Chapter 1

Planarizing Distortions at Carbon

1.1 Introduction

In 1874 it was suggested independently both by van't Hoff[1] and le Bel[2] that the arrangement in space of the substituents at a tetracoordinate carbon is such that they form a tetrahedral geometry. Van't Hoff wrote that,[†]

> "… theory is brought into accord with the facts if we consider the affinities of the carbon atom directed toward the corners of a tetrahedron of which the carbon atom itself occupies the center."

Similarly, le Bel, who was considering the same problem of isomerism in the fatty acids, wrote that,

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[†] Van't Hoff's proposal was general but was born of the problem of uniting the structural theory and experimental evidence for the isomers (both structural and "physical") of the fatty acids.

> "… we are obliged to admit that the four atoms A occupy the angles of a regular tetrahedron, whose planes of symmetry are identical with those of the whole molecule MA_4; in this case no bisubstitution product can have rotatory power."

These concepts quickly propelled structural chemistry into the three-dimensional realm which today seems only too natural. Remarkably, van't Hoff was attacked vehemently for his theory by Hermann Kolbe.[†] Kolbe[3] called it a "play of imagination" which "forsakes the solid ground of fact and is quite incomprehensible to the sober chemist." It is likely that Kolbe's tirade was the inspiration for van't Hoff's inaugural address as professor of chemistry in Amsterdam, which dealt with the role of the "imaginative faculty" in science.

It was almost 100 years later before the very real prospect of exceptions to what has become the van't Hoff/le Bel precept was seriously considered. In 1970, Hoffmann, Alder and Wilcox[4] proposed in their seminal work on this subject, that it might be possible to stabilize a structure in which the four substituents attached to a tetracoordinate carbon atom are arranged in a plane. There ensued a great interest in the possibility of *planar-tetracoordinate carbon.*

At first examination it was clear to Hoffmann *et al.* that because molecules with a simple chiral center at carbon do not racemize we should expect that an achiral geometry, such as a planar one, will lie *at least* 250 kJ mol^{-1} above the tetrahedral form. Their initial calculations suggested that the barrier to inversion was in fact considerably greater than this proposed lower limit and that it was unlikely that a simple carbon compound could be found that actually prefers a planar arrangement. It was suggested, instead, that the possibility of a planar geometry at tetracoordinate carbon might arise, in a more indirect fashion, as the transition structure involved in non-dissociative racemization of a suitably substituted methane derivative.

However, the challenge had been laid and a search to find systems which might contain planar-tetracoordinate carbon began. Some degree of success came very quickly with the work of Pople, Schleyer and coworkers, published in 1976.[5] They identified a number of small lithium- and boron-containing molecules (which included **1-1** – **1-3**) that were predicted from *ab initio* calculations to prefer a planar-tetracoordinate geome-

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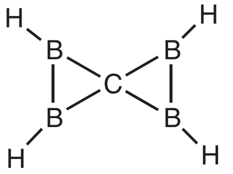
[†] O. T. Benfey gives some details of this affair in his translation of van't Hoff's article.[1]

try. These simple structures have, however, proven to be difficult to synthesize (see Section 1.4.1 on page 9). At about the same time experimental work began which was directed towards the synthesis of the fenestranes (**1-I**), and related hydrocarbons[6,7] that were expected to induce planarizing distortions at the central tetracoordinate carbon atom. Experimental success was then achieved in Erker's group[8] where a facile route was found to organometallic compounds with a planar carbon center which is clearly associated with four substituents, two of which are metals (**1-II**).[†]



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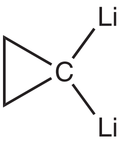

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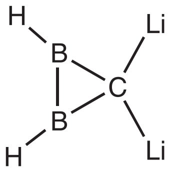

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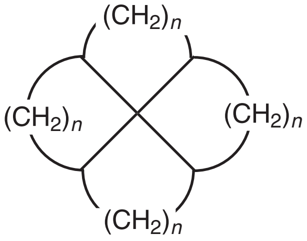

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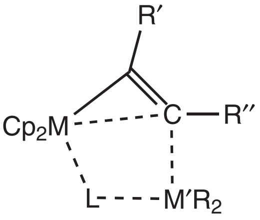

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Lack of success in achieving significant planarizing distortions at a quaternary carbon in purely organic systems (such as **1-I**) and the difficulty in synthesizing candidates of a purely organic nature led to a lull in this approach to planar-tetracoordinate carbon. However, it had always been recognized that the search for planar-tetracoordinate carbon was the sort of problem for which computational chemistry was well suited.[4] Computational techniques allow for the examination of a wide range of molecules, each of which might take years to synthesize in a laboratory. Exploitation of this computational approach led to the identification by McGrath, Radom and Schaefer of bowlane

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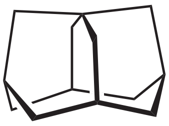
[†] However, as is explained later (see Section 1.4.2.2 on page 14), there is some ambiguity as to the nature of the planar-tetracoordinate carbon in these compounds, which might be better considered as a tricoordinate, planar, sp^2-hybridized carbon (typical of olefins), with a fourth, partially-bonded, in-plane ligand, than as a planarized, tetracoordinate carbon.

(**1-4**)[9] as a purely organic molecule with considerable flattening at a tetracoordinate carbon atom. Since then we have proposed other target molecules, including octaplane (**1-5**),[10] and spiro[2.2]octaplane (**1-6**).[11] Finally, we have identified dimethanospiro[2.2]-octaplane (**1-7**)[12] as the first saturated hydrocarbon predicted to contain a planar-tetracoordinate carbon atom.



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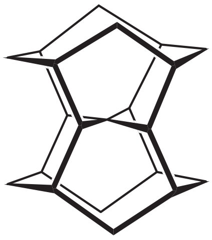

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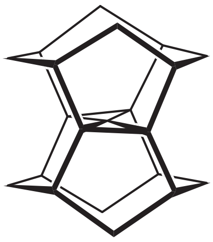

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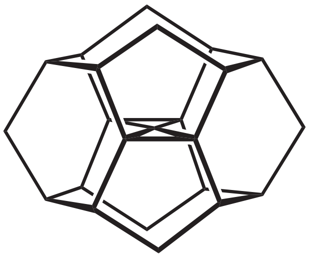

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This endeavour has proven to be well served by the use of both van't Hoff's "imaginative faculty" and detailed analysis. Previous work in the search to locate structures containing a planar-tetracoordinate carbon, their relevance to the present work, and further analysis by us that relates directly to these compounds, are described in detail in the remainder of this Chapter.

1.2 Inversion of Methane

Because methane is the simplest possible tetracoordinate carbon molecule, it serves as a good first model for examining the issues involved in designing a molecule containing a planar-tetracoordinate carbon atom. Many researchers have examined methane from the slightly different perspective of a model for the inversion (or, in the case of methane itself, the automerization) process at tetracoordinate carbon, which was thought originally to proceed via a square-planar transition structure (Figure 1-1).

Monkhurst[13] was the first to examine inversion of tetracoordinate carbon theoretically, although he was preempted by a brief paper on the deformation of a general AH_4 species by Saturno.[14] Monkhurst proposed that inversion may occur either through a planar or a pyramidal structure. Using methane as a model he then determined, via approximate electronic structure calculations, that the planar structure was lower in energy than the pyramidal structure and that the barrier to inversion was of the order of

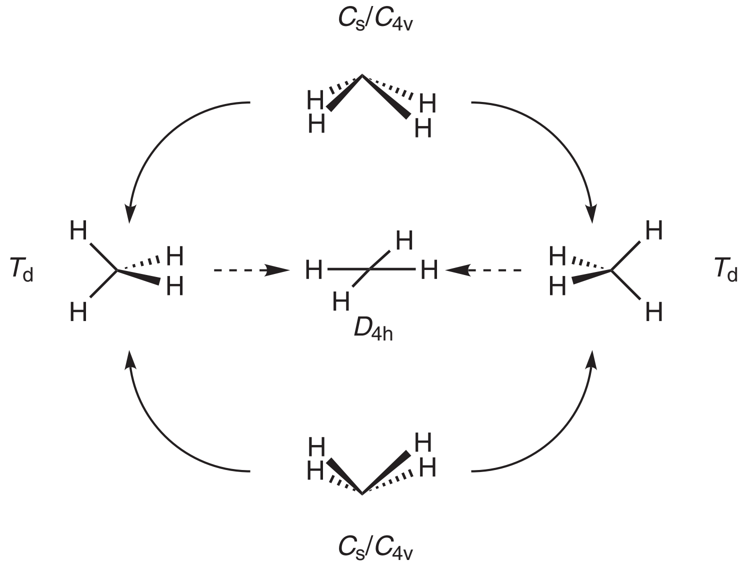


Figure 1-1. The automerization of methane, initially thought to proceed via a D_{4h} structure is expected to proceed via a pyramidal-like structure.

1000 kJ mol^{-1}. With such a large barrier, dissociation and recombination would clearly be the preferred pathway. Many workers[4,15–17] (including Hoffmann, Alder and Wilcox) made estimations of the difference in energy between the planar and tetrahedral geometries ($\Delta E_{PT} = E_{Planar} - E_{Tetrahedral}$) in methane which ranged from 600 to 1000 kJ mol^{-1}.

In 1977, Minkin et al.[18] used a number of methods including HF calculations employing a double-zeta basis to show that in fact the pyramidal C_{4v} symmetry structure is expected to be lower in energy than the planar D_{4h} structure. This preference was noted by others[19] and led to the elucidation in 1993 by Gordon and Schmidt[20] of the preferred route for the hypothetical classical inversion (automerization) of methane, which is seen to proceed via a pyramidal-type structure with C_s or possibly C_{4v} symmetry (Figure 1-1).

The most accurate calculations published to date for the relative energies of the various methane geometries come from the work of Pepper and coworkers.[21] Like Gordon and Schmidt before them, they find that the lowest-energy, planar structure for methane does not have four equivalent hydrogen atoms and D_{4h} symmetry, as had been supposed, but has C_{2v} symmetry and a structure that suggests a complex between CH_2 and H_2 (reminiscent of the structure[22] for CH_4^{2+}). Further, they find that the energy of the

C_{2v} (D_{4h}) symmetry, planar structure relative to the tetrahedral geometry is about 510 (546) kJ mol^{-1} (after correction for the zero-point vibrational energy (ZPVE)). This is significantly higher than the homolytic dissociation energy of the C–H bond in methane (435 kJ mol^{-1}).[23] Further, the C_s (C_{4v}) symmetry transition structure for the automerization process is found to lie 440 (437) kJ mol^{-1} above the tetrahedral ground state (after correction for ZPVE). This is very close in energy to the homolytic dissociation energy of the C–H bond (435 kJ mol^{-1}) and suggests that classical inversion without bond cleavage might in fact be possible under certain conditions.

Most recently, Yoshizawa and coworkers[24] have shown using B3-LYP calculations that this barrier can be reduced to 180–200 kJ mol^{-1} when methane is complexed to a transition metal cation (such as Fe^+, Co^+, Ni^+ or Cu^+). They suggest that inversion of stereochemistry at a carbon atom in catalytic reactions on hydrocarbons should be possible. They found this catalyzed inversion to proceed via a C_s symmetry structure, much like that of the uncatalyzed process.

It seems that pyramidal geometries at tetracoordinate carbon may, in general, be lower in energy than planar geometries (see also Section 1.3 below). A pyramidal geometry at tetracoordinate carbon is unusual in itself. Molecules with a pyramidal tetracoordinate carbon atom are considered further in Chapter 3.

1.3 Designing Planar Carbon

It was Hoffmann and coworkers[4] who initiated attempts to explicitly design systems in which a planar-tetracoordinate carbon would be preferred over the usual tetrahedral arrangement. Hoffmann and coworkers clearly recognized the audacity of their proposal. They wrote,

> "Attempts to subvert something as basic to organic chemistry as the tetrahedral tetracoordinate carbon atom should perhaps be viewed as acts appropriately described by the Yiddish word *chutzpah* and/or the Greek *hubris*."

Their caution was based, at least in part, on calculations which had determined the energy difference $\Delta E_{PT} = E_{Planar} - E_{Tetrahedral}$ in methane to be anywhere from 600 to 1000 kJ mol^{-1}, values[4,15–17] much greater than Hoffmann's proposed lower limit of 250 kJ mol^{-1}. Clearly, overcoming the preference for a tetrahedral geometry would be formidable. Consideration of the difference $\Delta E_{PT} = E_{Planar} - E_{Tetrahedral}$ shows that it can be reduced either by lowering E_{Planar} or by raising $E_{Tetrahedral}$. Raising $E_{Tetrahedral}$ can be achieved by devising polycyclic structures in which a tetrahedral arrangement at the central carbon is made unfavorable on steric grounds. Hoffmann's initial suggestion[4] for this approach was based on a symmetric fenestrane skeleton (**1-I** where $n < 3$). This can be considered as a structural approach, which relies on a rigid covalent bonding regime to apply constraints on the positioning of the substituents to carbon. This approach is explained in greater detail in Section 1.5 on page 19. The alternative, lowering E_{Planar}, requires replacement of hydrogen in methane with substituents that in some way electronically favour a planar bonding arrangement.

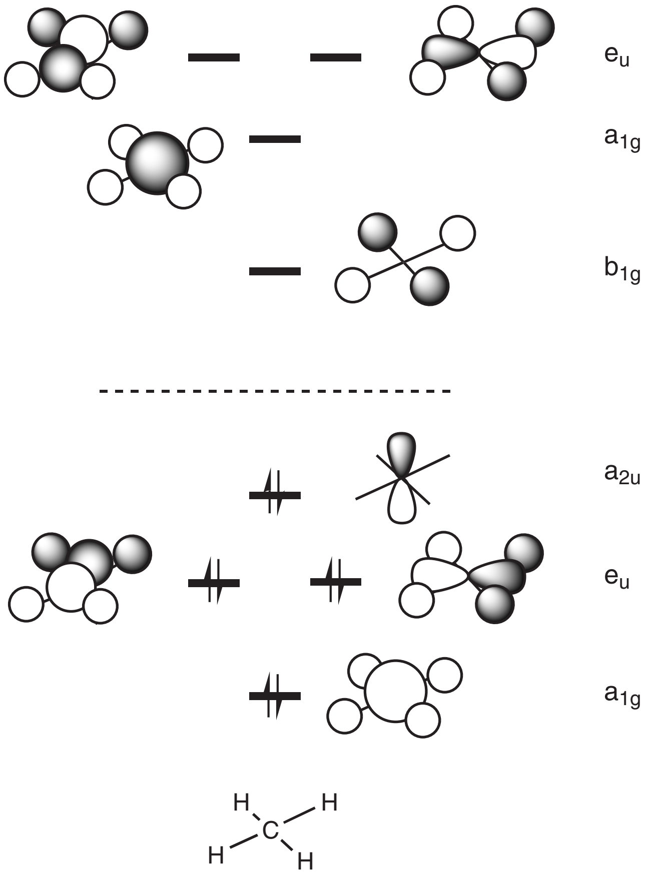


Figure 1-2. The electronic structure of square-planar methane showing the *p*-type lone-pair (HOMO) and six C–H bonding electrons.

Examination of the electronic structure of square-planar methane (Figure 1-2) reveals that the highest occupied molecular orbital (HOMO) (a_{2u}) is expected to be a *p*-

type lone pair, while the remaining six valence electrons are involved in forming four σ-deficient C–H bonds. Other ways to describe the bonding of the hydrogens to carbon have been suggested. One way sees square-planar methane as a resonance hybrid of structures that have a pair of regular C–H bonds and a three-center two-electron (3c-2e) bond between the remaining hydrogens and carbon. Our full-valence MCSCF calculations suggest that a unique five-center six-electron (5c-6e) bonding scheme is more appropriate. Whatever the best bonding description, it is clear that substituents which are strong σ-donors and/or π-acceptors (when bound with the correct orientation) will stabilize a planar over the tetrahedral geometry.

This electronic approach to designing molecules with a planar-tetracoordinate carbon atom has seen much activity and has had considerable success. Work in this area is summarized in the next section (Section 1.4 on page 9).

One other issue that becomes apparent when examining the electronic structure of methane, is the low-lying lowest unoccupied molecular orbital (LUMO). This has led some workers[17,19b] to suggest that the lowest state of planar methane (and its derivatives[5,27b]) may be a triplet (or perhaps an open-shell singlet biradical) species. Calculations by Schleyer and coworkers[19c] on a range of isoelectronic AH_4 systems (BH_4^-, CH_4, NH_4^+, AlH_4^-, SiH_4 and PH_4^+) showed that only planar (D_{4h}) BH_4^- preferred the triplet state and then by only 40 kJ mol^{-1} (at the MP2/6-31G(d)//HF/6-31G(d) level) over the lowest-energy, pyramidal singlet. But the method used is expected to overstate the stability of the triplet and they suggest that the singlet probably is the lowest-energy state in this case as well. However, the HOMO in the preferred singlet states of planar BH_4^-, AlH_4^-, SiH_4 and PH_4^+ is the b_{1g} orbital. Only CH_4 and NH_4^+ prefer the a_{2u} HOMO (see Figure 1-2). Interestingly, pyramidal (C_{4v}) singlet structures are preferred by CH_4, NH_4^+ and PH_4^+ but not by BH_4^-, AlH_4^- and SiH_4. A detailed examination of the three lowest electronic states of square-planar (D_{4h}) methane was carried out by Gordon and Schmidt[20] using multireference techniques. They also found that the singlet with an a_{2u} HOMO (*p*-type lone pair) is preferred over both the triplet and the open-shell singlet.

Although there is considerable evidence to suggest that planar-tetracoordinate carbon will indeed prefer a closed-shell singlet state with a *p*-type lone pair, it is possible that when hydrogen is replaced by other substituents the preferred electronic configuration may alter.

1.4 Electronic Stabilization

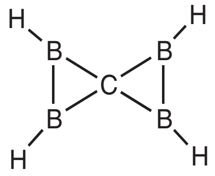
Initial suggestions of structures that exploited electronic stabilization at a planar-tetracoordinate carbon included a number of structures which either surrounded a central carbon atom with an annulene perimeter or incorporated the target atom into a delocalized π-system. Further attempts at designing molecules with a planar-tetracoordinate carbon atom involved calculations on structures which successively replaced the hydrogens of methane with σ-donors and/or π-acceptors like Li and B to form small polar organometallic molecules. Later attempts involved the use of transition metal substituents, and structures of this nature then began to show up incidentally from X-ray structure analyses.

Although there are a few notable exceptions, most of the compounds synthesized to date which achieve planar-tetracoordination at carbon do so by associating a fourth ligand in the plane of an already planar, sp^2-hybridized carbon atom. In this way, the planar-tetracoordinate carbon is stabilized to a large extent by direct incorporation into a π-system. As has been pointed out by Siebert and Gunale,[25,26] this removes the *p*-type lone-pair. It has been shown that in these molecules the carbon atom contributes a single electron to the π-system and three electrons to σ-bonding rather than the two and two split seen in square-planar methane (the electronic configuration at the planar carbon is $\sigma^3\pi^1$ rather than $\sigma^2\pi^2$). By removing the *p*-type lone pair, these compounds are greatly stabilized but are no longer expected to show properties which result from an electronic structure like that of square-planar methane.

Electronically-stabilized, planar carbon compounds (whether purely theoretical or experimentally isolated) can be separated into a number of distinct groups which are discussed in detail below.

1.4.1 Lithium and Boron Substituents

Pople, Schleyer and coworkers[5] identified through HF/4-31G calculations, six small, polarorganometallic molecules that appeared to prefer a planar arrangement at the central tetracoordinate carbon atom (**1-1** – **1-3** and **1-8** – **1-10**). All these molecules have either two lithium and/or two boron substituents, both of which appear to have a very strong stabilizing effect on the planar geometry. This was predicted by Hoffmann[4]



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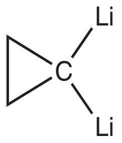

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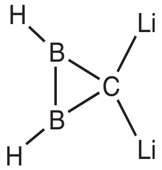
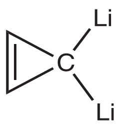


1-3

from his examination of the electronic structure of methane. Dilithiomethane (**1-11**) was found to be border-line because the planar and tetrahedral-like (C_{2v}) structures were of similar energy. More accurate calculations[27,28] on dilithiomethane (**1-11**) indeed indicated that there is little difference in the energy of the two geometrical isomers. Our best calculations, at the CCSD(T)/AVTZ level, indicate that the planar-tetracoordinate geometry is indeed a minimum but the tetrahedral geometry is also a minimum and is slightly preferred (5 kJ mol^{-1}). Further, the barrier to conversion of the planar into the



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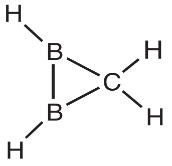

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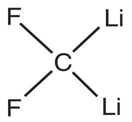

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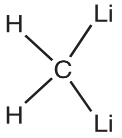

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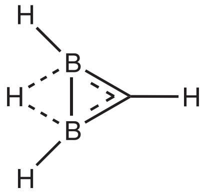
tetrahedral-like geometry is very small (about 3 kJ mol^{-1}). 3,3-Dilithiocyclopropene (**1-8**) has not been analyzed further in the literature. However, our calculations, at the MP2/6-311+G(2d,p) level, indicate that it is unstable with respect to dissociation. Diboracyclopropane (**1-9**) has received further attention[29] and the planar-tetracoordinate structure is found to be a transition structure. The preferred isomer of CB_2H_4 has a B–B bond bridged by hydrogen and CH (**1-12**). Further investigation of dilithiodifluoromethane (**1-10**) showed that very strong F–Li interactions lead to a pyramidal geometry (**1-13**) where a carbon atom sits on a $(LiF)_2$ base.[30] More recently, Sorger and Schleyer[31] have re-examined most of these molecules at the B3-LYP/6-311++G(d,p) level. In this work they find that **1-13** is a transition structure and that the preferred isomer is in fact **1-14**. Schleyer also identified four new, lithium- and boron-containing species (**1-15** – **1-18**)[32] that are predicted to contain planar-tetracoordinate carbon. Most



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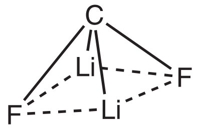
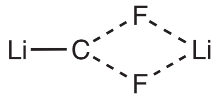


1-13 (C_{2v})



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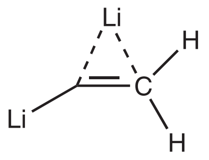

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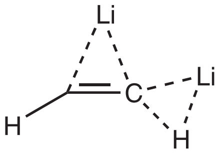

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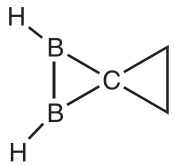

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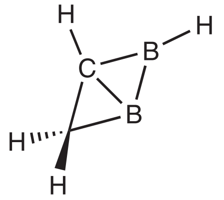

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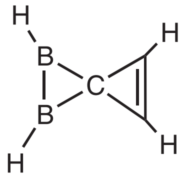

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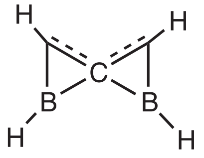

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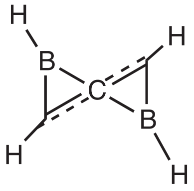

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recently, Gribanova, Minkin and Minyaev[33] have identified, through MP2(full)/6-31++G(d,p) calculations, a number of isomers of 1,2-diboraspiro[2.2]pent-4-ene (**1-19** – **1-21**) as also containing a planar-tetracoordinate carbon atom. In summary, it appears that there are ten small, lithium- and boron-containing species that have been identified as containing a planar-tetracoordinate carbon center (**1-1** – **1-3** and **1-15** – **1-21**).[†] Unfortunately, attempts at synthesis of the lithiated compounds has been frustrated by aggregation and lithium solvation effects (which disrupt the predicted planar-tetracoordination).[34] In fact, it seems unlikely that any of the small lithiated species identified

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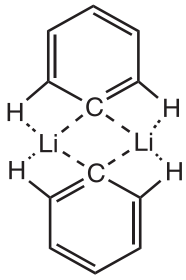
[†] Bolton, Laidig, Schleyer and Schaefer[32] have examined the $Li_2C_2H_2$ potential energy surface in great detail at the CCSD/DZP(+ZPVE) level and find a number of local minima (at least three) that exhibit planar-tetracoordinate carbon. The global minimum, which is considerably lower in energy (about 120 kJ mol^{-1}), was found to be a complex between LiH and HCCLi. Barriers to rearrangement of the species with a planar-tetracoordinate carbon to the global minimum are, in general, quite large (40–80 kJ mol^{-1}).

so far will exist as discrete compounds and attention seems to have turned to aggregations of these and similar species.[34]



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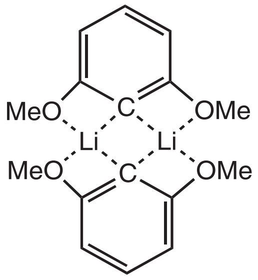

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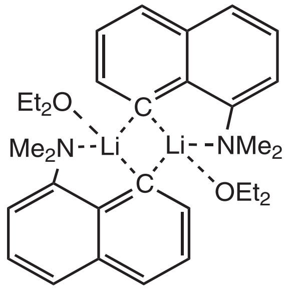


1-24

Lithiated compounds in which the target carbon atom for planar-tetracoordination is incorporated into an aromatic ring have also been considered.[35] These molecules are expected to aggregate into dimers (at least) and typical examples are [(2,6-dimethoxyphenyl)lithium]$_2$ (**1-23**) and [8-(dimethylamino)-1-naphthyllithium•Et$_2$O]$_2$ (**1-24**). Semi-empirical calculations of unsolvated dimers[35a] indicated that both **1-23** and the phenyllithium dimer (**1-22**) should prefer planar-tetracoordination at the lithiated carbon. X-ray crystal structure analysis of **1-23** showed further aggregation into tetramers which are stacked one on top of the other and rotated 90°. A tetracoordinate carbon environment can be discerned within these tetramers that has only minimal distortion from planar-tetracoordination (the distortion angle was given as 11°). However, the coordination at the *ipso*-carbon is actually five-fold. X-ray structure analysis of **1-24** (which does not aggregate into tetramers) shows a tetracoordinate environment about the lithiated carbon atoms that has only minimal distortion from planarity (again an angle of 11° was reported).[34c] No phenyllithium-type compound has yet been synthesized which has absolute planar-tetracoordination at the lithiated carbon.

Phenyllithium-type compounds (e.g. **1-22** – **1-24**) and the lithiated ethylene species **1-15** and **1-16** fall into the group of compounds that have a planar-tetracoordinate carbon incorporated into a π-system. The other eight molecules containing a planar-tetracoordinate carbon, **1-1** – **1-3** and **1-17** – **1-21**, do not rely on direct incorporation into a π-system and are expected to have the characteristic *p*-type lone-pair HOMO.

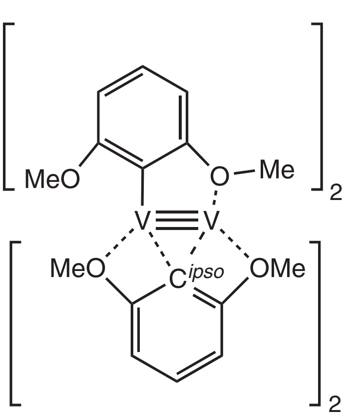
1.4.2 Dimetallic Complexes

The vast majority of compounds identified to date with a planar-tetracoordinate carbon atom have two metal ligands. Most of these compounds also make use of incorporation of the target carbon atom into a π-system.

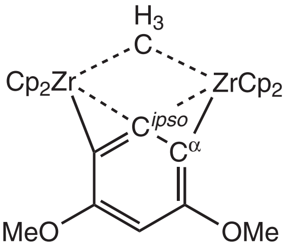
1.4.2.1 Complexed Aromatics

Although they did not report it at the time,† Cotton *et al.*[36] were the first to determine the crystal structure of a compound which has a planar-tetracoordinate carbon. The divanadium complex **1-25**, which has four 1,3-dimethoxy-substituted phenyl groups coordinated to a triple-bonded V_2 unit, has two planar-tetracoordinate carbon environments associated with the two carbon atoms (C^{ipso}) which are bonded to vanadium. It was Keese *et al.*[6] who first pointed out the planar-tetracoordination at C^{ipso} in **1-25**.

Buchwald *et al.* have identified a substituted 1,3-bis(dicyclopropenylzirconium) complex[37] (**1-26**) in which a pair of Cp_2Zr moieties form 3-center 2-electron (3c-2e) bonds with C^{ipso} and a neighboring aromatic carbon atom. The orientation of these Zr moieties is stabilized by a bridging methyl group so that (excluding the Cp groups) all atoms other than hydrogen lie in a plane which is only very slightly disturbed from exact planarity. Interestingly, the aromatic system remains intact; the C^{ipso}–C^{α} bond-lengths (1.39 and 1.40 Å) are only slightly increased from the aromatic ideal.



1-25



1-26

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† Cotton and Millar were, in fact, mostly interested in the triple-bond between the two vanadium atoms.

These two compounds, in similar fashion to **1-22** – **1-24**, rely on incorporation of the target carbon atom (C^{ipso}) into an aromatic π-system. Calculations by Poumbga, Bénard and Hyla-Kryspin on **1-25** and **1-26** have shown that the planar-tetracoordinate carbon atom (C^{ipso}) in each of these compounds bears a formal negative charge and has a $\sigma^4\pi^1$ configuration rather than the $\sigma^2\pi^2$ configuration of square-planar methane.[26c] In these compounds, stabilization is believed to depend on σ-electron density donation from the aromatic ligand to in-plane, empty, metal *d*-orbitals with metal–metal bonding character.[25]

1.4.2.2 Olefinic Complexes

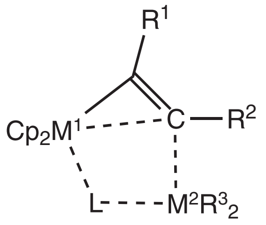
The most numerous examples, by far, of synthetically isolated compounds exhibiting a planar-tetracoordinate carbon atom fall into the category which is best described as complexes of an ethylene subunit. These compounds (**1-27** and **1-28**[†]) can be either neutral or cations and are characterized by a relatively undisturbed C=C double bond[26a,b] (with a normal C=C double-bond bond length) and a pair of metallic substituents (one must be either Ti, Zr or Hf and the other may be either B, Al or Ga for neutral species or Zr or Hf for the cationic species). The metal centers are bridged by either a methyl, ethyl or alkynyl ligand through a 3c-2e bond, or by chlorine through a pair of regular two-center two-electron (2c-2e) bonds. Erker and coworkers[8,38–40] have elucidated facile, and quite general, routes to the synthesis of these compounds (**1-27** and **1-28**[41]) and as a result have identified many species based on this formula.[‡]

In all of these compounds, the sp^2-hybridized planar-tetracoordinate carbon is involved in a 3c-2e bond with the pair of metals (M^1, M^2). Stabilization in these d^0 compounds was found[26a,b] to involve strong σ-acceptor character at M^1 and no delocalization of the π-electron density at the planar-tetracoordinate carbon.

Although the stabilization of the planar-tetracoordinate geometries is clearly quite different to that in compounds **1-27** and **1-28**, both 1,1-dilithioethene (**1-15**) and 1,2-dilithioethene (**1-16**)[32] can also be considered as members of the dimetallic olefinic category. Despite a normal C=C double-bond bond length (calculated at the CCSD/DZP

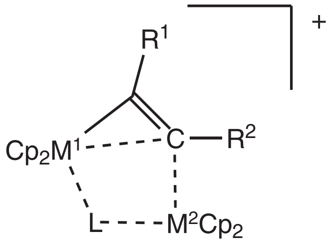
[†] Not all permutations of the given substituents have been synthesized. More detailed descriptions of the compounds that have been made can be found elsewhere.[38]

[‡] The list of compounds of this type is over 50 and growing.



M^1 = Ti, Zr, Hf; R^1, R^2 = Alkyl, Aryl, SiMe$_3$
M^{2}R$^3_2$ = BEt$_2$, Al*i*Bu$_2$, AlMe$_2$, AlEt$_2$, GaMe$_2$
L = Me, Et, CCMe, CCPh, CC*c*Hex, Cl

1-27



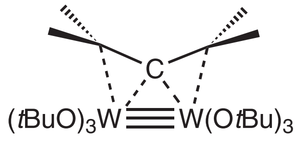
M^1, M^2 = Zr, Hf
R^1 = Me, Et, Pr, Ph, Bz
R^2 = Me, CC-Me; L = CC–R

1-28

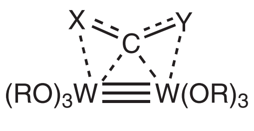
level to be 1.36 Å) in the 1,1-dilithioethene isomer (**1-15**), it was found that the C=C double bond was highly polarized, with electron density moved away from the planar-tetracoordinate carbon. Further, the two lithium substituents each donate an electron to the ethylene fragment leaving a purely electrostatic lithium interaction. Similarly, in the case of the 1,2-dilithioethene isomer (**1-16**), lithium bonding was found to be almost entirely ionic in nature. Clearly, lithium is not acting as a π-acceptor but is a strong σ-donor, and incorporation of the planar-tetracoordinate carbon into a π-system stabilizes the perpendicular *p*-orbital.

1.4.2.3 Allene Adducts and Analogues

Chisholm and coworkers[42] reported a ditungsten allene adduct (**1-29**) in which the terminal allene hydrogens are parallel (instead of the uncomplexed perpendicular arrangement). Further, on complexation the C–C bond lengths have increased to a normal C–C single-bond length and the geometry of the tetracoordinate bonding at the central carbon atom is planar. The bonding is unique. Allene was found to be acting as a



1-29



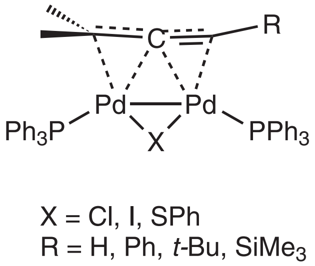
a X = Y = N-R
b X = O; Y = N–Ph

1-30

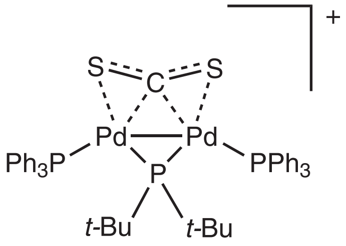
four-electron donor in a manner that completely disrupts the allene π-bonding. All four electrons are donated through in-plane orbitals and the perpendicular *p*-orbital at the central carbon is empty, allowing for positive overlap with filled metal–metal bonding orbitals.

Compounds of a similar nature (**1-30**) were identified earlier by Cotton and coworkers.[43] In these analogous complexes, it has been pointed out[42] that the bonding description need not be the same because the substituents at nitrogen lie roughly in the plane of the X–C–Y and W–W planes (the lone-pair on nitrogen, and possibly oxygen, appears to be involved in the X–C–Y to W–W bonding).

Two other complexes that are somewhat similar to **1-29** are worth noting, **1-31** and **1-32**. These dipalladium complexes have a pair of formally d^8 Pd centers connected via a 2c-2e bond. In **1-31**,[44] compounds described as μ-η^3-allenyl/propargyldipalladium complexes, the allenyl/propargyl unit is complexed to the dipalladium moiety in a way that puts the allenyl/propargyl carbon atoms, the two palladium atoms, the two phosphorous atoms and the bonding atom of ligand X, all in a plane. The C–C bonds in these complexes are short (1.26–1.40 Å) and the three carbon atoms almost lie in a line (∠CCC ≈ 175°). Reactivity studies and preliminary calculations suggest that the central tetracoordinate carbon atom (which is formally planar-tetracoordinate) has a high electron density. The cation complex **1-32**[45] appears to be an analogue of **1-30** and has the characteristic μ-η^2:η^2 bonding, in this case between the CS_2 and Pd_2 moieties. Once again, the carbon atom at the center is planar-tetracoordinate with only very slight deviations from exact planarity. The nature of the electronic structure at the planar-tetracoordinate carbon has not been analyzed but it seems likely that it is similar to that in **1-30**.



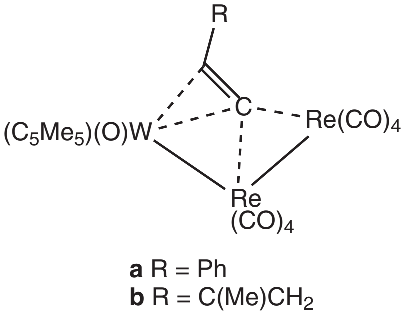
1-31



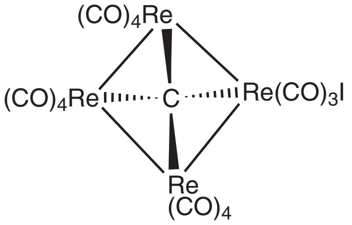
1-32

1.4.2.4 Other Transition-Metal Complexes

There have been a number of other reports of transition-metal complexes that contain a planar-tetracoordinate carbon atom. The cluster compound $[WRe_2(C_5Me_5)(O)(CO)_8(CCPh)]$ (**1-33**)[46] is of the complexed ethylene type. An examination of the structure shows that the C–C bond is effectively a C=C double bond (**1-33a**, 1.31 Å and **1-33b**, 1.34 Å). The other three substituents to the planar-tetracoordinate carbon atom are the three metal centers, $W(C_5Me_5)(O)$, $Re(CO)_4$, and $Re(CO)_4$. This three-transition-metal complex has an acetylide ligand in a unique μ-η^1:η^1:η^2-bonding mode. Beringhelli *et al.*[47] have reported a unique tetrarhenium anion cluster $[Re_4C(CO)_{15}I]^-$ (**1-34**). This complex does not have a planar-tetracoordinate carbon atom but the central carbon atom, which is in a tetrahedral-like environment, is considerably flattened from the tetrahedral ideal (∠ReCRe = 162°).

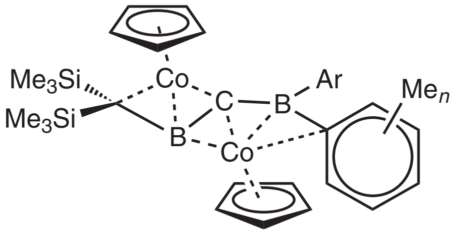


1-33



1-34

An intriguing group of dicobalt complexes (**1-35**) has been identified by Siebert and Gunale.[25,48] These compounds are essentially complex-stabilized diborylcarbenes. The central carbon atom is found to exist in a planar-tetracoordinate environment. Calculations on the electronic structure[26d] of the planar-tetracoordinate carbon revealed a $\sigma^{3.9}\pi^{1.4}$ configuration, while the electronic configuration of the bare diborylcarbene was found to be $\sigma^{3.0}\pi^{1.5}$. On these grounds, Siebert and Gunale argue that the stabilization of the planar-tetracoordinate carbon by Co is as was envisaged by Hoffmann,[4] i.e. σ-donation and π-acceptance, although they point out that there appears to be a push–pull effect between the two Co centers (so one Co acts as a σ-donor while the other acts as a σ-acceptor).[48] It seems likely that the two boron groups attached to the planar-tetracoord-



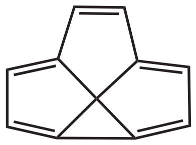
a Ar = Dur (2,3,5,6-tetramethylphenyl)
b Ar = Mes (2,4,6-trimethylphenyl)

1-35

inate carbon atom also act as σ-donor/π-acceptors, explaining the difference of σ and π densities (in the bare diborylcarbene) from that of the ideal square-planar carbon in methane (which should have a $\sigma^2\pi^2$ configuration).

1.4.3 Annulenes

Hoffmann's initial paper on the stabilization of planar-tetracoordinate carbon suggested many structures based on the idea of surrounding a central tetracoordinate carbon atom with an annulene perimeter (for example **1-36 – 1-39**). The intention here was



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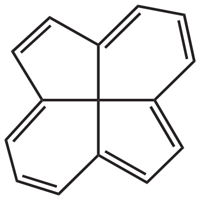

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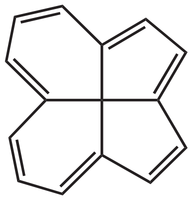

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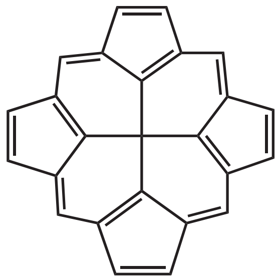
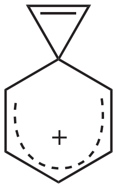


1-39

to make some use of structural constraints applied through the σ-framework and also to derive some stabilization through delocalization of the *p*-type lone pair through the annulene perimeter. It was shown quite conclusively by both Gleiter and coworkers[49] and Schleyer and coworkers[50] that such delocalization does not occur and any distortion from the tetrahedral ideal is purely a result of the structural constraints resulting from the σ-framework.

In a similar approach, which, like the annelation approach, tries to incorporate the



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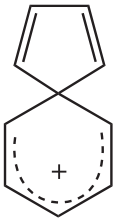
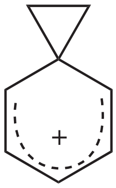


1-41



1-42

potentially planar-tetracoordinate carbon into a π-electron system, Hoffmann suggested structures like the cations **1-40** and **1-41**. MNDO/2 calculations by Schoeller[51] indicated that **1-40** and **1-42** have a greatly reduced preference for the tetrahedral-like geometry (the ΔE_{PT} values for **1-40** and **1-42** are 65 and 95 kJ mol^{-1}, respectively). Despite the potential for achieving planar-tetracoordinate carbon in a cation of this nature, this approach to planar-tetracoordinate carbon has not been pursued further. However, compounds like **1-40** (in which the target carbon atom is not much distorted from the tetrahedral ideal) have been the subject of more recent investigation.[52]

1.5 Structural Approach

This approach is the antithesis of the electronic approach. It relies almost exclusively on defining a suitably rigid bonding environment about the planar-tetracoordinate carbon atom. Because there would appear to be no question of significant electronic stabilization in a saturated hydrocarbon, these compounds form an excellent vehicle for the examination of structurally-constrained planar-tetracoordinate carbon.

The first step in devising a scheme to apply structural constraints to the positions of the four atoms bonded to a tetracoordinate carbon atom involves linking the four substituents together to give a polycyclic compound (Figure 1-3). In the tetrahedral ideal, the atoms bond to carbon with XCX angles of 109.5°. Shortening the links or 'straps' between the substituents X will reduce the XCX angle (α in Figure 1-3). In a square-planar geometry these angles are reduced to 90°. In other, less symmetrical, planar geometries the four XCX angles will add to 360°. Hydrocarbon systems of this type are a special type of polycyclic system (**1-III**) in which the central quaternary carbon atom, C^0, is common to all rings and the four carbon atoms bonded to it, C^α, are each com-

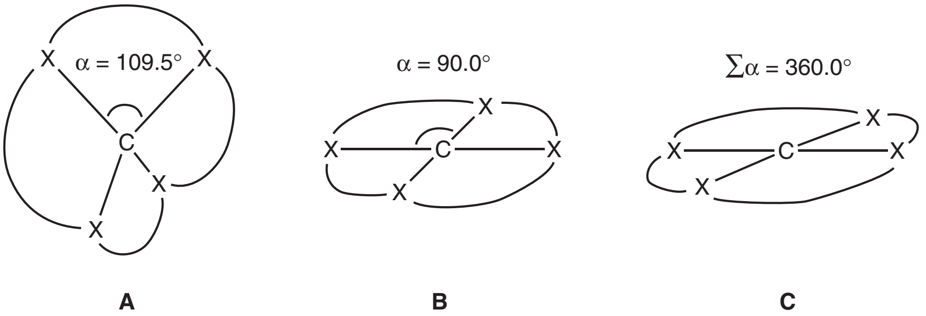
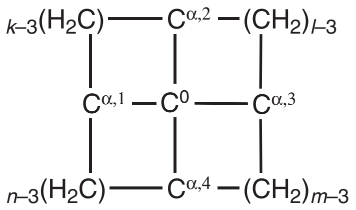
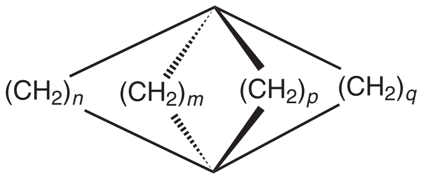


Figure 1-3. The structural approach to forming planar-tetracoordinate carbon involves binding the substituents at carbon. If the ‘straps’ are ‘tight’ enough, the XCX angles are reduced from **A**, the tetrahedral ideal of 109.5° to **B**, the square-planar ideal of 90.0°. It is likely that a less symmetric planar geometry, **C**, will result.

mon to a pair of rings. Compounds based on this structural motif have been labelled the fenestranes (see Section 1.5.2 on page 24).



1-III



1-IV

From a simplistic viewpoint, rings of less than six carbon atoms are needed to apply any planarizing distortion at the central quaternary carbon atom.[4] Cyclohexane is effectively unstrained, with CCC angles close to the tetrahedral ideal, and so cannot be expected to aid in reducing the opposite $C^{\alpha}C^{0}C^{\alpha}$ angles at the central carbon at all. However, because of configurational problems associated with fusing four six-membered rings at a single atom, some distortion from the tetrahedral ideal in this structure should be expected. Cyclopentane, cyclobutane and cyclopropane, however, all have CCC angles less than 109.5°. Fused ring systems of type **1-III** with combinations of three-, four- and five-membered rings are expected to exhibit a flattened central tetracoordinate carbon atom.

The main problem with this approach is that it can never actually achieve planar-tetracoordinate carbon except by coincidence. To achieve planar-tetracoordination, a symmetrical bonding environment, which results in a plane of symmetry through the central $C^0(C^\alpha)_4$ subunit, is required. In structures of type **1-III**, the four carbon atoms, C^α, bonded to the central carbon atom, C^0, have two other bonds to carbon (C^α–C^β) and one to hydrogen. Because of the constraints on the orientation of the C^α–C^β bonds (a result of the pericyclic ring fusion at C^0), the only way to achieve a symmetric environment at the central carbon, which contains a plane of symmetry through the $C^0(C^\alpha)_4$ subunit, is to make the four C^α atoms also planar-tetracoordinate. Since this is likely to be energetically prohibitive, a different approach is needed.

In many ways, the fenestrane approach is a two-dimensional approach to a three-dimensional problem. Clearly, a more three-dimensional structural design is necessary. The largely 'lateral' forces imposed by reducing the $C^\alpha C^0 C^\alpha$ angles need to be supplemented, or replaced, by perpendicular constraints (i.e. a bonding regime that constrains the positions of the C^α atoms from moving perpendicularly to the potential plane at C^0). A cage of some kind is required.

One attempt to devise such a cage, in which the lateral forces applied in the fenestrane approach are completely replaced by perpendicular constraints, can be seen in the small-ring paddlanes (**1-IV**). In these cage compounds, the target planar carbon atom is no longer central. Instead, a pair of bridgehead carbon atoms are subjected to planarizing distortions through their connection to one another. If such compounds are indeed stable, this should prove to be quite an effective way of applying the necessary perpendicular constraints. Bowlane[9] (**1-4**) acts in a similar manner to produce a single bridgehead carbon atom which is considerably flattened.[†] However, the bonding environment at the potentially planar-tetracoordinate carbon (C^0) is again not symmetrical and cannot be symmetrical.

The only way to obtain a truly planar-tetracoordinate carbon atom is to place it in a bonding arrangement that allows for the possibility of an identical spatial arrangement of the atoms both above and below the proposed plane. This is a necessary but not sufficient condition for planar-tetracoordination at carbon. Octaplane (**1-5**), first suggested by McGrath and Radom,[10] takes this approach. By attaching equivalent cyclooctane rings both above and below the central $C^0(C^\alpha H)_4$ moiety, it is possible to define a plane

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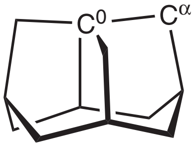
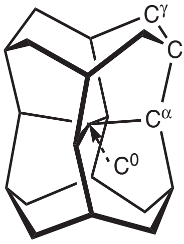
[†] Bowlane and a number of closely related molecules will be examined in detail in Chapter 3.



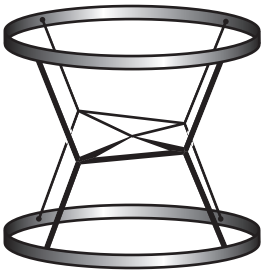
1-4 (C_{2v})



1-5 (S_4)

of symmetry through this central subunit without requiring undue distortion of the remaining tetracoordinate carbon atoms. In octaplane (**1-5**), the perpendicular constraints applied in bowlane are effectively duplicated on both sides of the central $C(CH)_4$ subunit. This approach leads to remarkable flattening at C^0 but not planarity; the ground state singlet is found to prefer distortion to S_4 symmetry with a tetrahedrally distorted central-quaternary carbon atom. The forces involved in constraining the positions of the C^α atoms are not enough to overcome the preference for distortion at C^0.[†]

1-V



1-VI

1-VII

In examining other alkaplanes (**1-V**) (see Chapter 4), we have explored variations on the exact nature of the perpendicular constraints used to hold the four C^α atoms in position. However, in all the alkaplanes of type **1-V** no use is made of the 'lateral'-type forces that are present in the fenestranes. The spiro[2.2]alkaplanes (**1-VI**), by introducing bonds between adjacent pairs of C^α atoms, introduce an effect that can be considered as 'lateral' in nature. However, unlike the case for the fenestranes, the spiroalkaplanes do not have a set of four small, fused rings, and so the effect is perhaps better likened to the beneficial effect of incorporating a potentially planar-tetracoordinate carbon

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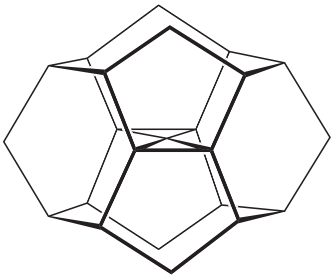
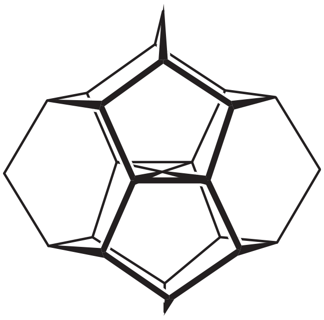
[†] Octaplane and many related molecules will be discussed in detail in Chapter 4.

atom into a three-membered ring (see Section 1.5.1 on page 23).

The spiroalkaplanes (**1-VI**) exhibit improved flattening at the central carbon atom over the alkaplanes (**1-V**) but fail to achieve a completely planar-tetracoordinate carbon atom. However, exact planarity at the central, tetracoordinate carbon atom results when the two caps, the cycloalkane units above and below the central $C(C)_4$ subunit, are linked by a pair of bridging methano groups to form the dimethanospiroalkaplanes (**1-VII**), dimethanospiro[2.2]octaplane (**1-7**) and dimethanospiro[2.2]binonaplane (**1-43**).† This remarkable result is detailed in Chapter 4.



1-7 (D_{2h})



1-43 (D_{2h})

The most important aspects of previous studies which have examined the flattening of planar-tetracoordinate carbon through structural means alone are outlined below. In some cases, results from our own calculations are quoted where they further clarify the discussion and no other recent results are available.

1.5.1 The Effect of Small Rings

The beneficial effect of incorporating a target planar-tetracoordinate carbon atom into a small, preferably three-membered, ring was first recognized by Pople, Schleyer and coworkers.[5] This effect appears to be due to the alleviation of the repulsive steric interactions that result if four non-bonding substituents are placed in a plane. The majority of the compounds already mentioned which have a planar-tetracoordinate carbon take advantage of this effect, **1-1** – **1-3**, **1-9**, **1-15** – **1-21** and **1-25** – **1-35**. In fact, the only exceptions are possibly dilithiomethane (**1-11**), which has an ambiguous geom-

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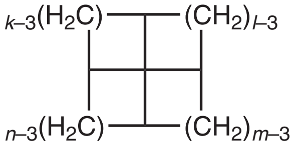
† For an explanation of the nomenclature of all the alkaplane families, see Appendix A.

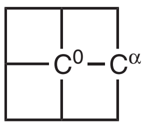
etry, and the phenyllithium dimers (**1-22 – 1-24**), which lose their planar-tetracoordinate geometry on complexation of solvent to lithium. Clearly this effect is significant and worth due consideration when designing systems that aim to achieve planar-tetracoordinate carbon.

1.5.2 Fenestranes

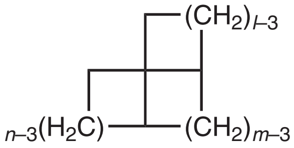
The first saturated hydrocarbons to be examined for flattening at the central, quaternary carbon atom from a synthetic approach were the [*k*.*l*.*m*.*n*]fenestranes (**1-VIII**). The term fenestrane was initially given by Georgian[53] to the symmetric [4.4.4.4]fenestrane (**1-44**) (*k*, *l*, *m*, *n* = 4) for its resemblance to a window.[†] As was indicated by Hoffmann,[4]



1-VIII



1-44



1-IX

these compounds (where *k*, *l*, *m*, *n* < 6), are the intuitive first suggestions for constraining the geometry at carbon. When the fused rings are smaller than six-membered, they must start to exert some angle strain on the central carbon atom; flat five-membered rings have the ideal angle of 108.0° for the included CCC angles, which is less than the tetrahedral ideal of 109.5°. However, it is possible for molecules with three fused rings at a central atom to exert some planarizing distortion at the central carbon atom. Molecules of this type are often labeled as [*l*.*m*.*n*]fenestranes (**1-IX**). The origin of the planarizing distortion at the central carbon atom in the [*l*.*m*.*n*]fenestranes is not the same as the 'strapping' effect referred to above for the [*k*.*l*.*m*.*n*]fenestranes but results from the orientation in which the rings are fused. An [*l*.*m*.*n*]fenestrane may be seen as two (overlapping) bicyclo[*x*.*y*.0]alkane subunits. These bicyclo[*x*.*y*.0]alkane subunits may be either *cis*- or *trans*-fused. For example, [4.4.4]fenestrane, can be considered as two overlapping bicyclo[2.2.0]hexane subunits. These bicyclo[2.2.0]hexane subunits can be either *cis*- and *trans*-bicyclo[2.2.0]hexane (**1-45** and **1-46**, respectively). Generally, *trans*-fused, small rings cause considerable angle strain at the bridgehead carbon atoms which are common to the two rings. Thus, *trans*,*trans*-[4.4.4]fenestrane (or simply *t*,*t*-

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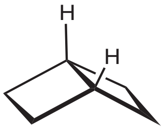
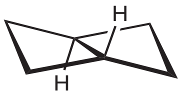
[†] [4.4.4.4]fenestrane has also been called windowpane.

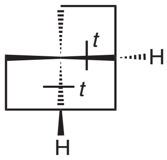
[4.4.4]fenestrane) (**1-47**)[†] might be expected to exhibit considerable distortion from the tetrahedral ideal at the central carbon (C^0). This same effect also applies to the [*k.l.m.n*]fenestranes (**1-VIII**).



1-45

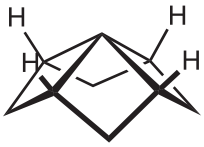


1-46

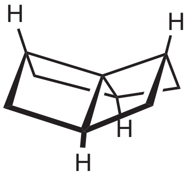


1-47

Considerable effort has gone into analyzing and synthesizing the fenestranes, particularly in the groups of Keese,[6,54–56] Agosta,[7,57] Wynberg[58] and Smit.[59] Wiberg[60] and Minkin[61] have also made important contributions, although mostly theoretical. Cook and coworkers[62] have concentrated on making unsaturated fenestranes. One aspect that has become clear in all the work on the fenestranes is that to effect considerable distortion at the central carbon atom from the tetrahedral ideal requires exploitation of the increased strain that results from incorporation of *trans*-fused bicyclo[*x.y.*0]alkane subunits.



1-48a (C_{4v})



1-49 (D_{2d})

Initial interest in the fenestranes centered around [4.4.4.4]fenestrane. Liebman and Greenberg[63] proposed a pyramidal structure for the all-*trans*[‡] isomer (**1-48**) and sug-

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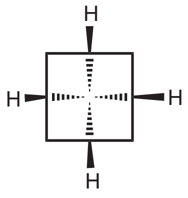
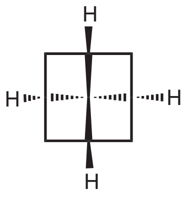
[†] The system of nomenclature for expressing the various isomers of the fenestranes can also be given by specifying the orientation of the hydrogen at the bridgehead carbon C^{α} as either α 'above' or β 'below' the projection plane. Thus, *trans*,*trans*-[4.4.4]fenestrane (**1-47**) is 1β,3α-[4.4.4]fenestrane. This nomenclature is less clear as to the degree of strain in the system and will not be used here. Some further discussion of fenestrane nomenclature is given in Appendix A.

[‡] The all-*trans* isomer of [4.4.4.4]fenestrane has also (somewhat confusingly) been called *cis*-[4.4.4.4]fenestrane. The latter nomenclature[64] refers to the fact that all hydrogens at C^{α} are on the same side of the 'plane' of the molecule.

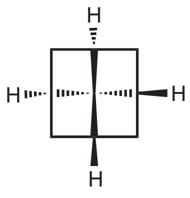
gested that this isomer may well be lower in energy than the all-*cis* isomer (**1-49**). Schleyer and coworkers[64] determined MNDO geometries for the all-*cis* and all-*trans* isomers and Schulman, Sabio and Disch[65] determined HF/STO-3G optimized structures. In both cases symmetry was imposed and the nature of the resulting stationary points were not examined through analysis of the force constant matrix. Our calculations at the MP2/6-311+G(3df,2p)//MP2/6-31G(d) level indicate that the C_{4v} symmetry structure (**1-48a**) proposed up until now for the all-*trans* isomer (**1-48**) is not a minimum on the potential energy surface but represents a transition structure connecting two equivalent C_{2v} symmetry structures (**1-48b**). An examination of the [4.4.4.4]fenestrane potential energy surface revealed three other minima which correspond to the all-*cis* (**1-49**), *trans*,*cis*,*trans*,*cis* (**1-50**), and *trans*,*cis*,*cis*,*cis* (**1-51**) isomers. No other local minima which are [4.4.4.4]fenestrane isomers could be found.[†] Perhaps surprisingly, the lowest-energy isomer is found to be the C_s symmetry, *trans*,*cis*,*cis*,*cis* isomer (**1-51**).



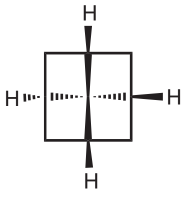
1-48



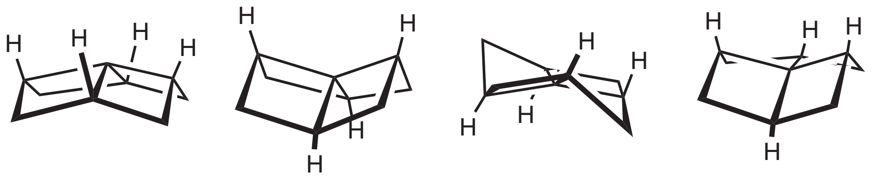
1-49



1-50



1-51



C_{2v}
E = 18.0
1-48b

D_{2d}
E = 0.0
1-49

C_2
E = 382.6
1-50

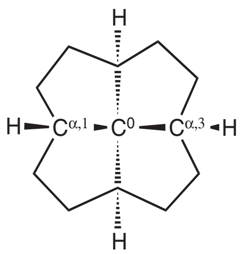
C_s
E = -60.0
1-51

Figure 1-4. Structural representations and relative energies (in kJ mol^{-1}) at the MP2/6-311+G(3df,2p)//MP2/6-31G(d) level of the four isomers of [4.4.4.4]fenestrane.

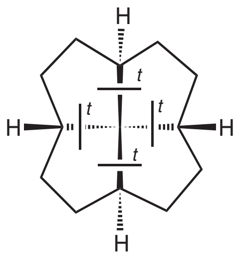
[†] Total energies are given in Table C-1 and optimized geometries are given in Table C-17 of Appendix C.

This result is less surprising when the geometries are examined in detail. The *trans,cis,cis,cis* isomer (**1-51**) has the least deformation at the central carbon atom while the most strained isomer (**1-50**) has the most flattened central tetracoordinate carbon (Figure 1-4).

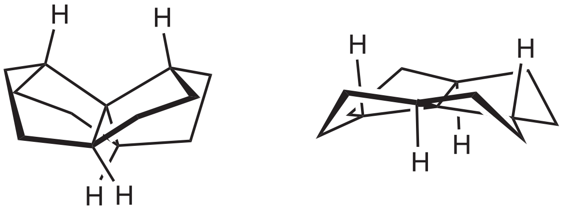
The smallest, fully-symmetric fenestrane to be synthesized is the all-*cis* isomer of [5.5.5.5]fenestrane (**1-52**) (also called staurane).[54] The structure of this D_2 symmetry molecule has been determined by electron-diffraction[54f] and it was found that distortion in the bonding at the central carbon atom from the tetrahedral ideal is minimal; the $C^{\alpha,1}C^{0}C^{\alpha,3}$ angle is widened from the tetrahedral ideal of 109.5° to 116.2° (in a planar-tetracoordinate fenestrane this angle would be 180°). Keese has determined structures for all isomers of [5.5.5.5]fenestrane using MNDO calculations[6b,54a] and finds that the all-*trans* isomer (**1-53**) has a remarkably flattened central, tetracoordinate carbon



1-52 (D_2)



1-53 (D_{2d})



D_2

E = 0.0

1-52

D_{2d}

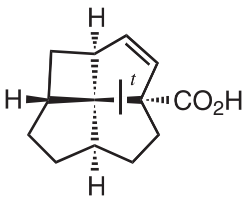
E = 582.3

1-53

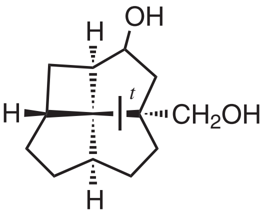
Figure 1-5. Structural representations and relative energies (in kJ mol^{-1}) at the MP2/6-311+G(3df,2p)//MP2/6-31G(d) level for all-*cis*-[5.5.5.5]fenestrane (**1-52**) and all-*trans*-[5.5.5.5]fenestrane (**1-53**).

($\angle C^{\alpha,1}C^0C^{\alpha,3}$ = 178.0°). Our calculations† at the MP2/6-31G(d) level give a similar result. However, we find that the $C^{\alpha,1}C^0C^{\alpha,3}$ angle for this D_{2d} symmetry molecule (**1-53**) is 164.1°. Further, **1-53** is calculated to be 582.3 kJ mol^{-1} higher in energy than **1-52** (calculated at the MP2/6-311+G(3df,2p)//MP2/6-31G(d) level) and, as can be seen from the orientation of the hydrogens at the peripheral bridgehead carbon atoms (C^{α}), these molecules differ only by inversion at C^0. Because of the considerable flattening at C^0 in **1-53**, this barrier is not expected to be particularly large (we calculate it to be about 25 kJ mol^{-1}). Given the very large thermodynamic preference for **1-52** and the low barrier for conversion of **1-53** to **1-52**, it seems likely that synthesis of **1-53** will prove prohibitively difficult.

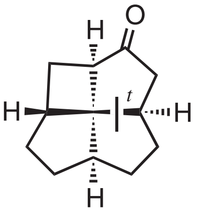
A number of workers[6b,66] have had success in incorporating a single *trans*-fused bicyclo[*x*.*y*.0]alkane subunit into small-ring fenestranes. In particular, *cis*,*trans*,*cis*,*cis*-[4.5.5.5]- and *trans*,*cis*,*cis*,*cis*-[5.5.5.5]fenestrane derivatives have been prepared (**1-54** – **1-57**). The X-ray crystal structures of all the *cis*,*trans*,*cis*,*cis*-[4.5.5.5]fenestrane derivatives show similar geometries at the central carbon atom; **1-54** has angles across the central carbon of 131.1° and 120.2°, **1-55** yields angles of 132.4 and 119.5°, while the X-ray structure of **1-56** gives angles of 134° and 119°. Wender's *trans*,*cis*,*cis*,*cis*-[5.5.5.5]fenestrane derivative (**1-57**) was not crystalline.[66] No structure for **1-57** is available yet but derivatization allowed positive assignment of the stereochemistry of ring fusion.



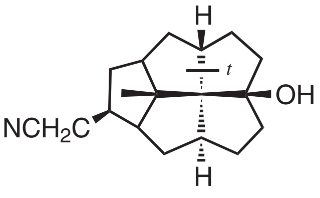
1-54



1-55



1-56



1-57

Keese[6b] has considered the introduction of bridgehead C=C double bonds in the [5.5.5.5]- and [4.5.5.5]fenestranes to give [5.5.5.5]- and [4.5.5.5]fenestrenes (e.g. **1-58** and **1-59**). While the bridgehead double bond was found (from MNDO calculations) to

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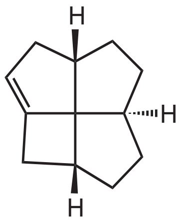
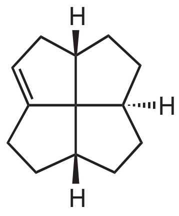
† Total energies are given in Table C-1 and optimized geometries are given in Table C-17 of Appendix C.

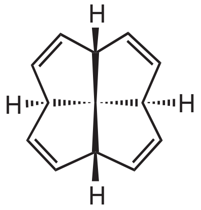
increase the planarizing distortion at C^0 relative to an all-*cis* isomer, it was less effective than the introduction of a *trans*-fused bicyclo[*x*.*y*.0]alkane subunit. The resulting molecules, with highly distorted C=C double bonds, are expected to suffer from significantly reduced kinetic stability.



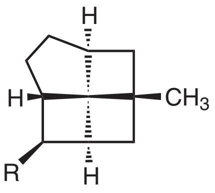
1-58



1-59



1-60

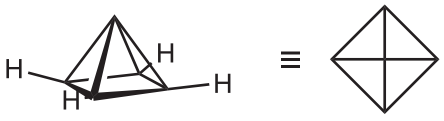


R = $CONHC_6H_4Br$

1-61

Cook and coworkers[62] have synthesized all-*cis*-[5.5.5.5]fenestratetraene (“staurane tetraene”) (**1-60**). No crystal structure is available yet but **1-60** (which has no bridgehead double bonds) is not expected to have any greater distortion towards planarity at the central carbon atom than all-*cis*-[5.5.5.5]fenestrane (see Section 1.5.3 on page 30).

The smallest fenestrane that has been synthesized to date, which is also the fenestrane with the most distorted central carbon atom, is an all-*cis*-[4.4.4.5]fenestrane derivative (**1-61**).[7,57] The angles across the central carbon atom are found from X-ray crystal structure analysis to be 128.3° and 129.2° (compared with the 180° required for planarity at the central carbon).



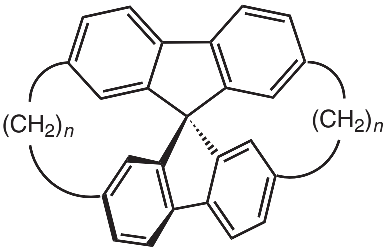
1-62

The smallest possible fenestrane is [3.3.3.3]fenestrane which is better known as pyramidane (**1-62**). Pyramidane has not been synthesized but has been examined in great detail theoretically.[61,67] Clearly, the bonding constraints placed on the four substituents to the central/apical carbon atom require a pyramidal-tetracoordinate arrangement. Pyramidane is the archetypal example of pyramidal-tetracoordinate bonding at carbon.[†]

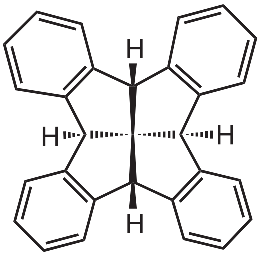
It would seem that the best hope of achieving planar-tetracoordinate carbon via the fenestrane route is in all-*trans*-[5.5.5.5]fenestrane. However, with a CCC angle of 162° **1-53** is still far from the planar ideal of 180°, and it is expected that this molecule will be unstable with respect to isomerization through inversion at the central carbon atom.

1.5.3 Vesiprenes and Fenestrindan

Two groups of compounds that are worthy of a brief mention are the vesiprenes (**1-63**) and fenestrindan (**1-64**) derivatives. The vesiprenes (n = 6 or 7) (**1-63**), synthesized by Prelog and Haas in 1969,[68] are fenestrane-like. They may be considered as unsaturated [5.m.5.m]fenestrane derivatives (with bridgehead double bonds to the four C^{α}'s) where m is large (13 or 14). Also referred to as spirobifluorenes, X-ray structures of these compounds showed some distortion from the tetrahedral ideal at the central carbon atom.[6a] This distortion is only minimal, and the importance of the vesiprenes is only in that they were the first fenestrane-like compounds to be considered.



1-63



1-64

Fenestrindan (**1-64**) is so called because it consists of four indan subunits fused in a similar manner to the four, fused cyclopentane rings in [5.5.5.5]fenestrane. This compound, synthesized by Kuck and coworkers,[69] has also been called tetrabenzo[5.5.5.5]fenestratetraene, tetrabenzocentrotetraquinene and centrotetraindan. The only stereoisomer of fenestrindan that has been synthesized is the all-*cis* isomer (**1-64**). The planarizing distortion at the central carbon is almost identical to that of the simple

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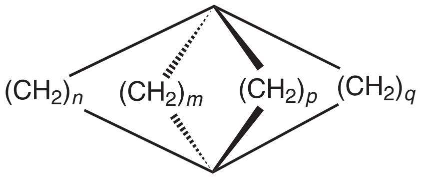
[†] For a detailed discussion of pyramidal-tetracoordinate bonding at carbon, see Chapter 3.

all-*cis*-[5.5.5.5]fenestrane (**1-52**); X-ray crystal structure analysis gives the $C^{\alpha}C^{0}C^{\alpha'}$ angle as 116.5°. Kuck has explored substitution at the bridgehead carbons (C^{α}) and finds some extra flattening at the central carbon atom in sterically crowded derivatives (e.g. tetramethyl-, tetrabromo-, tetracyanofenestrindan),[69b] but never by more than a few degrees beyond that seen in **1-64**.

1.5.4 Paddlanes and Bowlane

The paddlanes (**1-IV**), a family of saturated hydrocarbons, have been suggested as potential candidates for achieving planar-tetracoordinate carbon. The basic paddlane structure, and the usefulness of such a structure in applying a planarizing strain to tetracoordinate carbon, was first suggested by Wiberg *et al.*[70] in 1968.[†] The trivial name[‡] came later and is attributed to J. J. Bloomfield (see Hahn, Böhm and Ginsburg[71]). When the paddlane rings are all relatively small (*n*,*m*,*p*,*q* = 1–3), it is expected that the structural constraints placed on the bridgehead carbons will lead to a highly distorted tetracoordinate environment.



1-IV

Wiberg[70] has calculated *ab initio* geometries for the symmetric [*n*.*n*.*n*.*n*]paddlanes, [1.1.1.1]- and [2.2.2.2]paddlane. He determined high symmetry HF/6-31G(d) optimized structures of D_4 and D_{4h} symmetry for [1.1.1.1]paddlane (**1-65**) and [2.2.2.2]paddlane (**1-66**), respectively. Steric crowding in the equatorial plane (close H–H contacts between the methylene hydrogens) make the more symmetric D_{4h} structure for **1-65** unfavorable. Both calculated structures suggested close approaches between the two bridgehead carbon atoms (1.575 Å for **1-65** and 1.525 Å for **1-66**) which Wiberg took to

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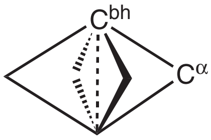
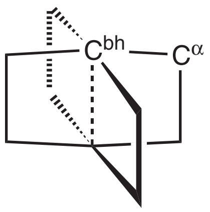
[†] Interestingly, Wiberg considered the possibility of a carbon atom approaching square-planar through structural imposition some years before Hoffmann's original paper[4] on the electronic structure of square-planar methane and design of planar-tetracoordinate carbon-containing systems.

[‡] The name paddlane comes from the resemblance of the structures to the paddles of the paddle-steamers on the Mississippi River.

indicate bonding between the two opposite bridgehead carbon atoms. The C^{bh}–C^{α} bonds are extremely long (1.668 and 1.787 Å, respectively) indicating a low bond-order, which added evidence for the notion of a bond between the bridgehead carbon atoms (C^{bh}). As a consequence of this likely C^{bh}–C^{bh} bond, the D_{4h} symmetry structure for [2.2.2.2]paddlane can be seen as a set of four fused cyclobutane rings and has an almost exactly planar-tetracoordinate carbon atom ($\angle C^{\alpha}C^{bh}C^{\alpha}$ = 178.8°). The bridgehead carbon atoms in [1.1.1.1]paddlane are clearly pyramidalized. Earlier semi-empirical calculations on [2.2.2.2]paddlane by Schleyer and coworkers[64] gave similar results.



1-65 (D_4)



1-66 (D_{4h})

Wiberg[70] and Schleyer[64] both indicated highly unfavorable thermodynamics for **1-65** and **1-66**. But neither calculated the second-derivative or force-constant matrix; the stationary points located were not examined to see if they were high-order saddle points, transition structures or minima. Our own calculations at the MP2/6-31G(d) level show that the high-symmetry structures reported by Wiberg and Schleyer are indeed high-order saddle points and not minima on the potential energy surface. Following the down-hill (negative) modes on the potential energy surface until a minimum is reached leads in all cases to disintegration of the paddlane structure through separation at one or more of the over-long C^{bh}–C^{α} bonds (which we calculate to be even longer at the MP2/6-31G(d) level than at the HF/6-31G(d) level). It seems unlikely that any small-ring paddlanes can exist.[†]

More recently, Dodziuk[72] has considered an unsaturated, hypothetical, conjugated paddlane (**1-68**). Although this cannot be considered a small-ring paddlane, it aims to distort the bridgehead carbons by using the rigid enediyne **1-67** as the 'arms' of the pad-

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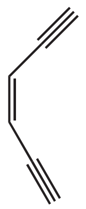
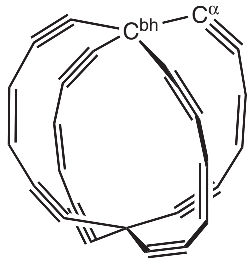
[†] A recent report of the synthesis and isolation of [1.1.1.1]paddlane from [1.1.1]propellane has appeared.[73] The product they report (with two ^{13}C-NMR signals with a 2:1 ratio and a single hydrogen environment) is not likely to be [1.1.1.1]paddlane; allene may be a possible product and is suggested from our calculations to be the preferred breakdown product of a short-lived [1.1.1.1]paddlane species.

dlane. The only minimum located for this $C_{28}H_8$ structure on the HF/6-31G(d) and B3-LYP/6-31G(d) potential energy surfaces has D_{4d} symmetry with a slightly distorted but still tetrahedral-like bridgehead carbon. The angle across the bridgehead carbon (C^{bh}) was found to be 117.6° at the B3-LYP/6-31G(d) level.

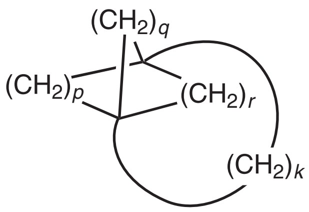


1-67

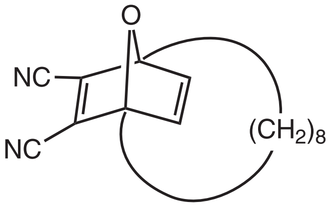


1-68 (D_{2d})

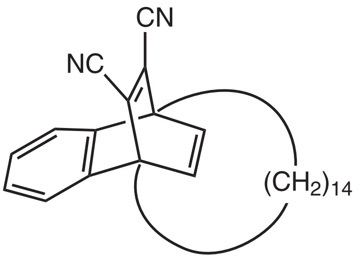
Experimentally-isolated paddlanes[6,7b,70,71,73,74] are mostly heteroatomic substitution derivatives of the parent paddlane systems (i.e. the skeleton is not purely carbon) and all have a [*k*.*p*.*q*.*r*]paddlane structure where $k \geq 8$ and $p,q,r \leq 3$ (**1-X**). In all of these compounds, there is little or no angle strain at the bridgehead carbons (see for example **1-69**[74b] and **1-70**[70b]).



1-X



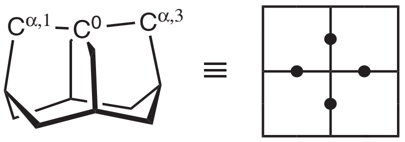
1-69



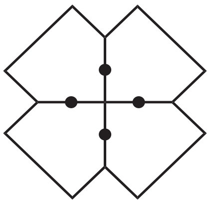
1-70

The lack of experimental progress in making small-ring paddlanes and the calculated instability of the symmetric small-ring paddlanes suggest that this will not be a very fruitful approach to forming planar-, or even highly-distorted, tetracoordinate carbon. However, a related approach to planar-tetracoordinate carbon, in which only a single carbon atom is highly distorted, has been suggested.

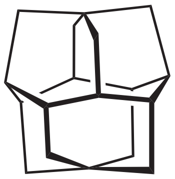
Bowlane (**1-4**) is a saturated hydrocarbon in which a $C(CH_2)_4$ neopentane-like subunit has been attached to a cyclooctane cap. The result of this is that all four substitu-



1-4 (C_{2v})



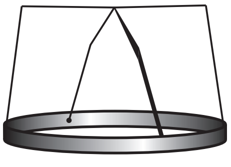
1-71



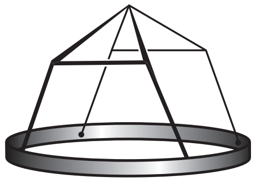
1-72

ents to carbon are drawn to one side of the molecule in a bowl-like structure. Semi-empirical calculations by Dodziuk[9b] indicated that the apical carbon (C^0) would be pyramidal. *Ab initio* calculations by McGrath, Radom and Schaefer[9a] at the HF/6-31G(d) level indicated that the apical carbon is tetrahedrally distorted but considerably planarized ($C^{\alpha,1}C^0C^{\alpha,3}$ = 170.8° and $C^{\alpha,2}C^0C^{\alpha,4}$ = 148.1°).[†]

Dodziuk has suggested other, larger bowlane-like structures[9b,75] (e.g. **1-71**) and a curious double-bowlane structure[75] (**1-72**) in which two bowlane molecules are fused via the cyclooctane bowl to give a structure that suggests that bowlane might well be considered as a half-paddlane-like molecule (with only a single highly distorted bridgehead carbon). The bowlane-like hemialkaplanes (**1-XI**) will be examined in detail in



1-XI



1-XII

Chapter 3. We have also considered a similar family of molecules that we call the hemispiroalkaplanes (**1-XII**). These bowl-like molecules also contain a single, highly distorted apical carbon atom. The substituents at the apical carbon atom are constrained to one hemisphere through attachment to a cycloalkane subunit (in the same manner as in the hemialkaplanes). However, the apical subunit, $C(CH)_4$, is based on spiropentane (rather than neopentane in the hemialkaplanes). The apical carbon in these molecules is

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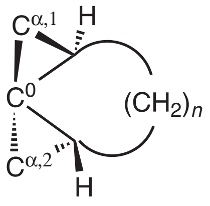
[†] Further details of our own calculations are provided in Chapter 3.

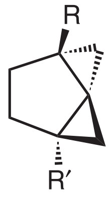
expected to be pyramidal, rather than planar-tetracoordinate. These molecules are also examined in detail in Chapter 3.

1.5.5 Bridged Spiropentanes

Recently, the desire to synthesize compounds with a highly distorted tetracoordinate carbon has led researchers to examine the simple bridged spiropentanes (**1-XIII**). This approach to forming highly distorted (though not planar) tetracoordinate carbon in purely organic molecules has proven to be remarkably successful. It appears that deformations from the preferred tetrahedral-like geometry at a spiro[2.2] carbon (i.e. the spiro carbon in spiropentane) can be accomplished more readily than distortions at a tetracoordinate carbon atom like that in neopentane or the [*k.l.m.n*]fenestranes (where *k*,*l*,*m*,*n* > 3).[56,60b] At the extreme, where the two three-membered rings approach planarity, it can be expected that steric repulsion, which results from the four methylene groups being packed into a plane, may be important. However, at the relatively small deformations that are typical in the systems that have been synthesized or where syntheses have been attempted, it seems that this effect should be small. It is likely that an electronic effect due to the peculiar bonding in the cyclopropane subunits is responsible.

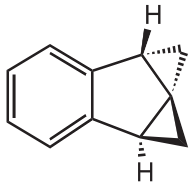


1-XIII

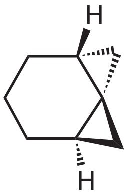


R, R′ = H, CH_3

1-73 (C_2)

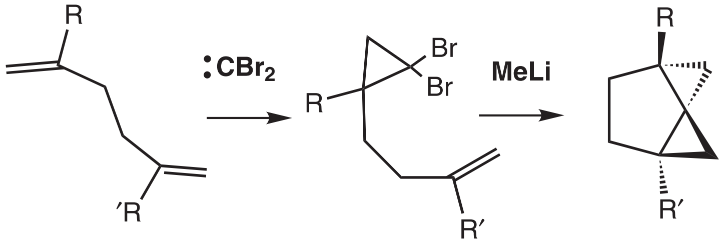


1-74 (C_2)



1-75 (C_2)

The first bridged spiropentanes (**1-XIII**) are due to Skattebøl,[76] who, in 1966 synthesized tricyclo[4.1.0.0^{1,3}]heptane and a series of alkylated derivatives (**1-73**) through intramolecular cyclopropylidene insertion into a C=C double bond (Scheme 1-1). Electron-diffraction analysis[77] of the structure of the unsubstituted tricyclo-[4.1.0.0^{1,3}]heptane (**1-73**) revealed a very highly distorted carbon atom (C^0). The angle across the apical carbon ($\angle C^{\alpha,1}C^0C^{\alpha,2}$) was found to be 162.4° from the electron-diffraction analysis and 158.2° from X-ray crystal structure analysis[78] (compared with 137.2° is spiropentane). The apical carbon atom is, however, not particularly flattened; the angles around the five-membered ring average 105°, although the ring-angle at the apical carbon is somewhat widened (110.1°). Further, the two three-membered rings are twisted at an angle of 80.0° (compared with the 90° twist in spiropentane and 0° twist in a planar-tetracoordinate structure). A number of workers[60b,78] have considered the relative difficulty of bending versus twisting at the spiro carbon in spiropentane and find that bending should be favoured over twisting. Tricyclo[4.1.0.0^{1,3}]heptane (**1-73**) shows this effect quite distinctly.



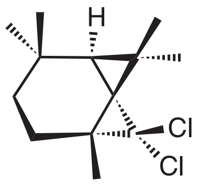
1-73

Scheme 1-1

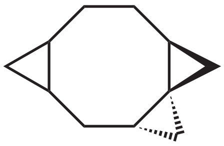
Brinker and coworkers[79] have synthesized a benzo derivative of tricyclo[4.1.0.0^{1,3}]-heptane (**1-74**) which is found to have a slightly larger angle at the apical carbon ($\angle C^{\alpha,1}C^{0}C^{\alpha,2}$ = 164.0°). This represents increased bending at C^0 but the angle between the three-membered rings is also increased to 85.2° (from 80.0° for **1-73**), indicating less twist. Interestingly, this molecule is found to be somewhat thermally labile with a half-life at 25° C of approximately 52 hours.[79,80] This is not the case for the saturated parent (**1-73**).[80] However, the importance of this low barrier to thermal isomerization, and its implications regarding the hemispiroalkaplanes, is explored in Chapter 3.

Brinker has tried to extend the use of the cyclopropylidene insertion reaction (Scheme 1-1) to make other bridged spiropentanes. Synthesis of tricyclo[5.1.0.0^{1,3}]octane (**1-75**)[81] via this process was reported by Skattebøl[76b] but proved problematic.[81] Both Brinker[81] and Wiberg[82] have synthesized this bridged spiropentane via an alternate route. No structure has been reported yet. However, it is expected that the larger bridge ($-(CH_2)_3-$) will lead to less deformation at C^{ap} than for **1-73**.

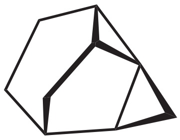
A number of other large-ring bridged spiropentanes (**1-XIII**, $n > 2$) have been



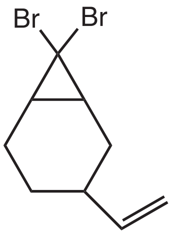
1-76



1-77

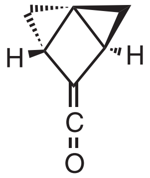


1-78

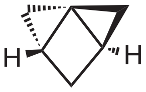


1-79

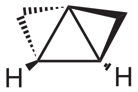
reported. A dichloropentamethyl derivative of **1-75** (**1-76**) has been reported by Köbrich and Baumann[83] and an $n = 5$ bridged spiropentane (**1-77**) was synthesized by Kuznetsova and coworkers.[84] The most unusual bridged spiropentane that has been synthesized is tetracyclo[$3.3.1.0^{2,4}.0^{2,8}$]nonane (**1-78**).[85] This bridged spiropentane was made by treating **1-79** with MeLi (Skattebøl's carbene cyclization). This molecule's tridendate spiropentane bridge is unique. No structure is available yet but our calculations at the MP2/6-311+G(2d,p) level indicate that the angle across the apical carbon is almost linear (174°) although the degree of twist between the planes of the two three-membered rings is still high (82°). This compound is only one step away from the hemispiroalkaplanes (**1-XII**) (which might be viewed as spiropentanes bound with a tetradentate bridge).



1-80 (C_2)



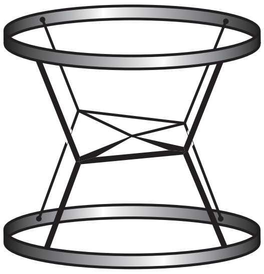
1-81 (C_2)



1-82 (C_1)

Bridged spiropentanes (**1-XIII)** with small bridges ($n < 2$) have been explored in detail by Wiberg.[82,86] Wiberg has had considerable success in synthesizing these [3.*m*.3]fenestranes (**1-IX**) (where $3 < m < 5$). Evidence for a one-carbon bridged species, presumably the small-ring ketene, tricyclo[$3.1.0.0^{1,3}$]hexane-4-ketene **(1-80),** was seen in a matrix at 15 K. This molecule (**1-80**) and its parent hydrocarbon (**1-81**) are expected to have a butterfly or half-planar geometry at the apical carbon; the angle across the apical carbon for both **1-80** and **1-81** is calculated to be very close to 180° but the twist between the two three-membered rings is found to be about 82° (similar to the twist in **1-73**). Wiberg has also found evidence for tricyclo[2.1.0.0^{1,3}]pentane (**1-82**) as the intermediate in the reaction of 1-bromo-2-chloromethylbicyclo[1.1.0]butane with phenylthiol. Calculated structures for **1-82** indicate that it will have C_1 symmetry, bond-lengths of 1.49 Å (for the C^0–C^α bonds) and 1.54 Å (for the single bridge bond), and a pyramidal tetracoordinate carbon atom.

1-V



1-VI

1-VII

It is our belief that spiropentane represents the best opportunity for distortion at a quaternary tetracoordinate carbon atom in a neutral saturated hydrocarbon. However, the bridged spiropentanes show considerable bending but little twisting of the cyclopropane subunits. This twisting is necessary to give planar-tetracoordinate carbon. Incorporation of a spiropentane subunit into our designs is likely to be of great assistance but a means of establishing (and maintaining) the necessary twist must be devised. Our approach to solving this problem has been to use a pair of tetradentate bridges (*cf.* the alkaplanes (**1-V**), spiroalkaplanes (**1-VI**) and dimethanospiroalkaplanes (**1-VII**)) (details are given in Chapter 4).

1.6 Concluding Remarks

A number of the various electronic approaches to forming planar-tetracoordinate carbon have clearly had great success. This is in part a tribute to the ingenuity of the workers and expeditious use of van't Hoff's "imaginative faculty", and in part serendipity.[†] However, as has been pointed out by Siebert and Gunale,[25] the planar-tetracoordin-

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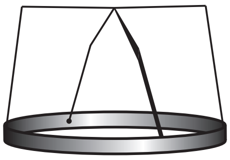
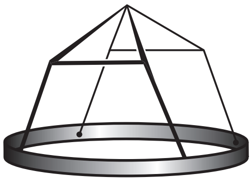
[†] For example, Cotton's dimethoxyphenyldivanadium complex (**1-25**) was not recognized as containing a planar-tetracoordinate carbon until some time after the X-ray crystal structure was published.

ate carbon compounds that result from most of these approaches have an electronic structure that differs markedly from the electronic structure proposed originally by Hoffmann for square-planar methane.[†] As a result, these compounds, none of which are organic molecules, will not have properties consistent with having a *p*-type lone pair and four electron-deficient σ-bonds. In fact, rather than stabilizing the unusual electronic structure expected for planar-tetracoordinate carbon, which has been described as a $\sigma^2\pi^2$ configuration at the planar carbon (*cf.* the normal σ^4 configuration seen in tetrahedrally-bonded carbon), most of these compounds alter the electronic structure to one that is more stable. This is generally done by removing one of the π-electrons, making it available for σ-bonding, and then stabilizing the remaining π-electron by involving it in a π-bonding system. The resulting electronic configuration at the planar-tetracoordinate carbon is usually $\sigma^4\pi^1$.

We think that the greater challenge involves taking a structural approach to forming planar-tetracoordinate carbon. Because such an approach relies on using covalent bonding in an organic framework, it is also more in the spirit of defying the van't Hoff/le Bel principle of tetrahedral tetracoordinate carbon, which was formulated for organic systems. Further, a structural approach should preserve the unusual electronic structure at the planar-tetracoordinate carbon. Because the electronic structure is not being disturbed by strongly electron-accepting or -withdrawing species, it is expected that a *p*-type lone pair of electrons will result. This unique feature should confer quite extraordinary properties on the resulting molecule. In choosing to restrict our search for planar-tetracoordinate carbon to saturated hydrocarbons, we hope to design molecules that will have unique bonding at the target carbon and remarkable properties for a purely organic system.



1-XI



1-XII

[†] Keese has also expressed his preference for the structural approach to planar-tetracoordinate carbon.[6b]

Our search for planar-tetracoordinate carbon in saturated hydrocarbon cage systems has indeed involved considerable use of van't Hoff's "imaginative faculty". Novel structures, in the form of the hemialkaplanes (**1-XI**) and hemispiroalkaplanes (**1-XII**), and their properties are detailed in Chapter 3. Chapter 4 then explores the three alkaplane-like families, the alkaplanes (**1-V**), the spiroalkaplanes (**1-VI**) and the dimethanospiroalkaplanes (**1-VII**) in detail.

References

(1) van't Hoff, J. H. "Sur les formules de structure dans l'espace," *Arch. Neerl. Sci. Exactes Nat.* **1874**, *9*, 445–454. For a translation see, van't Hoff, J. H. "A suggestion looking into the extension into space of the structural formulas at present used in chemistry. And a note upon the relation between the optical activity and the chemical constitution of organic compounds" in *Classics in the Theory of Chemical Combinations*; Benfey, O. T., Ed.; Dover: New York, **1963**; Vol. I, pp 151–160.

(2) le Bel, J. A. "Sur les relations qui existent entre les formules atomiques des corps organiques, et le pouvoir rotatoire de leurs dissolutions," *Bull. Chim. Soc. Fr.* **1874**, *22*, 337–347. For a translation see, le Bel, J. A. "On the relations which exist between the atomic formulas of organic compounds and the rotatory power of their solutions" in *Classics in the Theory of Chemical Combinations*; Benfey, O. T., Ed.; Dover: New York, **1963**; Vol. I, pp 161–171.

(3) (a) Kolbe, H. *J. prakt. Chem.* **1877**, *15*, 473. (b) A translation of Kolbe's comments appears in Wheland, G. W. *Advanced Organic Chemistry*, 2nd ed., Wiley: New York, **1949**, p. 132.

(4) (a) Hoffmann, R.; Alder, R.; Wilcox Jr, C. F. "Planar tetracoordinate carbon," *J. Am. Chem. Soc.* **1970**, *92*, 4992–4993; (b) Hoffmann, R. "The theoretical design of novel stabilized systems," *Pure Appl. Chem.* **1971**, *28*, 181–194.

(5) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. "Stabilization of planar tetracoordinate carbon," *J. Am. Chem. Soc.* **1976**, *98*, 5419–5427.

(6) (a) Keese, R.; Pfenninger, A.; Roesle, A. "35. Planarization of tetracoordinate carbon atom. Synthesis of 13-oxa-14-oxo-pentacyclo[5.5.2.1.$0^{4,15}$.$0^{10,15}$]pentadecane, a bridged 'tetraquinacane'," *Helv. Chim. Acta* **1979**, *62*, 326–334. (b) For a recent review see: Thommen, M.; Keese, R. "Fenestranes in recent synthetic developments," *Synlett* **1997**, 231–240.

(7) (a) Rao, V. B.; George, C. F.; Wolff, S.; Agosta, W. C. "Synthetic and structural studies in the [4.4.4.5]fenestrane series," *J. Am. Chem. Soc.* **1985**, *107*, 5732–5739; (b) Agosta, W. C. "Inverted and planar carbon" in *The Chemistry of the Alkanes and Cycloalkanes*; Patai, S. and Rappoport, Z., Ed.; Wiley: New York, **1992**, pp 927–962.

(8) Röttger, D.; Erker, G. "Compounds containing planar-tetracoordinate carbon," *Angew. Chem., Int. Ed.* **1997**, *36*, 813–827; *Angew. Chem.* **1997**, *109*, 840–856.

(9) (a) McGrath, M. P.; Radom, L.; Schaefer, H. F. “Bowlane: toward planar tetracoordinate carbon,” *J. Org. Chem.* **1992**, *57*, 4847–4850. (b) An earlier report of the molecule bowlane (**1-4**) calculated, using semi-empirical methods, that the apical carbon atom would be pyramidal: Dodziuk, H. “Bowlane (tetracyclo[3.3.3.$1^{3,10}$.$1^{7,10}$]tridecane): a new hypothetical molecule possessing a pyramidal tetracoordinated carbon atom in the ground state,” *J. Mol. Struct., Theochem.* **1990**, *239*, 167–172.

(10) (a) McGrath, M. P.; Radom, L. “Alkaplanes: a class of neutral hydrocarbons containing a potentially planar tetracoordinate carbon,” *J. Am. Chem. Soc.* **1993**, *115*, 3320–3321; (b) Lyons, J. E.; Rasmussen, D. R.; McGrath, M. P.; Nobes, R. H.; Radom, L. “Octaplane: a saturated hydrocarbon with a remarkably low ionization energy leading to a cation with a planar tetracoordinate carbon atom,” *Angew. Chem., Int. Ed.* **1994**, *33*, 1667–1668; *Angew. Chem.* **1994**, *106*, 1722.

(11) Radom, L.; Rasmussen, D. R. “Planar Carbon Story,” *Pure Appl. Chem.* **1998**, 1977–1984.

(12) Rasmussen, D. R.; Radom, L. “Planar-tetracoordinate carbon in a neutral saturated hydrocarbon. Theoretical design and characterization,” *Angew. Chem., Int. Ed.* **1999**, *38*, 2876–2878; *Angew. Chem.* **1999**, *111*, 3051–3054.

(13) Monkhorst, H. J. “Activation energy for interconversion of enantiomers containing an asymmetric carbon atom without breaking bonds,” *J. Chem. Soc., Chem. Commun.* **1968**, 1111–1112.

(14) (a) Saturno, A. F. “Walsh’s rules for AH_4 systems derived from united atom molecular orbitals,” *Theoret. Chim. Acta* **1967**, *7*, 273–276. (b) See also, Gimarc, B. M. “The shapes of simple polyatomic molecules and ions. II. The series AH_2, AH_3, and AH_4,” *J. Am. Chem. Soc.* **1971**, *93*, 593–599.

(15) Firestone, R. “Linnett planar methane,” *J. Chem. Soc., Chem. Commun.* **1973**, 163.

(16) (a) Wiberg, K. B.; Ellison, G. B. “Distorted geometries at carbon,” *Tetrahedron* **1974**, *30*, 1573–1578; (b) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J. “Electronic states of organic molecules. I. Potential functions for the deformation of methane,” *J. Am. Chem. Soc.* **1976**, *98*, 1212.

(17) (a) Durmaz, S.; Murrell, J. N.; Pedley, J. B. “Calculation of the lowest energy state of planar methane,” *J. Chem. Soc., Chem. Commun.* **1972**, 933–934; (b) Murrell, J. N.; Pedley, J. B.; Durmaz, S. “Potential energy surfaces for the reaction $CH_2 + H_2 \rightarrow CH_4$,” *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1370–1380.

(18) Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I. “Semiempirical and ab initio calculations on the automerization of methane,” *J. Chem. Soc., Chem. Commun.* **1977**, 213–214.

(19) (a) Lathan, W. A.; Hehre, W. J.; Curtiss, L. A.; Pople, J. A. “Molecular orbital theory of the electronic structure of organic compounds. X. A systematic study of geometries and energies of AH_4 molecules and cations,” *J. Am. Chem. Soc.* **1971**, *93*, 6377–6387; (b) Crans, D. C.; Snyder, J. P. “Tetracoordinate planar carbon: a disinglet radical,” *J. Am. Chem. Soc.* **1980**, *102*, 7152–7154; (c) Krogh-Jesperson, M.-B.; Chandrasekhar, J.; Würthwein, E.-U.; Collins, J. B.; Schleyer, P. v. R. “Molecular orbital study of tetrahedral, planar, and pyramidal structures of the isoelectronic series BH_4^-, CH_4, NH_4^+, SiH_4, and PH_4^+,” *J. Am. Chem. Soc.* **1980**, *102*, 2263–2268.

(20) Gordon, M. S.; Schmidt, M. W. "Does methane invert through square planar?" *J. Am. Chem. Soc.* **1993**, *115*, 7486–7492.

(21) Pepper, M. J. M.; Shavitt, I.; Schleyer, P. v. R.; Glukhovtsev, M. N.; Janoschek, R.; Quack, M. "Is stereomutation of methane possible?" *J. Comput. Chem.* **1995**, *16*, 207–225.

(22) Wong, M. W.; Radom, L. "Methane dication: planar but not square," *J. Am. Chem. Soc.* **1989**, *111*, 1155–1156.

(23) Benson, S. W. *Thermochemical kinetics: Methods for the estimation of thermochemical data and rate parameters*; 2nd ed.; Wiley: New York, **1976**, p. 309.

(24) (a) Yoshizawa, K.; Ohta, T.; Yamabe, T.; Hoffmann, R. "Dioxygen cleavage and methane activation on diiron enzyme models – A theoretical study," *J. Am. Chem. Soc.* **1997**, *119*, 12311–12321; (b) Yoshizawa, K.; Suzuki, A.; Yamabe, T. "Inversion of methane on transition-metal complexes: A possible mechanism for inversion of stereochemistry," *J. Am. Chem. Soc.* **1999**, *121*, 5266–5273.

(25) Siebert, W.; Gunale, A. "Compounds containing a planar-tetracoordinate carbon atom as analogues of planar methane," *Chem. Soc. Rev.* **1999**, *28*, 367–371.

(26) For calculations on the electronic configuration of these and related compounds see: (a) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. "An ab initio study on stabilizing interactions in dinuclear Zr/Al complexes with a planar tetracoordinate carbon center," *Angew. Chem., Int. Ed.* **1993**, *32*, 754–756; *Angew. Chem.* **1993**, *105*, 753; (b) Gleiter, R.; Hyla-Kryspin, I.; Niu, S. Q.; Erker, G. "Stabilizing interactions and coordination in cationic zirconocene complexes - Cp_2ZrL^+ - a MO theoretical study," *Organometallics* **1993**, *12*, 3828–3836; Gleiter, R.; Hyla-Kryspin, I.; Niu, S. Q.; Erker, G. "Stabilizing interactions and coordination in cationic zirconocene complexes - Cp_2ZrL^+ - a MO theoretical study, (Vol 12, 3831, 1993)," *Organometallics* **1994**, *13*, 744; (c) Poumbga, C. N.; Bénard, M.; Hyla-Kryspin, I. "Planar tetracoordinate carbons in dimetallic complexes - Quantum chemical investigations," *J. Am. Chem. Soc.* **1994**, *116*, 8259–8265; Poumbga, C. N.; Bénard, M.; Hyla-Kryspin, I. "Planar tetracoordinate carbons in dimetallic complexes - Quantum chemical investigations (Vol 116, 8259, 1994)," *J. Am. Chem. Soc.* **1994**, *116*, 12135; (d) Hyla-Kryspin, I.; Gleiter, R.; Rohmer, M. M.; Devemy, J.; Gunale, A.; Pritzkow, H.; Siebert, W. "Quantum-chemical investigations of stabilizing interactions in μ-diborylcarbene dicobalt complexes with a planar tetracoordinate carbon atom," *Chem.-Eur. J.* **1997**, *3*, 294–299.

(27) (a) Streitwieser Jr., A.; Williams Jr., J. E.; Alexandratos, S.; McKelvey, J. M. "Ab initio SCF-MO calculations of the methyllithium and related systems. Absence of covalent character in the C–Li bond," *J. Am. Chem. Soc.* **1976**, *98*, 4778–4784; (b) Laidig, W. D.; Schaefer III, H. F. "Structures and energetics of planar tetrahedral dilithiomethane. A near degeneracy of singlet and triplet states," *J. Am. Chem. Soc.* **1978**, *100*, 5972–5973; (c) Bachrach, S. M.; Streitwieser Jr., A. "Structure and bonding in dilithiomethane," *J. Am. Chem. Soc.* **1984**, *106*, 5818–5824.

(28) See also, (a) Maerker, A.; Theis, M.; Kos, A. J.; Schleyer, P. v. R. "1,1-Dilithioethane," *Angew. Chem., Int. Ed.* **1983**, *22*, 733–734; (b) Ritchie, J. P.; Bachrach, S. M. "Bond paths and bond properties of carbon-lithium bonds," *J. Am. Chem. Soc.* **1987**, *109*, 5909–5916; (c) van Eikema Hommes, N. J. R.; Schleyer, P. v. R.; Wu, Y.-D. "Mechanism of the Zei-

gler dilithiomethane synthesis. An ab initio study of methyllithium pyrolysis," *J. Am. Chem. Soc.* **1992**, *114*, 1146–1151; (d) Ong, C. M.; Stephen, D. W. "Lithiations of bis-diphenyl-N-trimethylsilylphosphiniminomethane: An X-ray structure of a 1,1-dilithiomethane derivative," *J. Am. Chem. Soc.* **1999**, *121*, 2939–2940.

(29) (a) Krogh-Jesperson, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. "Molecular orbital theory of the electronic structure of molecules. 39. Highly unusual structures of electron-deficient carbon compounds. Reversal of van't Hoff stereochemistry in BBC ring systems," *J. Am. Chem. Soc.* **1979**, *101*, 4843–4851; (b) Jemmis, E. D.; Subramanian, G.; Srinivas, G. N. "Boron analogs of cyclopropenium cation: $B_3H_6^+$, the first three membered nonplanar 2π aromatic," *J. Am. Chem. Soc.* **1992**, *114*, 7939–7941; (c) Minyaev, R. M.; Quapp, W.; Subramanian, G.; Schleyer, P. v. R.; Mo, Y. R. "Internal conrotation and disrotation in $H_2BCH_2BH_2$ and diborylmethane 1,3 H exchange," *J. Comput. Chem.* **1997**, *18*, 1792–1803.

(30) (a) Watts, J. D.; Stamper, J. G. "A molecular orbital study of CLi_2F_2: planar 3-coordinate and pyramidal 4-co-ordinate carbon," *J. Chem. Soc., Chem. Commun.* **1985**, 5–6; (b) Watts, J. D.; Stamper, J. G. "On the computational realization of planar tetracoordinate carbon," *Tetrahedron* **1987**, *43*, 1019–1026.

(31) Sorger, K.; Schleyer, P. v. R. "Planar and inherently non-tetrahedral tetracoordinate carbon: a status report," *J. Mol. Struct., Theochem.* **1995**, *338*, 317–346.

(32) (a) Bolton, E. E.; Laidig, W. D.; Schleyer, P. V.; Schaefer, H. F. "Singlet $C_2H_2Li_2$ - Acetylenic and 1,2-dilithioethene isomers - A remarkably congested potential energy hypersurface for a simple organometallic system," *J. Am. Chem. Soc.* **1994**, *116*, 9602–9612; (b) Bolton, E. E.; Laidig, W. D.; Schleyer, P. v. R.; Schaefer, H. F. "Does singlet 1,1-dilithioethene really prefer a perpendicular structure," *J. Phys. Chem.* **1995**, *99*, 17551–17557.

(33) Gribanova, T. N.; Minyaev, R. M.; Minkin, V. I. "Planar tetracoordinate carbon in organoboron compounds: ab initio computational study," *Coll. Czech. Chem. Commun.* **1999**, *64*, 1780-1789.

(34) (a) Sorger, K.; Schleyer, P. v. R.; Stalke, D. "Towards planar tetracoordinate carbon in the puckered ladder structure of dilithiated 1-di-*tert*-butylhydroxymethyl-3,3-dimethycyclopropene," *J. Chem. Soc., Chem. Commun.* **1995**, 2279–2280; (b) Sorger, K.; Schleyer, P. v. R.; Stalke, D. "Dimeric [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium–tetramethylenediamine: distortion of the cyclopropenyl geometry due to strong rehybridization at the lithiated carbon," *J. Am. Chem. Soc.* **1996**, *118*, 1086–1091; (c) Sorger, K.; Schleyer, P. v. R.; Fleischer, R.; Stalke, D. "Toward planar tetracoordinate carbon in the puckered ladder structures of chelated cyclopropenyllithium aggregates," *J. Am. Chem. Soc.* **1996**, *118*, 6924–6933.

(35) (a) Chandrasekhar, J.; Schleyer, P. v. R. "Planar tetracoordinate carbon candidates. MNDO calculations on substituted phenyllithium dimers," *J. Chem. Soc., Chem. Commun.* **1981**, *6*, 260–261; (b) Dietrich, H.; Mahdi, W.; Storck, W. "Kristall- und Molekülstruktur von 2,6-Dimethoxyphenyllithium," *J. Organomet. Chem.* **1988**, *349*, 1–10; (c) Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. "Planar tetracoordinate carbon atoms hidden in the tetrameric aggregate of (2,6-dimethoxyphenyl)lithium," *J. Am. Chem. Soc.* **1988**, *110*, 7802–7806; (d) Harder, S.; Ekhart, P. F.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; Schleyer, P. v. R.

"Crystal structure of [2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium," *Organometallics* **1992**, *11*, 2623–2627.

(36) Cotton, F. A.; Millar, M. "The probable existence of a triple bond between two vanadium atoms," *J. Am. Chem. Soc.* **1977**, *99*, 7886–7891.

(37) Buchwald, S. L.; Lucas, E. A.; Davies, W. M. "A bimetallic zirconium complex containing an in-plane bridging aromatic ring," *J. Am. Chem. Soc.* **1989**, *111*, 397–398.

(38) (a) Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. "Planar tetracoordinate carbon in $Cp_2Zr(\mu\text{-}\eta^1,\eta^2\text{-}Me_3SiCCPh)(\mu\text{-}Cl)AlMe_2$," *J. Am. Chem. Soc.* **1990**, *112*, 9620–9621; (b) Erker, G.; Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. "Eine einfache Synthese van dimetallischen Zirconium/Aluminim-Verbindungen mit planar-tetrakoordiniertem Kohlenstoff," *Chem. Ber.* **1992**, *125*, 1953–1956; (c) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S.; Binger, P.; Langhauser, F. "(Aryne)metallocene- and (Alkyne)metallocene-derived dimetallic zirconium/aluminium complexes containing planar-tetracoordinate carbon," *Organometallics* **1992**, *11*, 3517–3525; (d) Erker, G. "Planar-tetrakoordinierter Kohlenstoff," *Nach. Chem. Tech. Lab.* **1992**, *40*, 1099–1104; (e) Erker, G. "Planar-tetracoordinate carbon: making stable anti-van't Hoff/le Bel compounds," *Comments Inorg. Chem.* **1992**, *13*, 111–131; (f) Erker, G.; Röttger, D. "The energetic stabilization caused by a planar-tetracoordinate carbon atom: a dynamic NMR spectroscopic study of the dimetallabicycle $[(Cp_2Zr)_2(\mu\text{-}CCCH_3)(\mu\text{-}H_3CCCCH_3)]BPH_4$," *Angew. Chem., Int. Ed.* **1993**, *32*, 1623–1625; (g) Albrecht, M.; Erker, G.; Krüger, C. "The synthesis of stable, isolable planar-tetracoordinate carbon compounds," *Synlett* **1993**, 441–448; (h) Röttger, D.; Erker, G.; Fröhlich, R.; Grehl, M.; Silverio, S. J.; Hyla-Kryspin, I.; Gleiter, R. "Determination of the stabilization energy of planar-tetracoordinate carbon in dynamic dinuclear (μ-hydrocarbyl)bis(zirconocene) cation complexes and detection of an organometallic memory effect in their formation," *J. Am. Chem. Soc.* **1995**, *117*, 10503–10512; (i) Röttger, D.; Erker, G.; Fröhlich, R. "Formation of a $[\mu\text{-}(\eta^1\text{-}N\text{-}\eta^2\text{-}C,N)$-aryl cyanide biszirconocene cation by ligand exchange reaction," *Chem. Ber.* **1995**, *128*, 1045–1046; (j) Röttger, D.; Pflug, J.; Erker, G.; Kotila, S.; Fröhlich, R. "Reaction of the organometallic planar tetracoordinate carbon compound $[(Cp_2Zr)_2(\mu\text{-}C\text{-}CCH_3)(\mu\text{-}(\eta^1\text{-}C\text{-}\eta^2\text{-}C,C)\text{-}CH_3CCCH_3)]^+ [BPh_4]^-$ with alkyl isocyanides," *Organometallics* **1996**, *15*, 1265–1267; (k) Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. "Stabilization of a planar-tetracoordinate carbon center in an organometallic complex containing both a zirconocene and a hafnocene moiety," *Chem. Ber.* **1996**, *129*, 1–3; (l) Röttger, D.; Erker, G.; Fröhlich, R. "Formation of stable organometallic planar-tetracoordinate carbon compounds containing a cationic $(\mu\text{-}R^1CCR^2)[\mu\text{-}Cl(ZrCp_2)_2]$ framework," *J. Org. Chem.* **1996**, *518*, 221–225; (m) Ahlers, W.; Erker, G.; Fröhlich, R.; Peuchert, U. "Synthesis, structure, and dynamic behavior of (μ-aldimido)$(\mu\text{–}\eta^1,\eta^2$-alkyne)-biszirconocene cation complexes that contain planar-tetracoordinate carbon," *Chem. Ber. -Recueil* **1997**, *130*, 1069–1077; (n) Schottek, J.; Erker, G.; Fröhlich, R. "Formation of metallocene-stabilized planar-tetracoordinate carbon compounds by a protonation route," *Eur. J. Inorg. Chem.* **1998**, 551–558; (o) Schottek, J.; Röttger, D.; Erker, G.; Fröhlich, R. "Formation of hypercoordinated carbon inside a (μ-hydrocarbyl)bis(group 4 metallocene) framework by a simple protonation route," *J. Am. Chem. Soc.* **1998**, *120*, 5264–5273; (p) Erker, G. "Using bent metallocenes for stabilizing unusual coordination geometries at carbon," *Chem. Soc. Rev.* **1999**, *28*, 307–314.

(39) (a) Binger, P.; Sandmeyer, F.; Krüger, C.; Kuhnigk, J. R.; Goddard, R.; Erker, G. “New titanium–boron complexes with a planar tetracoordinate carbon or a planar tricoordinate phosphorus center,” *Angew. Chem., Int. Ed.* **1994**, *33*, 197–198; (b) Binger, P.; Sandmeyer, F.; Krüger, C.; Erker, G. “New bimetallic complexes (M^1-Ti; M^2-B) containing planar tetracoordinate carbon,” *Tetrahedron* **1995**, *51*, 4277–4290; (c) Binger, P.; Sandmeyer, F.; Krüger, C. “Reactivity of bimetallic compounds containing planar tetracoordinate carbon toward unsaturated organic substrates,” *Organometallics* **1995**, *14*, 2969–2976.

(40) Choukroun, R.; Cassoux, P. “Planar tetracoordination of carbon in groups 4 and 5 organometallic chemistry,” *Acc. Chem. Res.* **1999**, *32*, 494-502.

(41) The first cation of type **1-28**, where $M^1 = M^2 =$ Zr, L = CC–*t*-Bu, $R^1 =$ *t*-Bu, $R^2 =$ Me, was reported by Horton and Orpen: Horton, A. D.; Orpen, A. G. “A structurally distorted ligand in an electron-deficient dizirconocene cation: unusual 1,2- and 1,1-dimetallioalkenes,” *Angew. Chem., Int. Ed.* **1992**, *31*, 876–878; *Angew. Chem.* **1992**, *104*, 912.

(42) (a) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Hampden-Smith, M. J.; Huffman, J. C.; Folting, K.; Ellis, P. D.; Huggins, B. A. “Versatile modes of allene bonding in the structures of $[W_2OtBu)_6(C_3H_4)]$, $[W_2OtBu)_6(C_3H_4)(CO)_2]$ and $[W_2(O\text{-}tBu)_6(C_3H_4)_2]$,” *Angew. Chem., Int. Ed.* **1989**, *28*, 1523–1525; (b) Chacon, S. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. “Allene adducts of ditungsten hexaalkoxides. Three modes of allene coordination to dinuclear centers as seen in the structures of $W_2(O\text{-}tBu)_6(C_3H_4)$, $W_2(O\text{-}tBu)_6(C_3H_4)_2$, and $W_2(O\text{-}tBu)_6(C_3H_4)(CO)_2$,” *Organometallics* **1991**, *10*, 3722–3735.

(43) (a) Cotton, F. A.; Shamshoum, E. S. “Mechanistic insight into the reaction of phenyl isocyanate with ditungsten hexa-*tert*-butoxide: isolation and characterization of early intermediates,” *J. Am. Chem. Soc.* **1985**, *107*, 4662-7; (b) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. “Addition of di-*p*-tolylcarbodiimide to ditungsten hexa-*tert*-butoxide. Preparation and structure of $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$,” *Organometallics* **1985**, *4*, 461–465.

(44) Ogoshi, S.; Tsutsumi, K.; Ooi, M.; Kurosawa, H. “Synthesis, Structure and Reactivity of η^3-Allenyl/Propargyl Dinuclear Palladium Complexes,” *J. Am. Chem. Soc.* **1995**, *117*, 10415–10416.

(45) (a) Leoni, P.; Pasquali, M.; Pieri, G.; Albinati, A.; Pregosin, P. S.; Rüegger, H. “A stable palladium(I) dimer with one 14e palladium center and its reversible reaction with CS_2, affording a new complex with a planar four-coordinate carbon,” *Organometallics* **1995**, *14*, 3143–3145. (b) For a related hexacoordinate carbon species see: Leoni, P.; Pasquali, M.; Fadini, L.; Albinati, A.; Hofmann, P.; Metz, M. “Synthesis and structure of $Pd_4(\mu\text{-}(PtBu_2)_2(\mu\text{-}CS_2)(PPh_3)_2I_2$, a neutral palladium(I) derivative with a hexacoordinate carbon and a CS_2 molecule bridging four palladium centers,” *J. Am. Chem. Soc.* **1997**, *119*, 8625–8629. For similar platinum based complexes see: (c) Farrar, D. H.; Gukathasan, R. R.; Morris, S. A. “Reaction of CS_2 with trinuclear Pd and Pt clusters. Crystal structure of $Pt_2(\mu\text{-}CS_2)_2(P(tBu)_2Ph)_2$,” *Inorg. Chem.* **1984**, *23*, 3258–3261; (d) Farrar, D. H.; Gukathasan, R. R.; Won, K. “Reactions of carbon disulphide with palladium(0) complexes,” *J. Organomet. Chem.* **1984**, *275*, 263–271.

(46) Chi, Y.; Cheng, P.-S.; Wu, H.-L.; Hwang, D.-K.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. "Heterometallic carbonyl cluster oxide. Formation, structure and reactivity of WRe_2 oxo-acetylide cluster compounds," *J. Chem. Soc., Chem. Commun.* **1994**, 1839–1840.

(47) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. "A new metallic environment for carbon in a carbido metal cluster," *J. Chem. Soc., Chem. Commun.* **1985**, 978–979.

(48) (a) Gunale, A.; Pritzkow, H.; Siebert, W.; Steiner, D.; Berndt, A. "Dicobalt and diplatinum complexes of diborylcarbenes," *Angew. Chem., Int. Ed.* **1995**, *34*, 1111–1113; (b) Gunale, A.; Steiner, D.; Schweikart, D.; Pritzkow, H.; Berndt, A.; Siebert, W. "Unusual mono- and dinuclear cobalt and platinum complexes of rearranged boriranylideneborane and diboretanylideneborane ligands - Dicobalt-μ-diborylcarbene complexes as derivatives of planar methane," *Chem. Eur. J.* **1998**, *4*, 44–52.

(49) Böhm, M. C.; Gleiter, R.; Schang, P. "On the planarity of tetracyclo[5.5.1.$0^{4,13}$.$0^{10,13}$]tridecahexaene," *Tetrahedron Lett.* **1979**, *28*, 2575–2578.

(50) Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R. "On the planarity of tetracoordinate carbon enclosed by annulene perimeter," *Tetrahedron* **1981**, *37*, 921–927.

(51) Schoeller, W. W. "On the question of a planar tetravalent carbon centre in the ethylene- and acetylene-benzenium ion - a semi-empirical SCF-LCAO-study," *J. Chem. Soc., Chem. Commun.* **1974**, 872.

(52) For more recent studies that have considered these phenonium ions, see for **1-40**: (a) Sieber, S.; Schleyer, P. v. R.; Gauss, J. "The accurate C_{2v} phenonium and benzenonium ion structures confirmed by correlated GIAO-MP2 NMR chemical shift calculations," *J. Am. Chem. Soc.* **1993**, *115*, 6987–6988; (b) Rappoport, Z.; Kobayashi, S.; Stanger, A.; Boese, R. "Crystal structure of 1,2-diphenyl-5,7-di-*tert*-butylspiro[2.5]octa-1,4,7-trien-6-one, a possible model for diphenylvinylidenephenonium ions," *J. Org. Chem.* **1999**, *64*, 4370–4375. (c) For **1-41** see: Wang, H.; Weiner, B.; Frenklach, M. "Theoretical study of reaction between phenylvinyleum ion and acetylene," *J. Phys. Chem.* **1993**, *97*, 10364-10371. (d) For **1-42** see: Olah, G. A.; Head, N. J.; Rasul, G.; Prakash, G. K. S. "Protonation of benzocyclobutene with superacid: Cram's phenonium ion (spiro[5.2]octa-5,7-dien-4-yl cation) revisited," *J. Am. Chem. Soc.* **1995**, *117*, 875-82.

(53) Georgian, V. "Synthesis directed toward saturated "flat" carbon," *Tetrahedron Lett.* **1972**, *42*, 4315–4317.

(54) (a) Keese, R. "Tetrakoordinierter Kohlenstoff mit planoider Konfiguration," *Nach. Chem. Tech. Lab.* **1982**, *30*, 844–849; (b) Keese, R. *Planarization of tetracoordinate carbon. Synthesis and structure of [5.5.5.5]fenestranes*; Chizhov, O. S., Ed.; Blackwell: Oxford, **1986**, pp 43–52; (c) Luef, W.; Keese, R. "62. Angular distortions at tetracoordinate carbon. Planoid distortions in α,α′-bridged spiro[4.4]nonanes and [5.5.5.5]fenestranes," *Helv. Chim. Acta* **1987**, *70*, 543–553; (d) van der Waals, A.; Keese, R. "Synthesis of a [5.5.5.5]fenestrenedione via tandem Pauson-Khand tetracyclization," *J. Chem. Soc., Chem. Commun.* **1992**, 570–571; (e) Keese, R.; Guidetti-Grept, R.; Herzog, B. "Synthesis of [5.5.5.5]fenestranes by Pd-catalyzed carbonylation-cyclization," *Tetrahedron Lett.* **1992**, *33*, 1207–1210; (f) Brunvoll, J.; Guidetti-Grept, R.; Hargittai, I.; Keese, R. "204. Synthesis and electron-diffraction structure of all-*cis*-[5.5.5.5]fenestrane," *Helv. Chim. Acta* **1993**, *76*, 2838–2846; (g) Guidetti-Grept, R. G.; Herzog, B.; Debrunner, B.; Silje-

govic, V.; Keese, R.; Frey, H.-M.; Hauser, A.; König, O.; Lüthi, S.; Birrer, J.; Nyffeler, D.; Förster, M.; Bürgi, H.-B. “A [5.5.5.5]fenestrane derivative,” *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *C51*, 495–497.

(55) (a) Keese, R. “Two stereoisomeric [4.5.5.5]fenestranes formed by intramolecular [2 + 2] cycloaddition,” *Angew. Chem., Int. Ed.* **1992**, *31*, 344–345; (b) Hirschi, D.; Luef, W.; Gerber, P.; Keese, R. “147. Synthesis and structure of [4.5.5.5]fenestranes (= tetracyclo[5.4.1.0^{4,12}.0^{9,12}]dodecanes),” *Helv. Chim. Acta* **1992**, *75*, 1897–1908.

(56) (a) Luef, W.; Keese, R. “Angular distortions at tetracoordinate carbon: planoid distortions in small spiroalkanes,” *J. Mol. Struct., Theochem.* **1992**, *257*, 353–368; (b) Luef, W.; Keese, R. “Planarizing distortions in carbon compounds,” *Adv. Strain Org. Chem.* **1993**, *3*, 229–267.

(57) (a) Venepalli, B. R.; Agosta, W. C. “Fenestranes and the flattening of tetrahedral carbon,” *Chem. Rev.* **1987**, *87*, 399–410; (b) Venugopal, D.; Agosta, W. C. “Cation, carbene, and radical centers in a [4.4.4.5]fenestrane,” *Tetrahedron* **1992**, *48*, 6757–6762.

(58) (a) Hoeve, W. T.; Wynberg, H. “Synthetic approaches to planar carbon. 1,” *J. Org. Chem.* **1980**, *45*, 2925–2930; (b) Hoeve, W. T.; Wynberg, H. “Synthetic approaches to planar carbon. 2,” *J. Org. Chem.* **1980**, *45*, 2930–2937.

(59) Smit, W. A.; Buhanjuk, S. M.; Simonyan, S. O.; Shashkov, A. S.; Struchkov, Y. T.; Yanovsky, A. I.; Caple, R.; Gybin, A. S.; Anderson, L. G.; Whiteford, J. A. “An efficient protocol for the synthesis of fenestrane derivatives,” *Tetrahedron Lett.* **1991**, *32*, 2105–2108.

(60) (a) Wiberg, K. B.; Olli, L. K.; Golombeski, N.; Adams, R. D. “Tricyclo[4.2.0.0^{1,4}]octane,” *J. Am. Chem. Soc.* **1980**, *102*, 7467–7475; (b) Wiberg, K. B.; Wendoloski, J. J. “Enthalpies of formation of fused cyclobutane derivatives,” *J. Am. Chem. Soc.* **1982**, *104*, 5679–5686; (c) Wiberg, K. B. “Structures and energies of the tricyclo[4.1.0.0^{1,3}]heptanes and the tetracyclo[4.2.1.0^{2,9}.0^{5,9}]nonanes. Extended group equivalents for converting *ab initio* energies to heats of formation,” *J. Org. Chem.* **1985**, *50*, 5285–5291.

(61) For work by Minkin and coworkers relating to pyramidane (**1-62**) and other fenestranes see: (a) Minyaev, R. M.; Minkin, V. I. “Pyramidal tetracoordinate carbon,” *J. Org. Chem. USSR (Engl. Transl.)* **1978**, *14*, 1–12; *Zh. Org. Khim.* **1978**, *14*, 3–15; (b) Minyaev, R. M.; Minkin, V. I.; Zefirov, N. S.; Zhdanov, Y. A. “An approach to the synthesis of pyramidane,” *J. Org. Chem. USSR (Engl. Transl.)* **1979**, *15*, 1815–1821; *Zh. Org. Khim.* **1979**, *15*, 2009–2016; (c) Minkin, V. I.; Minyaev, R. M. “Stabilization of pyramidal tetracoordinated carbon in organic molecules,” *J. Org. Chem. USSR (Engl. Transl.)* **1979**, *15*, 197–204; *Zh. Org. Khim.* **1979**, *15*, 225–234; (d) Minkin, V. I.; Minyaev, R. M.; Natanzon, V. I. “Structure of fenestranes and the eight-electron rule,” *J. Org. Chem. USSR (Engl. Transl.)* **1980**, *16*, 589–596; (e) Natanzon, V. I.; Minyaev, R. M. “Stabilization of the carbon atom by two collinear double bonds,” *Theor. Exp. Chem.* **1981**, *17*, 207–209; *Teor. Éksp. Khim.* **1981**, *17*, 264–268; (f) Minkin, V. I.; Minyaev, R. M. “The nonclassical polyhedral organic molecules and ions” in *Progress in Theoretical Organic Chemistry*; Csizmadia, I. G., Ed.; Elsevier: Amsterdam, **1982**; Vol. 3, pp 121–155; (g) Minkin, V. I.; Minyaev, R. M.; Orlova, G. V. “Pyramidane and isoelectronic cations,” *J. Mol. Struct., Theochem.* **1984**, *110*, 241–253; (h) Minyaev, R. M.; Minkin, V. I. “Structure of hetero derivatives and of the pentacoordinated anion of [4.4.4.4]fenestrane,” *J. Org. Chem. USSR*

(Engl. Transl.) **1985**, *21*, 1239–1248; (i) Minkin, V. I.; Minyaev, R. M.; Zhdanov, Y. A. “Nontetrahedral tetracoordinate carbon atom in organic compounds” in *Nonclassical Structures of Organic Compounds*; Mir: Moscow, **1987**, pp 248–306 (translated by B. V. Rassadin); (j) Minkin, V. I.; Ya Simkin, B.; Glukhovtsev, M. N. “Quantum-chemical studies of the structure and reactivity of carbenes,” *Russ. Chem. Rev.* **1989**, *58*, 622–635.

(62) (a) Gupta, A. K.; Fu, X.; Snyder, J. P.; Cook, J. M. “General approach for the synthesis of polyquinenes via the Weiss reaction,” *Tetrahedron* **1991**, *47*, 3665–3710; (b) Fu, X.; Kubiak, G.; Zhang, W.; Han, W.; Gupta, A. K.; Cook, J. M. “General approach for the synthesis of polyquinenes via the Weiss reaction XV. Synthesis of the [5.5.5.5]fenestrane system via the aldol approach and the studies directed toward the [5.5.6.6]fenestranes,” *Tetrahedron* **1993**, *49*, 1511–1524.

(63) (a) Liebman, J. F.; Greenberg, A. “A survey of strained organic molecules,” *Chem. Rev.* **1975**, *76*, 311–365; (b) Greenberg, A.; Liebman, J. F. “A potpourri of pathologies” in *Strained Organic Molecules*; Academic Press: New York, **1978**; Vol. 38, pp 342–385.

(64) Würthwein, E.-U.; Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. “The [4.4.4.4]fenestranes and [2.2.2.2]paddlane. Prospects for the realization of planar tetracoordinate carbon?” *Tetrahedron Lett.* **1981**, *22*, 843–846.

(65) Schulman, J. M.; Sabio, M. L.; Disch, R. L. “Structure and energetics of [4.4.4.4]fenestrane,” *J. Am. Chem. Soc.* **1983**, *105*, 743–744.

(66) (a) Wender, P. A.; Dore, T. M.; deLong, M. A. “An arene-alkene photocycloaddition-radical cyclization cascade: the first syntheses of *cis,cis,cis,trans*-[5.5.5.5]-fenestranes,” *Tetrahedron Lett.* **1996**, *37*, 7687-7690; (b) Wender, P. A.; DeLong, M. A.; Wireko, F. C. “Novel oxidative rearrangement product of the first *trans,cis,cis,cis*-[5.5.5.5]fenestrane derivative,” *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1997**, *C53*, 954-956.

(67) Lewars, E. “Pyramidane - an *ab initio* study of the C_5H_4 potential energy surface,” *J. Mol. Struct., Theochem.* **1998**, *423*, 173–188.

(68) (a) Haas, G.; Prelog, V. “Optically active 9,9′-spirobifluorene derivatives,” *Helv. Chim. Acta* **1969**, *52*, 1202–1218; (b) Prelog, V.; Bedekovic, D. “Chiral 2,2′-polyoxaalkano-9,9′-spirobifluorenes,” *Helv. Chim. Acta* **1979**, *62*, 2285–2302.

(69) (a) Kuck, D.; Boegge, H. “Benzoannelated centropolyquinanes. 2. (all-*cis*)-tetrabenzotetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane, ‘fenestrindan’,” *J. Am. Chem. Soc.* **1986**, *108*, 8107–8109; (b) Kuck, D.; Schuster, A.; Krause, R. A. “Benzoannelated centropolyquinanes. Part IX. Synthesis and conformational behavior of fenestrindans (tetrabenzo[5.5.5.5]-fenestranes) with four bridgehead substituents,” *J. Org. Chem.* **1991**, *56*, 3472–3475; (c) Kuck, D. “Benzoannelated fenestranes with [5.5.5], [5.5.5.6], and [5.5.5.5] frameworks: the route from 1,3-indandione to fenestrindan,” *Chem. Ber.* **1994**, *127*, 409–25; (d) Kuck, D.; Schuster, a.; Gestmann, D.; Posteher, F.; Pritzkow, H. “Benzoannelated centropolyquinanes. Part 20. Centropentaindan, a fenestrane bearing five mutually fused indan units: syntheses, molecular structure, and bridgehead substitution,” *Chem. Eur. J.* **1996**, *2*, 58–67; (e) Seifert, M.; Kuck, D. “Naphtho-annulated [5.6.5]- and [6.5.5.5]fenestranes,” *Tetrahedron* **1996**, *52*, 13167–13180; (f) Kuck, D. “Benzoannelated fenestranes,” *Adv. Theor. Interesting Mol.* **1998**, *4*, 81–155; (g) Kuck, D. “The centropolyindans and related centro-fused polycyclic organic compounds. Polycycles between neopentane $C(CH_3)_4$ and the carbon nucleus $C(CC_3)_4$,” *Top. Curr. Chem.* **1998**, *196*, 167–220; (h)

Bredenkotter, B.; Barth, D.; Kuck, D. "Synthesis and base-induced epimerization of *cis,cis,cis,trans*-tribenzo[5.5.5.6]fenestranes," *Chem. Commun. (Cambridge)* **1999**, 847-848.

(70) (a) Wiberg, K. B.; Hiatt, J. E.; Burgmaier, G. J. "Distorted geometries about bridgehead carbons," *Tetrahedron Lett.* **1968**, 5855–5857; (b) Wiberg, K. B.; O'Donnell, M. J. "Preparation and Diels-Alder reactions of the [*n*](1,4)naphthalenophanes. Isolation of a paddlane derivative containing the tricyclo[14.2.2.2^{1,6}]docosane ring system," *J. Am. Chem. Soc.* **1979**, *101*, 6660–6666; (c) Wiberg, K. B. "Bonding in small ring paddlanes," *Tetrahedron Lett.* **1985**, *26*, 5967–5970.

(71) Hahn, E. H.; Bohm, H.; Ginsburg, D. "The synthesis of paddlanes: compounds in which quaternary bridgehead carbons are joined by four chains," *Tetrahedron Lett.* **1973**, 507–510.

(72) Dodziuk, H.; Leszczynski, J.; Nowinski, K. S. "The quest for a planar and pyramidal carbon atom. 4. An unsuccessful search for pyramidal carbon atoms in hypothetical unsaturated conjugated paddlane," *J. Mol. Struct., Theochem.* **1997**, *391*, 201–205.

(73) Lee, W. B.; Oh, D. W. "The reaction of [1.1.1]propellane with methylene," *Bull. Korean Chem. Soc.* **1999**, *20*, 629-630.

(74) (a) Wynberg, H.; Helder, R. "The synthesis of [2.2](9,10)anthraceno(2,5)furanophane and its reaction with dimethyl acetylenedicarboxylate," *Tetrahedron Lett.* **1971**, *45*, 4317–4320; (b) Helder, R.; Wynberg, H. "Diels-Alder addition of dicyanocetylene to [8](2,5)furanophane. Synthesis of a paddlane," *Tetrahedron Lett.* **1973**, 4321-4; (c) Wynberg, H.; Hulshof, L. A. "Optical activity of hydrocarbons," *Tetrahedron* **1974**, *30*, 1775-82; (d) Vögtle, F.; Koo Tze Mew, P. "Triptycenophanes – Synthesis via 'double nonbenzylic sulfone pyrolysis'," *Angew. Chem., Int. Ed.* **1978**, *17*, 60–61; (e) Warner, P.; Chem, B.-L.; Bronski, C. A.; Karcher, B. A.; Jacobson, R. A. "Synthesis of some [*n*.1.3.1]- and [*n*.1.2.1]paddlanes," *Tetrahedron Lett.* **1981**, *22*, 375-6; (f) Eaton, P. E.; Leipzig, B. D. "Toward tricyclo[2.2.2.2]decane. 1. [*n*.2.2.2]Paddlane systems, n = 10-14," *J. Am. Chem. Soc.* **1983**, *105*, 1656–1658; (g) Tobe, Y.; Fujita, H.; Wakaki, I.; Terashima, K.; Kobiro, K.; Kakiuchi, K.; Odaira, Y. "Water-soluble macrocyclic paddlanes and propellane as a new class of host molecules," *J. Chem. Soc., Perkin Trans. 1* **1984**, 2681-4; (h) Schwartz, M. H.; Rosenfeld, S. M.; Lee, C. I.; Jasinski, J. P.; Dardon, E. H. "The structure of 9,10-dihydro-9,10-bis(hydroxymethyl)-9,10-ethanoanthracene-11,12-anhydride," *Tetrahedron Lett.* **1992**, *33*, 6275-8.

(75) Dodziuk, H. "Unusual saturated hydrocarbons: Interaction between theoretical and synthetic chemistry," *Top. Stereochem.* **1994**, *21*, 351–380.

(76) (a) Skattebøl, L. "Chemistry of *gem*-dihalocyclopropanes. II. The reaction of dienes with dibromocarbene," *J. Org. Chem.* **1964**, *29*, 2951–2956; (b) Skattebøl, L. "Chemistry of *gem*-dihalocyclopropanes. V. Formation of tricyclo[4.1.0.04,6]heptane and derivatives," *J. Org. Chem.* **1966**, *31*, 2789–2794; (c) Frey, H. M.; Hopkins, R. G.; Skattebøl, L. "Thermal unimolecular isomerization of tricyclo[4.1.0.0^{1,3}]heptane," *J. Chem. Soc. B* **1971**, 539–541; (d) Becher, G.; Skattebøl, L. "Thermal reactions of *meso*- and racemic deca-2,3,7,8-tetraene," *Tetrahedron Lett.* **1979**, *14*, 1261–1264.

(77) Smith, Z.; Andersen, B.; Bunce, S. "Electron-diffraction study of gaseous tricyclo[4.1.0.0^{1,3}]heptane," *Acta Chem. Scand. A* **1977**, *31*, 557–562.

(78) Boese, R.; Bläser, D.; Gomann, K.; Brinker, U. H. “Spiropentane as a tensile spring,” *J. Am. Chem. Soc.* **1989**, *111*, 1501–1503.

(79) (a) Brinker, U. H.; Streu, J. “4,5-Benzotricyclo[4.1.0.$0^{1,3}$]hept-4-ene,” *Angew. Chem., Int. Ed.* **1980**, *19*, 631–632; *Angew. Chem.* **1980**, *92*, 641. See also: (b) Brinker, U. H.; Wilk, G.; Gomann, K. “Thermolysis and reactions of 4,5-benzotricyclo[4.1.0.$0^{1,3}$]hept-4-ene and *o*-(propadienyl)styrene,” *Angew. Chem., Int. Ed.* **1983**, *22*, 868–869; *Angew. Chem.* **1983**, *95*, 892; (c) Brinker, U. H.; Gomann, K.; Zorn, R. “Tricyclo[4.1.0.$0^{1,3}$]hept-4-enes as intermediates,” *Angew. Chem., Int. Ed.* **1983**, *22*, 869–870; *Angew. Chem.* **1983**, *95*, 893; (d) Gleiter, R.; Krennrich, G.; Brinker, U. H. “Electronic structure of spiropentane and some derivatives,” *J. Org. Chem.* **1986**, *51*, 2899–2901.

(80) (a) Flowers, M. C.; Frey, H. M. “The thermal isomerization of spirobicyclopropane,” **1961**, *J. Chem. Soc.*, 5550–5551; (b) Roth, W. R.; Wollweber, D.; Offerhaus, R.; Rekowski, V.; Lennartz, H.-W.; Sustmann, R.; Müller, W. “Zur Energiedelle von Diradikalen. IV. 2-Methylen-1,4-cyclohexadiyl,” *Chem. Ber.* **1993**, *126*, 2701–2715.

(81) (a) Miebach, T.; Wuster, H.; Brinker, U. H. “Carbene rearrangements. 42. Intramolecular addition versus novel carbon hydrogen bond insertion reactions of N-alkenyl-substituted cyclopropylidenes,” *J. Org. Chem.* **1993**, *58*, 6520–6523; (b) Miebach, T.; Brinker, U. H. “*trans*-Tricyclo[5.1.0.$0^{1,3}$]octane,” *J. Org. Chem.* **1993**, *58*, 6524–6525.

(82) (a) Wiberg, K. B.; McClusky, J. V.; Schulte, G. K. “The reaction of a bridged spiropentane with Zeise’s dimer,” *Tetrahedron Lett.* **1986**, *27*, 3083–3086; (b) Wiberg, K. B.; McClusky, J. V. “Tricyclo[2.1.0.$0^{1,3}$]pentane,” *Tetrahedron Lett.* **1987**, *28*, 5411–5414; (c) Wiberg, K. B.; Chaves, A. “Predominant inversion of configuration in an intramolecular carbene addition to an alkene,” *J. Am. Chem. Soc.* **1989**, *111*, 8052–8053; (d) Wiberg, K. B.; McMurdie, N.; McClusky, J. V.; Hadad, C. M. “Tricyclo[2.1.0.$0^{1,3}$]pentane,” *J. Am. Chem. Soc.* **1993**, *115*, 10653–10657; (e) Wiberg, K. B.; Snoonian, J. R. “Bridged spiropentanes - ring expansion,” *Tetrahedron Lett.* **1995**, *36*, 1171–1174; (f) Wiberg, K. B.; Snoonian, J. R.; Lahti, P. M. “Ring contraction of a two-carbon bridged spiropentane,” *Tetrahedron Lett.* **1996**, *37*, 8285–8288; (g) Wiberg, K. B.; Snoonian, J. R. “Synthesis, reactions, and structural studies of two-carbon bridged spiropentanes,” *J. Org. Chem.* **1998**, *63*, 1402–1407; (h) Wiberg, K. B.; Snoonian, J. R. “Ring expansion and contraction of a two-carbon bridged spiropentane,” *J. Org. Chem.* **1998**, *63*, 1390–1401.

(83) Köbrich, G.; Baumann, M. “Bridged methylenecyclopropanes as test cases for Brett’s rule: 2,5,5,7,7-pentamethylbicyclo[4.1.0]hept-1-ene,” *Angew. Chem., Int. Ed.* **1972**, *11*, 52–53; *Angew. Chem.* **1972**, *84*, 62–63.

(84) Kuznetsova, T. S.; Eremenko, O. V.; Kokoreva, O. V.; Zatonsky, G. V.; Zefirov, N. S. “Synthesis of alicyclic derivatives of spiropentane based on 1,5-cyclooctadiene,” *Russ. Chem. Bull.* **1996**, *45*, 1662–1666.

(85) Baird, M. S. “Tetracyclo[3.3.1.$0^{2,4}$.$0^{2,8}$]nonane. A strained spiro-compound,” *J. Chem. Soc., Chem. Commun.* **1974**, 197–198.

(86) See also: (a) Dodziuk, H.; Nowinski, K. S. “In quest for planar and pyramidal carbon atom. Part 2. AM1 study of small bridged spiropentanes,” *J. Mol. Struct., Theochem.* **1994**, *311*, 97–100; (b) Dodziuk, H.; Leszczynski, J.; Nowinski, K. S. “The quest for a planar and pyramidal carbon atom. 3. Can a tetrahedrally coordinated carbon form a nearly linear C-C-C bond angle,” *J. Org. Chem.* **1995**, *60*, 6860–6863.