 1.2)

The manner in which ethyl Grignard reagents[93] (and many other metal alkyls with hydrogen atoms attached to their β-carbon atoms) can function as reducing agents by alkene elimination and β-hydrogen transfer probably also involves hypercarbon species [Eq. (1.5)]. Similar hypercarbon species appear



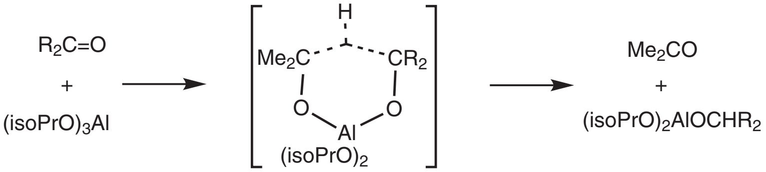
Scheme 1.2

to be involved when alkyls of lithium [Eq. (1.6)] and aluminum (Scheme 1.3) undergo β-hydrogen elimination reactions and in Merwein–Ponndorf–Verley reductions and Oppenauer oxidations[94,95] [Eq. (1.7)]. Related 6-membered ring species appear possible in olefin exchange reactions of alkylboranes[96] [Eq. (1.8)]:

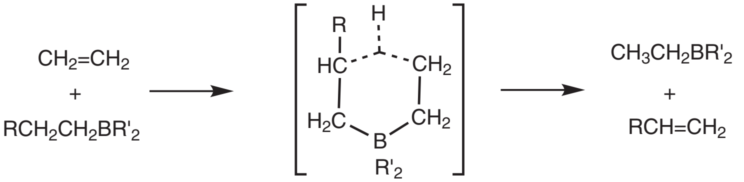


(1.5)

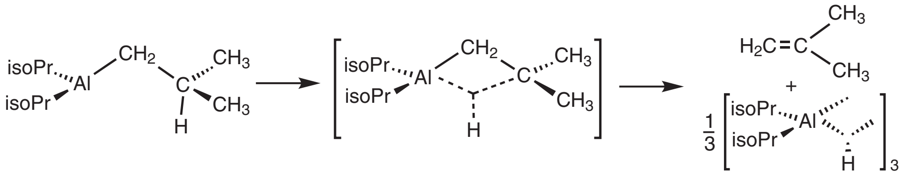
$$1/n\,[CH_3CH_2CH_2CH_2Li]_n \xrightarrow[-CH_3CH_2CH{=}CH_2]{\text{reflux in octane}} 1/n\,[LiH]_n \tag{1.6}$$



(1.7)



(1.8)

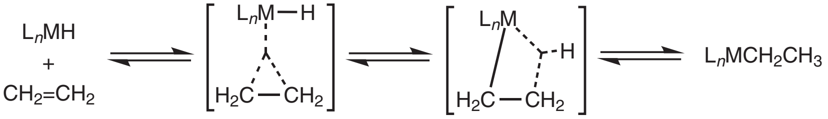


$sec\text{-}BuAl(isoPr)_2 \longrightarrow 1/3\ [(isoPr)_2AlH]_3 + \text{isobutylene}$

Scheme 1.3

The involvement of hypercoordinated carbon species in S_N2 reactions was commented on in Section 1.4 (Fig. 1.10). Compounds have been synthesized[97] that keep the displaced and displacing atoms close to the carbon atom undergoing nucleophilic substitution, in order that the relative energies of the classically bonded reagent or product and the hypercoordinated transition state can be both more readily assessed and modified (see Chapter 6).

The many reactions that involve insertion of alkenes or alkynes into metal–carbon or metal–hydrogen bonds provide further examples of hypercoordination of carbon atoms during reactions.[98] For example, an alkene may coordinate to the coordinatively unsaturated metal atom of a metal hydride complex prior to inserting into the metal–hydrogen bond [Eq. (1.9)]:



(1.9)

The hydroboration reaction, the dehydroboration reaction[99] (not to be confused with olefin exchange reactions of alkylboranes), and organoborane rearrangement reactions[100–103] (in which organoboryl residues R_2B migrate along alkyl chains) are examples of this type of reaction (Fig. 1.22). This last reaction was commonly supposed to entail successive dissociation and association steps in which a dialkylborane residue R_2BH separated from the carbon chain and then recombined in the reverse orientation.[99] That this mechanism was not general was shown by the way that, in some cases, the hydrocarbon chain retained its stereochemical integrity,[100,101,103] a feature incompatible with the intermediacy of an alkene. The retention of the hydrocarbon stereochemistry poses no problem, however, if the boryl group, R_2B, becomes attached to the next carbon atom along the chain before becoming detached from its original site (Fig. 1.22). Its mode of travel along the hydrocarbon chain, as if swinging from branch to branch, has been aptly described as "molecular brachiation."[104]

Oxidative-addition reactions of transition metal complexes with the C–H bonds of saturated or unsaturated organic groups, whereby organometal

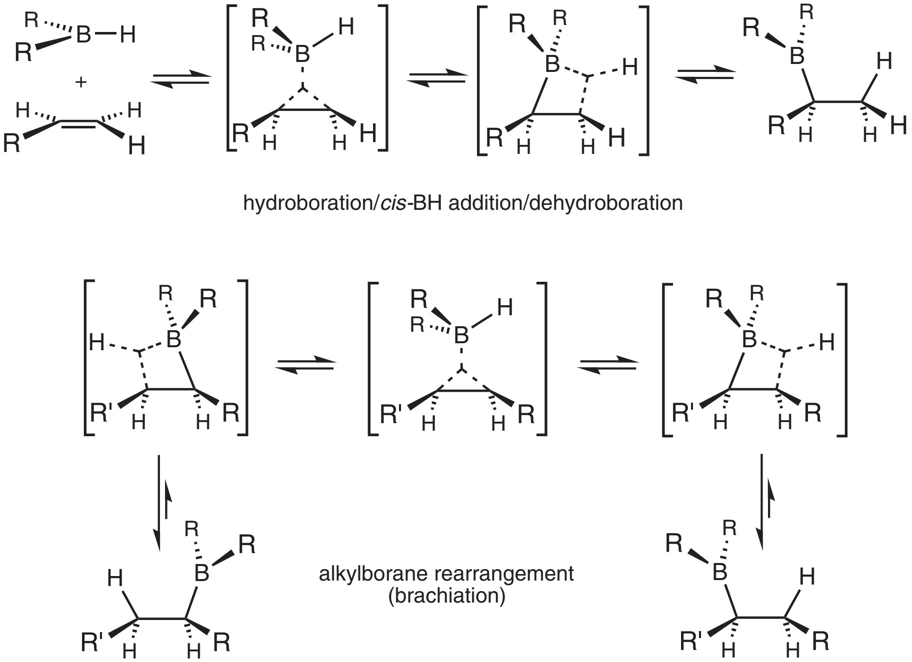
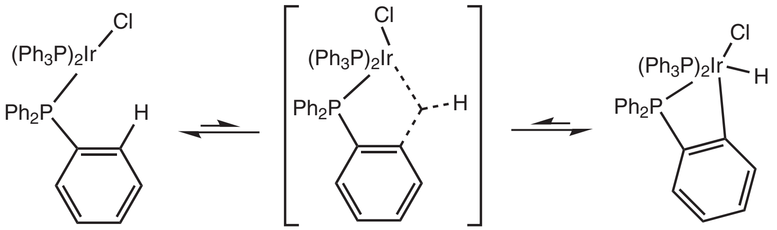


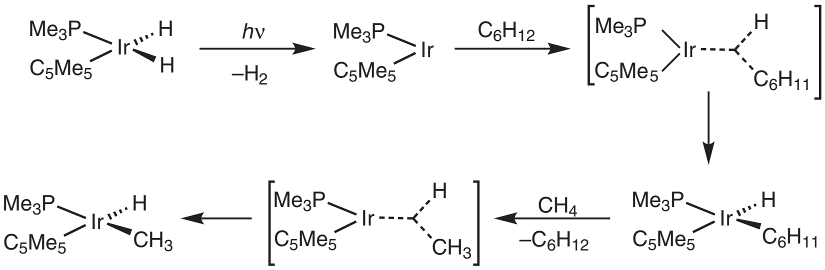
Figure 1.22. Involvement of hypercarbon intermediates in the hydroboration, dehydroboration and alkylborane rearrangement (brachiation) reactions.

hydride complexes are formed, and their reverse reactions, *reductive eliminations*, provide yet further examples of important reactions that involve hypercoordinated carbon atoms. The largest group of such reactions, *orthometallation reactions*, involves the intramolecular formation of a metal–carbon bond to the nearest carbon atom of an aromatic ring already linked to the metal atom through another atom[105] [Eq. (1.10)]:



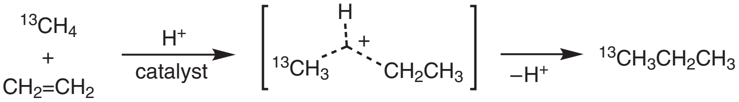
(1.10)

Intermolecular reactions between coordinatively unsaturated metal atoms and the C–H groups of relatively unreactive hydrocarbons such as cyclohexane and even methane have been reported (Scheme 1.4).[106] Insertion reactions of carbenes R^1R^2C into C–H or other bonds are clearly of the same type, the carbene carbon atom playing the role of the coordinatively unsaturated metal

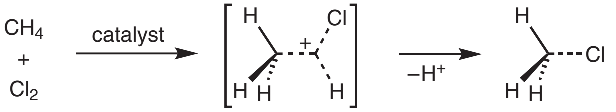


Scheme 1.4

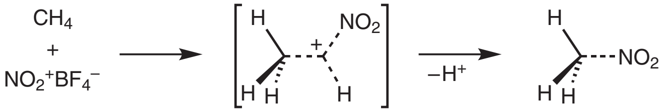
in the reactions just cited (see also insertion reactions of nitrenes, etc.) Typical electrophilic substitution reactions of alkanes, including methane, are exemplified in the ethylation of the latter (labeled with ^{13}C) with ethylene over superacid catalyst [Eq. (1.11)].[107] The key step is the insertion of the highly electron-deficient trivalent carbon atom of an ethyl cation $(MeCH_2)^+$ into a methane $^{13}C–H$ bond forming the pentacoordinate carbocation $(H_3{}^{13}CHCH_2Me)^+$ shown. Similar substitutions of methane include electrophilic chlorination [Eq. (1.12)],[108] nitration [Eq. (1.13)],[109] and related reactions:[5]



(1.11)



(1.12)



(1.13)

These and other reactions believed to involve hypercarbon intermediates are discussed in Chapter 6.

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