Chem. Rev. **2006,** *106,* 4787−4808

Carbon Flatland: Planar Tetracoordinate Carbon and Fenestranes

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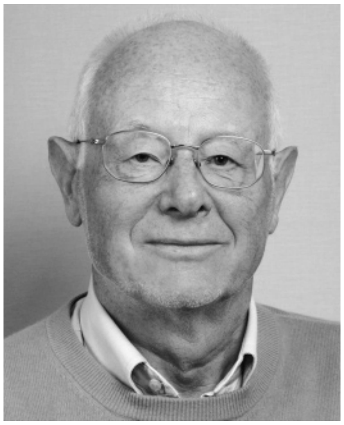
Received April 20, 2006

Contents

1. Introduction—Some Historical Remarks

The common structural features of optically active compounds, known in 1874, led van’t Hoff and, independently, Le Bel to the conclusion that tetracoordinate carbon compounds of type Cabcd must have a tetrahedral rather than a planar arrangement.[1,2] Since van’t Hoff related these structural features to the orientation of valence bonds rather than to a distorted tetrahedron, his rationalization appealed immediately to chemists doing experiments. This ‘quantum step’ in structural organic chemistry, in combination with the graphical representation of bonds and symbols for atoms, was the starting point for the explosive expansion in the realm of organic compounds and their structures.



Reinhart Keese was born in Mannheim, Germany, and studied chemistry at the University of Bonn, where he received his Dr. rer. nat. degree under the guidance of F. Korte (on unsaturated α-lactones) in 1961. Following two years of postdoctoral work with H. E. Zimmerman at the University of Wisconsin, Madison, he became Research Assistant of A. Eschenmoser at the Swiss Federal Institute of Technology, Zürich, Switzerland. His Habilitation dealing with Bredt’s rule was completed in 1974. He then joined the Institute of Organic Chemistry at the University of Bern, where he was Professor of Chemistry until his retirement in 1999. His main research interests were in the area of the chemistry of architectural molecules and biofunctional chemistry. Computational exploration of the planarizing deformation of tetracoordinate carbon and silicon as well as synthesis of appropriate polycyclic compounds were pursued. In addition, theoretical and mechanistic investigations of coenzyme B_{12}-catalyzed rearrangements and reactions were of major concern. At present he is actively engaged in the chemistry of functional vitamin B_{12} derivatives for surface coating and electrochemical transformations.

The open flank of a possible racemization—the extent of the kinetic stability—remained for many decades. This problem was of no concern in Berlin, where van’t Hoff worked during 1896−1911. According to B. Helferich, research assistant to E. Fischer during these years in Berlin (later Professor at Leipzig and Bonn), this question was not discussed.[3] An autoracemization of optically active organic compounds was eventually considered unlikely when no exemption was found from a racemization mechanism of optically active compounds occurring by breaking a bond to the asymmetric carbon atom.[4] New interest in the configurational inversion was initiated by Hoffmann, Alder, and Wilcox in 1970 in their discussion of the MO’s for planar tetracoordinate carbon.[5]

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10.1021/cr050545h CCC: $59.00

On the basis of extended Hückel MO calculations they evaluated the stabilization of tetracoordinate planar carbon "so that it could serve as a thermally accessible transition state for a classical racemization experiment". For organic chemists the potential of the semiempirical MO approach for organic reactions had previously been established in the context of pericyclic reactions.[6]

With the rapid development of advanced quantum chemical methods, which essentially replaced the classical valence-bond theory with its 'ties' to hybridization, the realm of nonclassical structures could now be explored.

The structures drawn on the basis of the MO calculations show the connectivities between nearest neighbors of atoms rather than localized two-center bonds containing two electrons and associated with hybridization. This feature, well known in coordination chemistry, makes it rather difficult or almost impossible to evaluate the stability of a newly formulated nonclassical organic structure without computational control. Furthermore, the MO methodology provides information about transition states and the relative stability of structurally related or isomeric atom assemblies.

These aspects, creation of new atom assemblies for forming molecules and extended networks, verification of their structures as local minima, the location of transition states nearby, and the relative stability of possible isomers have to be kept in mind for an appropriate evaluation of compounds containing planar tetracoordinate carbon.

In this review the more recent results in the wider area of planarizing distortions of tetracoordinate carbon are presented. First, the wealth of computational results is surveyed. Subsequently, experimental results of structures containing planar tetracoordinate carbon will be discussed. Finally, experimental exploration of planoid distortions in molecules containing $C(C)_4$ substructures will be exemplified. Theoretical, organometallic, and organic aspects of the earlier work in these areas have been reviewed.[7−19]

2. Computational Results

The nonclassical structure of planar tetracoordinate carbon gained considerable interest when the structural prerequisites for its stabilization became known. These concepts were developed by Hoffmann, Alder, and Wilcox and presented in 1970 using extended Hückel molecular orbital theory.[5] To date, the 'flat carbon' was almost exclusively the domain of computational explorations. In this way, an increasing number of structures were found. Prior to presentation of the key results it is appropriate to describe briefly the computational aspects of these investigations.

2.1. Computational Methods

Development of MO theory including the ab initio methodology and density functional theory (DFT) led to the computer-based exploration of the structural space in chemistry. The computational elucidation of structures, their energy content, and a variety of spectroscopic properties now provides reliable results.[20,21] Extension of this methodology to nonclassical structures and new atomic assemblies leads to new insights into structural possibilities. Thus, it comes without surprise that these theoretical tools are used for modeling structures containing planar tetracoordinate carbon.[5,6] Local (and global) minima, transition states, and plateaus on the potential-energy surface (PES) are detected by the number of imaginary frequencies. In addition, the HOMO−LUMO gap has to be rather high, and low-lying triplet states have to be absent. Furthermore, it has to be established whether the number of electrons at the planar tetracoordinate carbon (plc) is compatible with the octet rule with normal-range bond lengths. Also, evaluation of aromaticity in π systems surrounding and including the key carbon atom is appropriate. This property may be identified in terms of the $(4n + 2)$-Hückel rule or the magnetic properties extracted from nucleus-independent chemical shift (NICS) parameters.[22−26] The electron localization function (ELF) has been developed for inspection of the electron distribution.[27,28] Determination of the coordination number is of particular interest for those clusters where the number of ligands surrounding the planar tetracoordinate carbon exceeds four.[29] If not stated otherwise, the structures discussed in the sections below were obtained by high-level ab initio and DFT calculations, in many cases corrected by the zero-point vibrational energy (ZPE).

2.2. Stereomutation of CH_4

With their paper, Hoffmann, Alder, and Wilcox triggered unabated interest in both computational and experimental studies on planar tetracoordinate carbon.[5] They raised the question whether the stereomutation of CH_4 is possible and how structures containing tetracoordinate planar carbon could be generated. Prior to the outline of how to stabilize planar tetracoordinate carbon, a brief discussion of the prospects to the stereomutation in CH_4 is appropriate.[30−32] Detailed and extensive ab initio calculations on the methane potential-energy surface by Shavitt, Schleyer, Janoschek, Quack et al.[30] led to the following conclusion: The transition state for stereomutation is best described by a structure with C_s symmetry formally derived from singlet methylene and a side-on hydrogen molecule. It is located 105 kcal/mol above the T_d ground state of methane. Dissociation into singlet methylene ($^1A_1$) and H_2 would require an additional 13 kcal/mol, whereas decay of the transition state into triplet methylene and dihydrogen would still be endothermic by 4 kcal/mol. Bond cleavage of methane to give methyl and a hydrogen atom is 3 kcal/mol exothermic. According to these results, it is highly unlikely that methane could undergo stereomutation without breaking a bond. Yoshizawa et al. considered the possibility of inversion of methane by interaction with transition-metal complexes.[31] In their computational exploration by the DFT methodology they systematically explored the stabilizing interaction of first-row transition-metal ions (M^+) with the CH_4 transition state of C_s symmetry. According to their results the barrier height for the CH_4 stereomutation is decreased to ∼48 kcal/mol in complexes of the late-transition-metal complexes ($M^{+\bullet}CH_4$) with M = Fe to Cu in a low-spin state and to 59−43 kcal/mol in a high-spin state. They surmised that inversion of the configuration at a chiral carbon atom might be possible without bond cleavage in catalytic, including enzymatic, reactions.

More recently they compared the transition-state structure for the stereomutation of CH_4 with those of SiH_4 and GeH_4. In contrast to CH_4 with a calculated transition state of C_s symmetry, SiH_4 and GeH_4 should undergo inversion of configuration via a square-planar D_{4h} structure with activation energies of 88.6 and 93.7 kcal/mol, respectively.[32] Possible stereomutation of appropriate cyclopropyllithium derivatives was discussed.[33]

2.3. Stabilization of Planar Tetracoordinate Carbon

In their analysis of how to stabilize planar tetracoordinate carbon Hoffmann et al. first discussed the MO sequence of planar (D_{4h}) methane.[5] These MO's are correlated with those of tetrahedral CH_4 (Scheme 1). In a localized perspective this structure contains two two-center two-electron bonds, one three-center two-electron array, and a lone pair in an orthogonal 2p-AO.

It was clearly stated that the planar arrangement could be stabilized by σ-donating and π-accepting ligands. Replacement of hydrogen by less electronegative groups for in-plane bonding and concomitant π-conjugation might be achieved by ligands with a prospensity for back-bonding or incorporation of the planar carbon atom into the center of an annulene ring, achieving an aromatic ring system with $4n + 2$ electrons (Chart 1). The early extended Hückel calculations showed that **1p** is less stable than **1t** by 96.8 kcal/mol and that the planar arrangement derived from **2t** is only 66.9 kcal/mol above the tetrahedral structure. The energy of the planar structure of $C(BH_2)_4$ is calculated to be only 41.4 kcal/mol above the tetrahedral configuration. Also, the [14]annulene **3**, containing an aromatic perimeter, was evaluated for a possible planarization (see also section 3.1 and the discussion of **94** and **95** ($\equiv$ **3**).[5,10,85,86]

Scheme 1. Walsh Diagram for the Occupied MO's of Tetrahedral and Square Planar CH_4

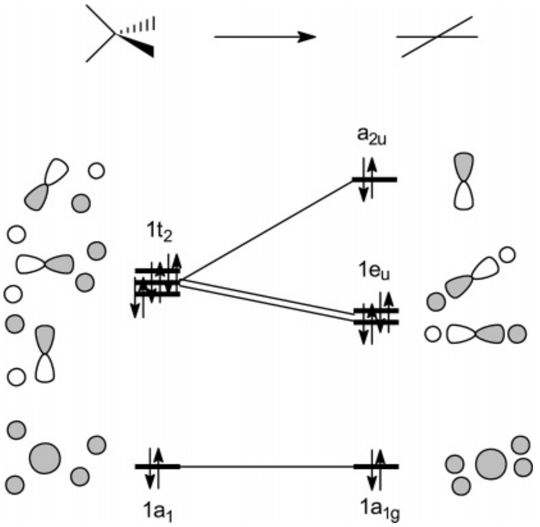
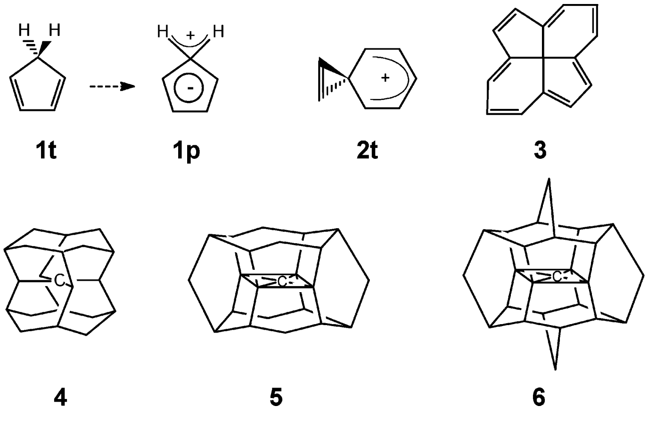


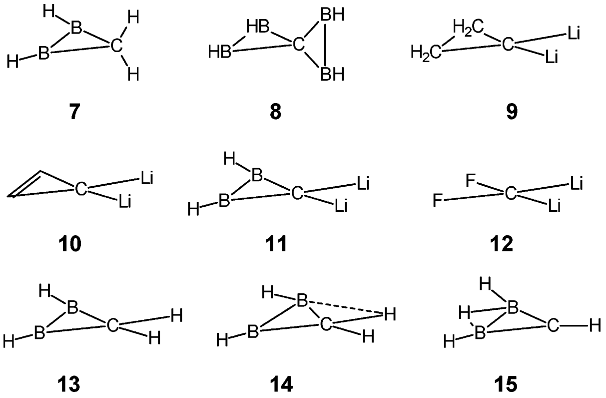
Chart 1



These leading propositions were later supported and expanded by extensive calculations performed by Schleyer and his group (see below).[33]

More recently Radom computationally explored the alkaplanes, a hypothetical family of strained hydrocarbon cage compounds, and found that the octaplane **4** with S_4 symmetry should contain a central carbon atom with opposite bond angles close to 180°.[34−38] Furthermore, it was shown that structures **5** (D_{2h}) as well as **6** (D_{2h}) contain a planar tetracoordinate carbon.[36] This concept, to place a carbon atom in the center of a saturated or unsaturated hydrocarbon skeleton, is based on the robust resistance of the ligand system to larger distortions from tetrahedral or planar arrangements, which reinforces planarizing distortions for the central carbon atom. In most cases low-lying reaction channels for ring opening and fragmentation into more stable isomeric structures have not been elucidated. However, exploratory computations led to the conclusion that **5** lies in a "relatively deep potential well" and that the HOMO is indeed the $2p_z$ AO at the planar tetracoordinate carbon. Later calculations at a computationally higher level showed **5** to be a transition state.[39] Emanating from the basic concepts of Hoffmann et al., the main developments for stabilization of planar tetracoordinate carbon are concerned with the computational exploration of the π-acceptor and σ-donor properties of mainly electropositive substituents. For reduction of the bond angle strain, the carbon atom 'under planarizing pressure' should be incorporated into a saturated or an unsaturated three-membered ring. For further stabilization of the planar configuration, the two electrons may be removed from the nonbonding $2p_z$ AO of the planar tetracoordinate carbon atom. These aspects are exemplified below (Chart 2).

Chart 2

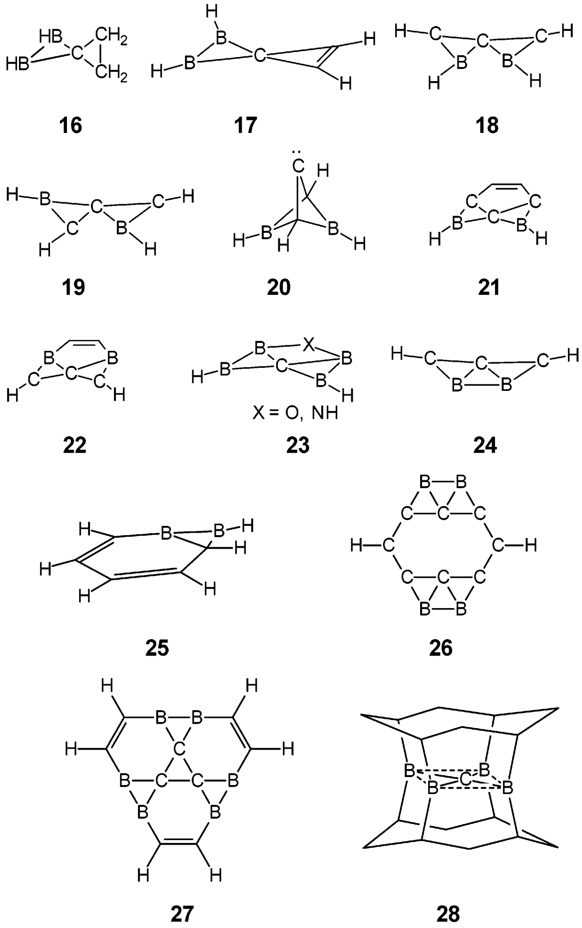


In 1976 Schleyer's calculations showed that diboracyclopropane **7** and tetraboraspiropentane **8** are more stable in the conventional tetrahedral configuration by 20 and 6 kcal/mol, respectively.[33] In contrast, **9**−**12** were calculated to prefer a planar structure.[7] Later, the DFT methodology revealed that **13**, the planar structure of **7**, is more stable but associated with a transition state and that the nonsymmetrical structure **14** and the hydrogen-bridged structure **15** are more stable by ~30 kcal/mol. The delicate balance of σ-donating effects of electropositive ligands and orthogonal π systems, both included in a three membered ring, is apparent.

These structural motifs have stimulated several groups to establish computationally a large variety of structures containing planar tetracoordinate carbon. Some of the most recent results are exemplified here with spirocyclopentane and its modifications and congeners as the most important building blocks.

According to high-level, high-precision ab initio calculations by Gribanova et al., the tetrahedral structure **16** is related to its enantiotopomer by a planar transition state only 0.23 kcal/mol higher in energy[40] with the PES in the region of the planar structure of **16** being extremely flat (Chart 3).

Chart 3



The diboraspiro[2.2]pent-4-ene **17** was found to prefer a planar configuration. The two isomers of the $C_3H_4B_2$ family, **18** and **19**, are also local minima on the potential-energy surface. Structure **18** is the more stable isomer and energetically only 3.9 kcal/mol less stable than the $C_3B_2H_4$ singlet carbene **20**. Variation of these structural motifs led to **21**−**23** also showing computed preferences for planar tetracoordinate carbon.[41] Representative examples of more complex molecules using such structural units are **24**−**26** which all contain a planar tetracoordinate carbon on a high ab initio level.[41]

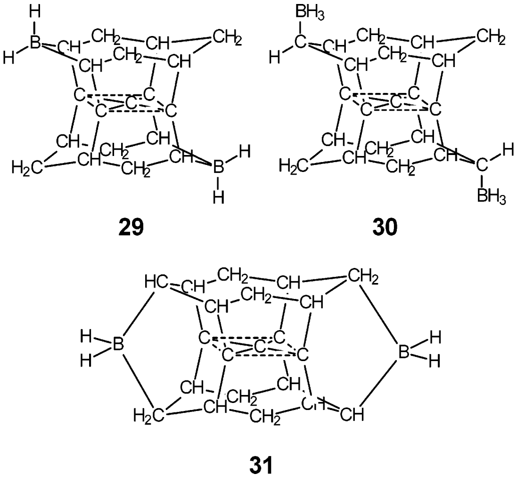
All these structures are stabilized by three-center, two-electron σ- and π-MO systems. The (Mulliken) charge calculated for the π system of the central C_3 unit in **27** is +1.2 e, reminiscent of a cyclopropenyl cation.

Wang and Schleyer found unique structures in the alkaplane family.[42] In contrast to Radom's octaplane, the σ-donating and π-accepting properties of the four boron atoms surrounding the central carbon atom in the tetraboraoctaplane **28** lead to a planar CB_4 unit.

The surrounding carbon skeleton is required as it enhances the mechanical strain exerted by the cage structure. The HOMO is delocalized over an in-plane MO of the CB_4 substructure and is best described by a 4-center 2-electron bond.[42] The LUMO is the empty $2p_z$ AO of the planar carbon.

The intriguing concept of removing the two electrons of the planar tetracoordinate carbon center completely and placing them into the MO system of the periphery leads to hypothetical structures containing for the first time planar $C(C)_4$ substructures (Chart 4).[43] This is achieved by replacing two carbons remote from the central CC_4 unit by boron atoms. Typical examples of this concept are the neutral structures **29**−**31** which formally contain a planar spiropentadiene dication and are best described as zwitterions generated by a novel charge-compensation strategy. According to the computational results, the positive charge on the planar tetracoordinate carbon is partially compensated for most likely by hyperconjugation with the boronate groups having a formal charge less negative than −1.

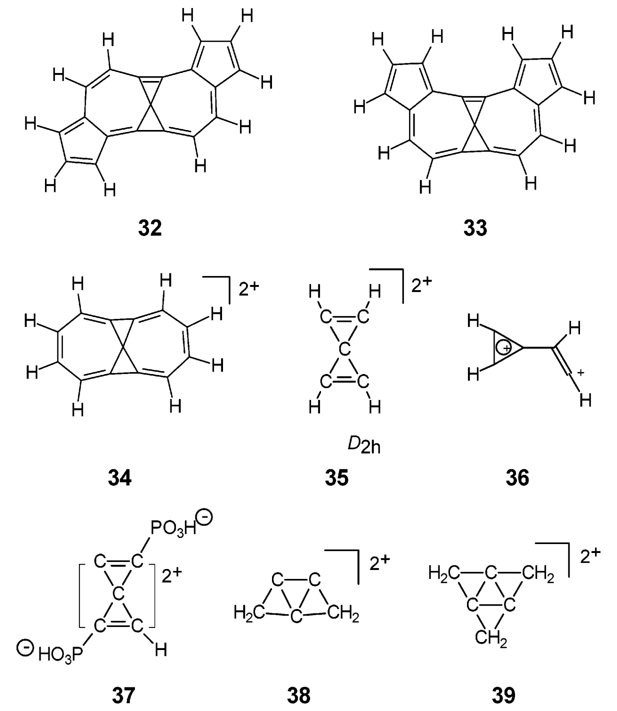
Chart 4



Schleyer's charge-compensation concept for the stabilization of planar tetracoordinate carbon and his earlier ab initio investigations of cumulene dications which favor anti-van't Hoff geometries[44] stimulated further computational explorations. On the basis of this concept, Esteves, Ferreira and Corrêa[45] have recently shown that neutral molecules **32** and **33** are local minima on the potential-energy surface of **32** and **33** (Chart 5). The two electrons of the planar tetracoordinate carbon are delocalized as the charge at the planar tetracoordinate carbon is only +0.10 and +0.12 e for **32** and **33**, respectively. As the barrier for opening one of the spiropentadiene rings in **32** and **33** is only 2.2 and 1.4 kcal/mol, respectively, it is highly unlikely that these molecules can be prepared.[45]

The dication **34** was also found to be planar. The 'planarizing pressure' of the peripheral double bonds adjacent to the spiro ring and the delocalization provided by the π systems have to be taken into account for the interpretation of the central CC_4 substructure (and the complete molecule **34**) to prefer a planar configuration. Another concept for the charge compensation in molecules with a spiropentadiene dication substructure is shown in **37** for which a planar minimum structure was computed.[45] These investigations and those to be described below are based on the dication of spiro[2.2]penta-1,4-diene **35**.[43,44] Incidentally, the planar structure **35** is a low-lying transition state (ΔE = 3.8 kcal/mol) for the 1,2-shift to the dication **36**. A complete planarization of **35** can be achieved by its incorporation in

Chart 5



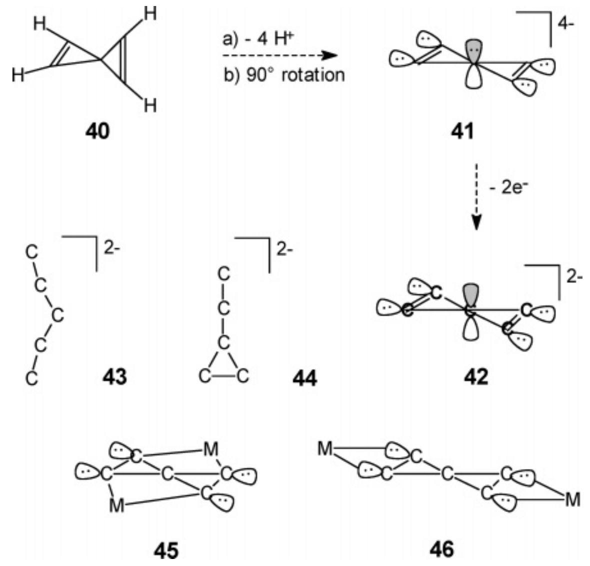
small ring systems. A recent example is given by the dication **38**, where all hydrogen atoms are shown.[46] Expansion of this structural entity led Priyakumar and Sastry to the computed structure **39** as a local minimum, which contains three planar tetracoordinate carbon atoms in a cyclic arrangement.[47] However, this structure was found to be 97.8 kcal/mol higher in energy than the fulvalene dication, which is the global minimum on the $C_6H_6^{2+}$ potential-energy surface.

2.4. 'Brave New World' of C_5^{2-}

Summarizing the computational endeavors in 1997, we observed that "despite considerable computational efforts, no structures with a planar $C(C)_4$ structure have been found".[17] Such structural islands were subsequently detected, first in the doubly bridged octaplanes such as **5** and **6** by Rasmussen and Radom[36] and later in the charge-compensated octaplanes such as **29**−**31** by Wang and Schleyer.[43] The basic principles for generating planar tetracoordinate carbon with four carbon atoms as ligands may be summarized as follows: a delicate balance of electronic effects via σ-donating and π-accepting properties of substituents, a cage covalently attached to the four ligands of the central carbon atom exerting mechanical distortions, and the charge compensation.[5,43] These concepts were creatively applied to the C_5 cluster, the smallest carbon skeleton possible for formation of a planar tetracoordinate carbon.

Spiropentadiene **40**, prepared by Billups and Haley in 1991 as a highly reactive compound, may serve as a structural entry since it found increasing computational attention as a precursor for structures containing a planar tetracoordinate carbon atom in the spiro position (Scheme 2).[48,49] Formally, 4-fold deprotonation and 90° rotation leads to hypothetical structure **41**, from which the planar dianion **42** is generated by removal of the nonbonding electron pair at the central carbon. Neutral structures may then be obtained from the C_5^{2-} species **42** by interaction with counterions or by charge compensation in larger structures containing this hypothetical building block.[52]

Scheme 2. Conceptual Development of the Planar C_5^{2-} Structure 42 and Additional Features



In 2003 Vela et al. described the hypothetical dianion C_5^{2-} **42** as the leading structural entity for formation of neutral (and charged) molecules with a planar tetracoordinate carbon.[50] The high-level ab initio calculations clearly show **42** to be a minimum on the potential-energy surface.[51] However, the extensive screening of the C_5^{2-} potential-energy surface revealed the two molecular fragments **43** and **44** to be more stable than **42** by 48.2 and 44.0 kcal/mol, respectively. In addition, the HOMO of C_5^{2-} in **42** has a positive eigenvalue, 'precluding the existence of this dianion'.[51] To achieve stabilization cations were added. The interaction of the dianion **42** with the metal ions investigated is predominantly ionic. The doubly bridged structure **45** with $M = Li^+$ is more stable by 36.9 kcal/mol than isomer **46**.[52] It may be speculated whether such complexes are formed in the calcium carbide process.

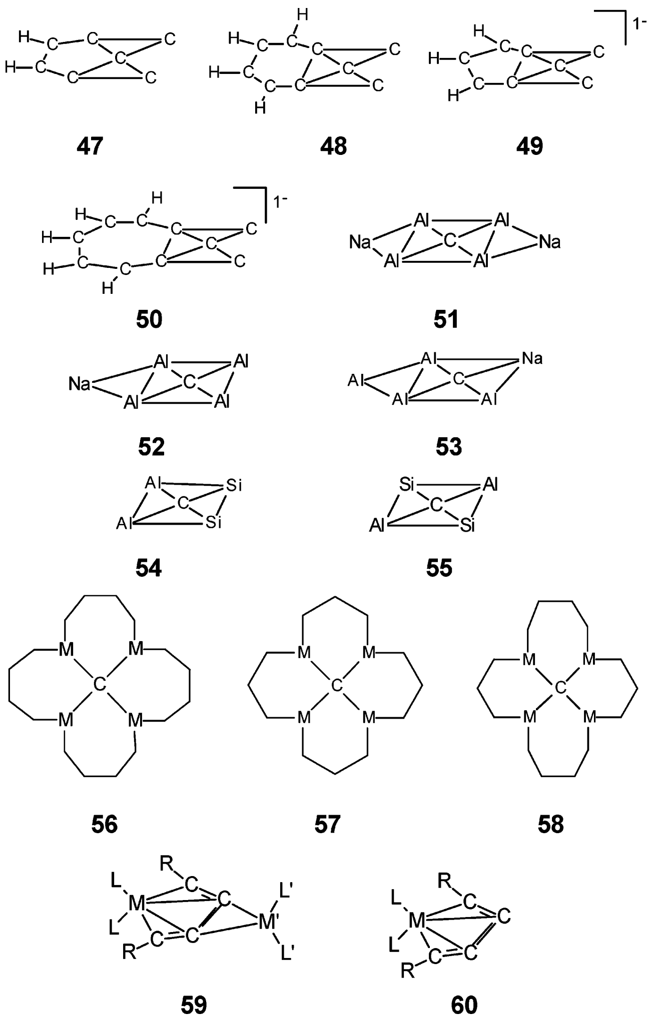
Vela, Hoffmann et al. used this structural concept for an exploration of the possible oligomerization and polymerization of the C_5^{2-} fragment in the presence of countercations.[52] Their results give clues for a variety of stability 'islands' of oligomers and polymers containing an array of planar tetracoordinate carbons.

Recently, Vela et al. found that the charges in the C_5^{2-} moiety can be compensated by attachment of dications, formally derived by removal of two hydrides from ethane and 1,3-butadiene as well as from allyl and pentadienyl anions (Chart 6; only the skeletons are shown). The constructs **47**−**50** were calculated to be minima on the potential-energy surface.[53]

2.5. Planar Tetracoordinate Carbon Tamed by Metal Complexes

Apart from four carbon atoms surrounding a planar carbon atom, main-group elements and transition metals have been envisaged as ligands for stabilization of planar tetracoordinate carbon. It is evident that this concept requires a four-membered ring sufficiently large for enclosure of the carbon atom. In addition, strong binding between the ligands is required and the combination of these metals must provide the appropriate number of valence electrons consistent with the symmetry desired. Schleyer and Boldyrev first discussed

Chart 6



this new strategy in 1991 for planar tetracoordinate carbon harnessed by second-row elements (Chart 6).[54]

According to very high level ab initio calculations by Zubarev and Boldyrev Al_4C has a tetrahedral structure.[55] Al acts as a monovalent ligand, and the central carbon preserves its usual sp^3 hybridization. Addition of one electron leads to Al_4C^-, which is predicted to have a planar square and a quasiplanar almost square structure by DFT and high-level ab initio calculations, respectively.[56] Subsequent theoretical investigations by Boldyrev et al. revealed that the closed-shell 18-valence electron dianion Al_4C^{2-} as well as $(Na^+)_2Al_4C^{2-}$ **51** have a planar structure.[57] The structure of **51** with the two Na^+ occupying opposite edges was calculated to be a global minimum on the potential-energy surface. A global minimum was also found for the monoanion $Na^+Al_4C^-$ **52** with Na^+ bonded to an edge of Al_4C^-. The isomer **53** is a local minimum and 25.4 kcal/mol higher in energy. Binding between the perimeter atoms is considered highly important for stabilization of the planar structures. In addition, the authors concluded that 18 valence electrons are required for complete occupation of all binding MO's, three σ and one π bond as well as one ligand−ligand bond and four lone pairs. The anionic moieties Al_4C^- and $Na^+Al_4C^{2-}$ have been detected experimentally by photoelectron spectroscopy.[56] This is the first experimental evidence for the existence of molecules containing a planar tetracoordinate carbon (see below).

This concept is further illustrated by the mixed silicon−aluminum arrays **54** and **55**. The planar structures of the cis/trans isomers **54** and **55** (as well as CAl_3Si^- and CAl_3Ge^-) are calculated to be minima on the potential-energy surface.[54,58,59] More recent higher order calculations showed **54** and **55** to be slightly pyramidal local minima with the planar structures being higher inversion barriers by <0.014 kcal/mol.[58] Again, *cis*- and *trans*-CSi_2Ga_2 and *cis*- and *trans*-CGe_2Al_2 are true minima in their planar configurations with the corresponding tetrahedral entities 25−28 kcal/mol higher in energy as transition states.

In further pursuit of their experimental and theoretical studies, Boldyrev and Wang reported the experimental observation in the gas phase of CAl_3Si and CAl_3Ge as well as their anions CAl_3Si^- and CAl_3Ge^-.[59,60] According to their high- level calculations all species have a planar structure. Meanwhile, the structure of the dimer $(Na_2[CAl_4])_2$ was computationally explored as a building block for solid materials containing an array of planar tetracoordinate carbon atoms.[61] Another approach for a metal framework harnessing planar tetracoordinate carbon was recently reported by Su.[62] His computational results suggest that complexes **56**−**58** with M = Cu, Ag, and Au prefer a planar structure. Bonding between the central carbon and the metal ligands and between the metal ligands themselves was found. Other recent examples for computational results of nonclassical structures containing planar tetracoordinate carbon atoms are complexes of type **59** (M/M′ = Zr/Zr, Zr/Ti, Ni, V, Ti/Zr, Ti/Ti, Ti/V, and Ti/Ni), which are based on the known metallcumulenes **60** (M = Zr, Ti, V).[63] Jemmis, Parameswaran, and Phukan interpreted their results in terms of bonding interactions between M and the two central carbons.[63]

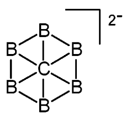
2.6. Planar Hypercoordinate Carbon−Boron Cages

A variety of islands in the 'swampy plains of the carbon flatland' have been described above. The principal guides for exploration of these vast plains are electronic stabilization and mechanical distortions as well as an appropriate choice of metal ligands. The tools for detection and verification are first of all computational in nature; valence-bond considerations are not helpful. The electronic stabilization is due to the σ-donating and π-accepting properties of the ligands around the central carbon atom. More specifically, π aromaticity in the cyclic array, detectable in the computational MO results by the $(4n + 2)$ rule and evaluation of the magnetic properties, is an important guideline.[23−25] In recent years higher coordination numbers of flat carbon were described in terms of π aromaticity by Schleyer et al.,[64−67] Boldyrev,[68]and independently by Minkin et al.[69,70]

2.6.1. Hexacoordination

According to density functional theory (DFT) calculations CB_6^{2-}, **61**, CB_6H_2, **62**, and the three C_3B_4 isomers **63**−**65** are minima on the potential-energy surface. All of these species have a π system with six electrons and are NICS aromatic. The MO system of **63** reveals that the HOMOs are the degenerate pair of π MOs found in benzene, whereas the lower lying π MO involves the p AO at the central carbon. Further analysis shows that the octet rule is not violated by the planar carbon in the center. Rearrangement of these isomers into more stable isomers of the C_3B_4 family requires an "appreciable" activation energy. In an independent investigation Minkin et al. found the planar hexacoordinate structure **66**, which is related to **23** (Chart 7).[69,10]

Chart 7



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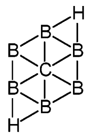

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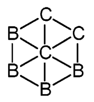

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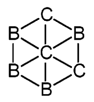

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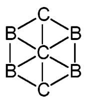

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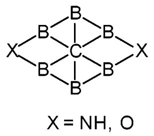

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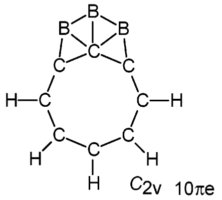

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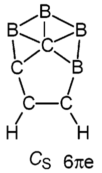

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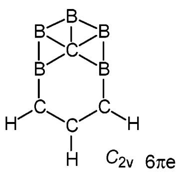

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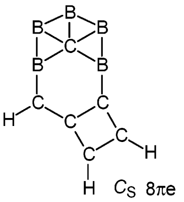

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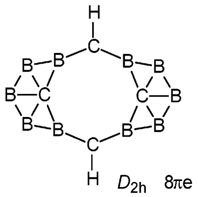

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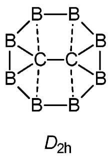

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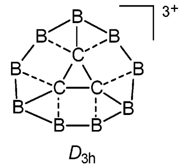

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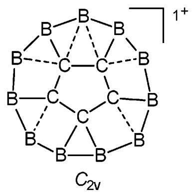

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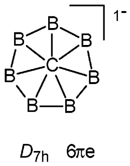

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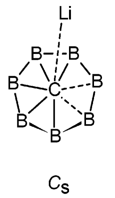

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2.6.2. Pentacoordination

A large variety of structures containing planar pentacoordinate carbon have been generated by replacing the $-(CH)_3-$ units in aromatic or antiaromatic hydrocarbons by the borocarbon units with planar pentacoordinate carbons $-C_3B_3-$, $-C_2B_{4-}$, and $-CB_5-$, leading to the so-called hyparenes.[65] These borocarbon units contribute two, one, or no π electrons to the parent conjugated system. The hyparenes such as **67**−**71** (Chart 7; only the atoms and their connectivities are shown) are low-lying local minima with normal C−B, B−B, and C−C bond lengths. The structure of **71**, two $-(CH)_3-$ units in cyclooctatetraene are replaced by two $-CB_{5-}$ entities, has been found to be completely planar including the antiaromatic character of the eight-membered C_4B_4 ring. In further pursuit of such concepts, 'aromatic boron wheels' containing more than one planar pentacoordinate carbon in a boron cage have been designed.[66] Important examples are **72**−**74**, where dashed lines indicate C−B contacts with significantly longer interatomic distances than conventional C−B bond lengths (1.60 Å). As mentioned earlier, bonding between the atoms defining the fence is required for stabilization of the planar carbon.

2.6.3. Higher Coordination

Whereas heptacoordination and a planar arrangement with D_{7h} symmetry has been calculated for the anion **75**, octacoordination involving a planar structure with D_{8h} symmetry is unstable.[65,70] **76** was generated from the anionic species **75** by association of the central carbon with a cation like Li^+, resulting in lower symmetry and topomerizations via low-lying transition states.[70]

The impressive number of hypothetical molecules containing planar tetra- or hypercoordinated carbon is a solid basis for further explorations and computational verifications. Concomitant with these developments the expectation is explicitly or implicitly expressed that synthetic chemists may take up the challenges suggested by the computational results. Indeed, the computationally designed nonclassical molecules containing planar tetracoordinate carbon may become attractive targets for synthesis, particularly those structures for which the relative stability was determined and the depth of the potential well on the potential-energy surface is thoroughly evaluated. In view of the increasing experimental experience and results in the chemistry of boron chemistry and carboranes it is not unreasonable to expect that more boron-containing compounds and heterocycles with a planar tetracoordinate carbon will become available.[71−79] Such achievements are highly desirable and will add to the experimental results of Boldyrev and Wang mentioned[57,75] and the transition-metal complexes presented below.

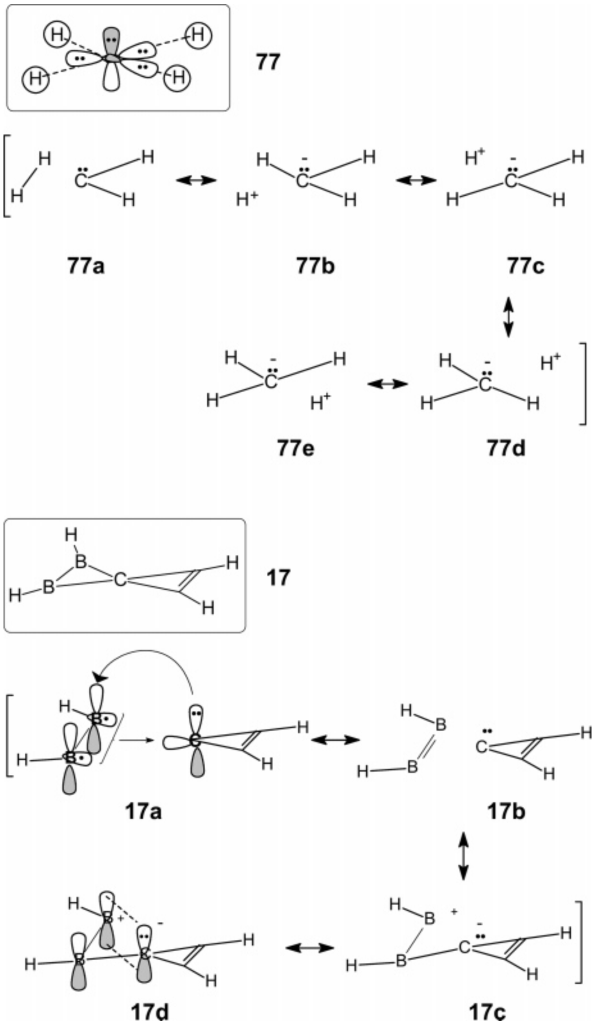
Key concepts for the computational harnessing of planar tetracoordinate carbon and hypercoordinate carbon are now known. Unfortunately, in many cases the potential-energy surface has not been explored with respect to the lowest adjacent transition states for isomerization or fragmentation.

2.7. Resonance Structures and MO Approach

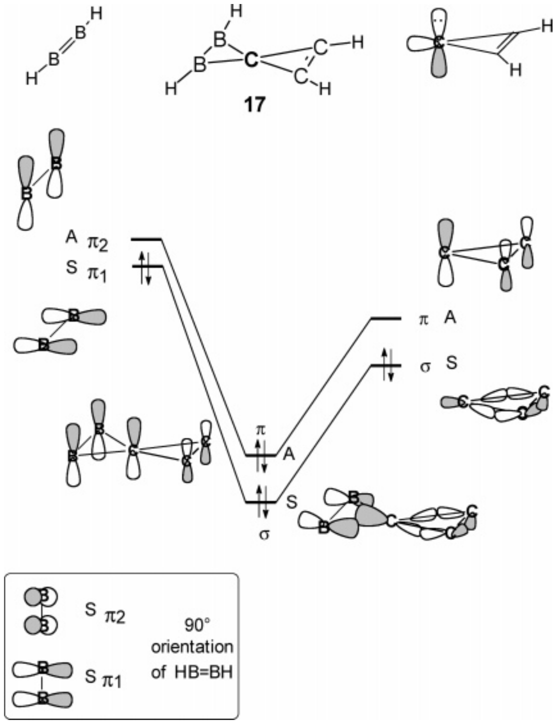
Prior to the rise of MO theory organic chemists used resonance theory for evaluation of relative stability. The concept of a chemical bond containing two electrons, hybridization, and aromaticity led to rules for a graphical procedure for evaluation of a qualitative perspective of stability. The problems associated with this approach are apparent when structures containing planar tetracoordinate carbon are to be evaluated (Scheme 3).

In planar methane the bonding is described in terms of the sp^2 hybridization of the carbon atom, leading to the arrangement depicted in **77**. Two hydrogens are bonded via a 3-center 2-electron bond, while the two electrons in the nonbonding $2p_z$ orbital do not contribute to the bonding. The resonance structures **77a**−**e**, all with no-bond forms and charge separations, clearly show that a planar arrangement is much less stable than the tetrahedral structure of methane. For the 1,2-diboraspiropent-4-ene **17** the interacting orbitals for formation of the BBC ring through the σ-donating property of the B_2H_2 fragment and the π-back-bonding from the planar carbon are shown in **17a**. Two (of several more) resonance structures, **17b** and **17c**, show again a no-bond situation. The orbitals in **17d** illustrate the π interaction without an underlying σ bond but do not allow evaluation

Scheme 3. Resonance Structures for the Planar Structures of CH_4 77 and Planar 1,2-diboraspiropent-4-ene 17



Scheme 4. Frontier Orbital Analysis for Planar 1,2-diboraspiropent-4-ene 17



of a stabilizing interaction. In comparison with a tetrahedral arrangement, where four 2-electron σ bonds can be formulated, the resonance structures for the planar geometry suggest an unstable species—in contrast to the computational MO results for **17**. It is obvious that only MO theory can cope with such structural aspects. The frontier orbital interactions of MO's in appropriate substructures are helpful for the qualitative evaluation of whether a planar or tetrahedral geometry may be more stable. Thus, the $(HB)_2C(CH)_2$ structure may be considered as a complex of H_2B_2 with C_3H_2 (Scheme 4). The σ and π MO have the sp^2/2p orientation required for a planar carbon with four ligands.

The stabilization of the planar tetracoordinate carbon in **17** may qualitatively be described by the interaction between the frontier orbitals with appropriate symmetry of the H_2B_2 and C_3H_2 fragments. This approach, the linear combination of group orbitals in combination with rules from perturbation theory, is well suited for a qualitative evaluation of stabilizing interactions. It is based on Hoffmann's extended Hückel method and is well developed.[6,80] The interaction of π_1 in the H_2B_2 fragment with the σ MO in C_3H_2, both of S symmetry (defined by the plane of the C_3H_2 fragment), leads to the σ-bonding MO in $H_2B_2C_3H_2$ and stabilization. The orthogonal π MO in $H_2B_2C_3H_2$ is formed by the interaction of π_2 in H_2B_2 and the π MO in C_3H_2, both with A symmetry. Here the stabilization is due to π conjugation. When the H_2B_2 fragment is rotated by 90° for formation of a tetrahedral geometry, the bonding interaction π_1/σ is still possible but affected by interaction with the π MO. The MO π_2 in the 90° orientation has S symmetry. Hence, it does not interact with the π MO of C_3H_2 and thus provides no stabilization. According to this qualitative comparison of the HOMO/LUMO interactions in the two geometries, a planar tetracoordination of the central carbon is to be preferred. Obviously verification has to come with high-level calculations. The σ and π MO's in $H_2B_2C_3H_2$ are the core MO's for stabilization of structures containing a planar tetracoordinate carbon. In a variety of publications the corresponding MO's are shown by contour diagrams.

3. Structural Landscape between Tetrahedral and Planar Carbon

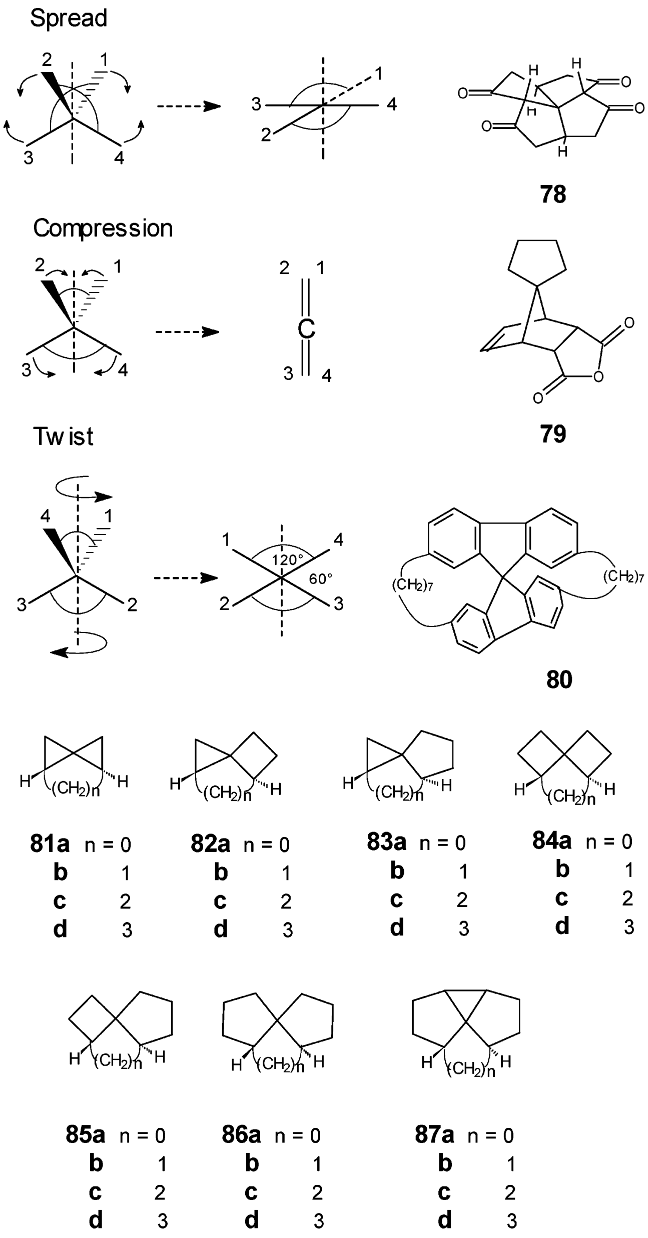
This is the domain of the α,α′-bridged spiroalkanes and the fenestranes, defined as doubly α,α′-bridged spiroalkanes. Due to their unique structures with bent bonds the members with small rings of this class of cyclic hydrocarbons have in the past found considerable interest in synthesis.

3.1. Spiroalkanes and Fenestranes

We analyzed the central $C(C)_4$ substructures in a large variety of such structures using symmetry deformation coordinates (Chart 8).[9] The structures were generated by semiempirical calculations.

Within the concept of symmetry deformation coordinates the planarizing distortions in $C(C)_4$ substructures are mainly described by the opening of two opposite bond angles (spread) and twisting, which leads to rotation of one plane, defined by two ligands and the central carbon atom, relative to the other fragment. In the case of opening of the opposite bond angles to 180° a square planar geometry would be obtained, whereas twist would lead to a rectangular arrange-

Chart 8

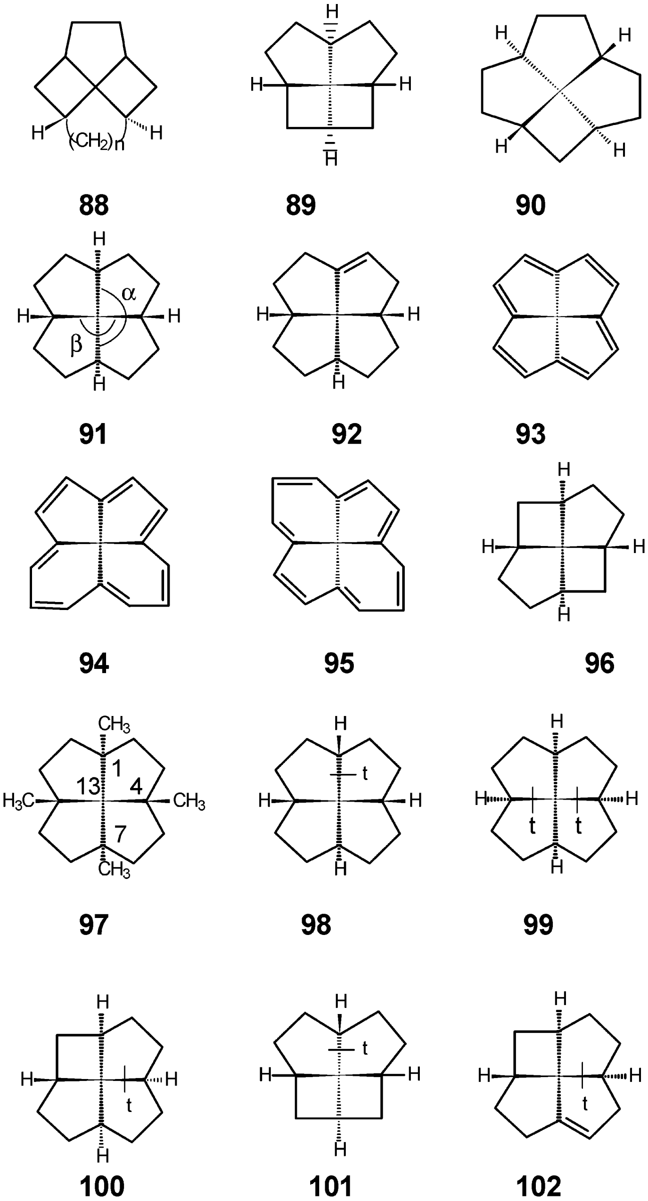


ment. Closing of two opposite bond angles (‘compression’) would approach an unrealistic linear arrangement. Typical examples are given by the fenestrane-tetrone **78** prepared by Cook and Weiss,[81] the spiro compound **79**,[82] and Prelog’s vespirene **80**,[83] where the values of bond angle deformations in the corresponding $C(C)_4$ fragments are based on X-ray structures. Whereas torsional deformations are essentially absent in **78** and **79**, the amount of twist in **80** is almost 50% of that of opening of the opposite bond angles.

Throughout the series **81b**−**84d** and **87a** the extent of twist is larger than that of spread. (Wiberg’s theoretical and experimental results for **81a** (≡ **111**) are discussed in section 3.3.) The spread is reduced with the increase of the number of CH_2 groups in the α,α′ bridge. In the α,α′-bridged spiro[3.4]-compounds **85a**−**d** and **86a**−**d** as well as in **87b,c** the amount of opening of the opposite bond angles and that of torsion are more or less balanced out.

The fenestranes, doubly α,α′-bridged spiroalkanes, are a unique class of hydrocarbons. The bond angle distortions in the central $C(C)_4$ substructures are due to a large extent to opening of two opposite bond angles as in the [4.5.5.5]-fenestrane **90** and are exclusively due to this effect in structures such as **88**, **89**, and **91** (Chart 9). Here and in all subsequent formulas the structure of the fenestranes are drawn using Fischer projections. According to our semiempirical results the opposite nonbridge bond angles, α and *β*, in **91** are 113.8°, whereas electron diffraction analysis shows 116.2° with the remaining four being 103.7°.[84]

Chart 9



The planoid deformation in the [5.5.5.5]fenestranes can be enhanced by introduction of bridgehead double bonds, contraction of at least one ring, inversion of the configuration at one or more bridgeheads, and to smaller extent methyl substituents at the bridgehead positions (see section 5.5.5 for the X-ray structure of **184** with R = CH_3).

In **92**, a [5.5.5.5]fenestrene, the two bond angles relevant for bond angle opening were calculated to be 120° and 116°.[9] For the [5.5.5.5]fenestrane-1,4,7,10-tetraene (not shown) containing four nonconjugated bridgehead double bonds the two opposite bond angles were calculated to be 137°.

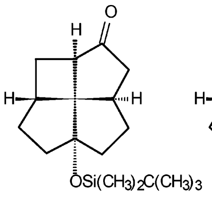
More recently, the structural features of cyclic polyenes **93**−**95** were investigated by ab initio methodology.[10] These results confirmed earlier semiempirical calculations with geometry optimization that the planar structures are highly strained.[85,86] The opposite bond angles calculated for **93**, **94**, and **95** are 137.8°, 128.2°, and 129.2°, respectively. The aromaticity in the 14-membered rings of **94** and **95** is retained, and the effective radius of the central carbon atom and, as a consequence, the strain decrease as well. In the fully unsaturated **93** "the charge on the central carbon atom is calculated to be lower by 2e (+1.9), and as a consequence, the conjugated 12-membered ring contains 14 π electrons, which complies with the aromaticity condition".[10]

The [4.5.4.5]fenestrane **96** illustrates the impact of ring contraction on the opening of the opposite bond angles which are 126°. Methyl substituents at all four bridgehead position of the all-*cis*-[5.5.5.5]fenestrane lead to calculated bond angles of 120° in **97**. For the all-*cis*-benzofenestrane **184** ($R = CH_3$) X-ray structure analysis gave 118.6° for two opposite bond angles at the central carbon.[19]

Stereoisomeric fenestranes are generated by inversion of bridgehead substituents. In this way *trans*-bicyclo[3.3.0]-octane subunits are formed in [5.5.5.5]fenestrane and its congeners. X-ray structure analysis of compounds containing the structural unit of a *trans*-bicyclo[3.3.0]octane show bond angles at the two bridgeheads of 127° and 131°.[9] For the *trans,cis,cis,cis*-[5.5.5.5]fenestrane **98**, *t,c,c,c*-[5.5.5.5]fenestrane, containing one *trans*-bicyclo[3.3.0]octane subunit, the calculated opposite bond angles α and β (cf. formula 91) at the central carbon are 118° and 126°. A derivative of this hydrocarbon has recently be prepared by Wender (see below).[87,88] Introduction of two opposite trans-fused bicylo-[3.3.0]octane subunits gave calculated bond angles of 130° and 137° in **99**.[9] Additional ring contraction gives rise to bond angles in **100** of 121° and 134°, respectively.

Similar values of bond angles are calculated for *c,c,t,c*-[4.4.5.5]fenestrane **101** (136° and 125°). The combination of ring contraction, inversion at one bridgehead carbon atom, and introduction of a bridgehead double bond leads to structure **102** with opposite bond angles calculated to be 138° and 131°.[89] The synthetic approach to derivatives of this compound will be described below.[90] Further computational results for additional stereoisomeric and unsaturated fenestranes have been published.[10,17] Derivatives with the structural skeleton of **100** have been prepared by the author's group (Chart 10).[17] X-ray structural analyses of the two derivatives with a *c,t,c,c*-[4.5.5.5]fenestrane skeleton, **103** and **104**, revealed opposite bond angles of 120.2°/131.1° and 119.2/134.9°, respectively.[91,92]

Chart 10



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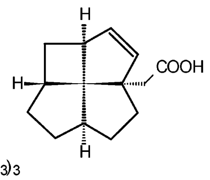

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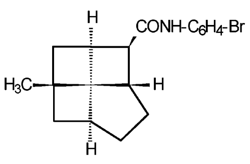

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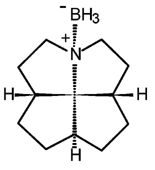

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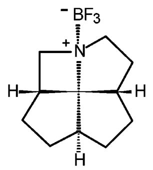

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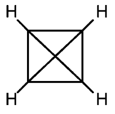
It should be noted that the bond angles at the outer side of the trans-fused bicyclo[3.3.0]octane subunit in **103** and **104** are 127° and 128°, respectively. The largest bond angles in a central $C(C)_4$ fragment have been observed in **105**, a derivative of an all-*cis*-[4.4.4.5]fenestrane reported by Agosta.[93] Here the bond angles are 129.2° and 128.3°, respectively. Comparison of the structural features in **106** and **107**, the first fenestranes with a nitrogen atom at a bridgehead, also supports the concept that ring contraction leads to an opening of the opposite bond angles: albeit modest, the bond angles are increased from 116.6°/116.1° in **106** to 119.8°/120.7° (119.2°/121.2° in a second structure) in **107**.[94,95] It is apparent that the distortions in fenestranes are mainly or exclusively due to opening of two opposite bond angles at the central carbon (spread). The values for the opposite bond angles in the fenestranes prepared are smaller than 130°. No fenestranes with both opposite bond angles larger than 130° have been prepared yet. Thus, it may be concluded that the tetrahedral configuration of $C(C)_4$ substructures is rather robust, bond angle deviations from 109.4° toward planoid structures being smaller than 20°. It is a synthetic challenge to prepare fenestranes with both bond angles beyond 130° and study their chemistry and structural integrity.

3.2. Pyramidanes

The smallest member of the fenestrane family is [3.3.3.3]-fenestrane **108**. It has found specific computational interest and been treated by several groups.[10,38,96−101] The results of a variety of high-level calculations all indicate that its structure is best described as a tetragonal pyramid **108a** rather than as a fenestrane. As mentioned above, the spiropentadiene **40** as an isomer of **108a** is less stable but separated from **108a** by a high-energy barrier (see below). Computational results for [4.4.4.4]fenestrane **109** indicate that this molecule has the structure **109a** best described by a half-planar (bisphenoidal) configuration.[102] Recently **110a**, a derivative of [3.4.3.4]fenestrane **110**, was discussed.[103] Computational analysis again shows a pyramidal structure for the tetracoordinate carbon atom (Chart 11).

Chart 11



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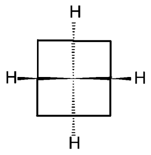

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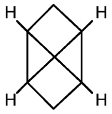

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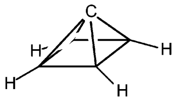
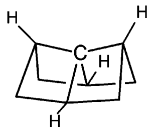
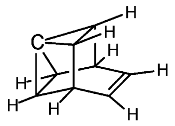


108a



109a



110a

A more extensive discussion of half planar and pyramidal arrangements in carbon compounds is beyond the scope of this review with its focus on planarizing distortions of tetracoordinate carbon.[102]

3.3. Strain and Stability

In most cases the planar configuration of a tetracoordinate carbon is discussed in relation to the corresponding tetrahedral arrangement. Beyond this reference point and the computational confirmation that the structures containing a planar tetracoordinate carbon are minima on the energy hypersurface the question remains about the global minima and low-lying transition states possibly leading to more stable isomers. In most cases these problems remain to be addressed. It is evident that such explorations require increasingly complex calculations with the increasing size of the structures to be scrutinized. For initiating the preparation of a complex compound containing a planar tetracoordinate carbon, however, such data would be highly desirable. A few computational results and experimental observations about the reactivity of relevant compounds are presented here.

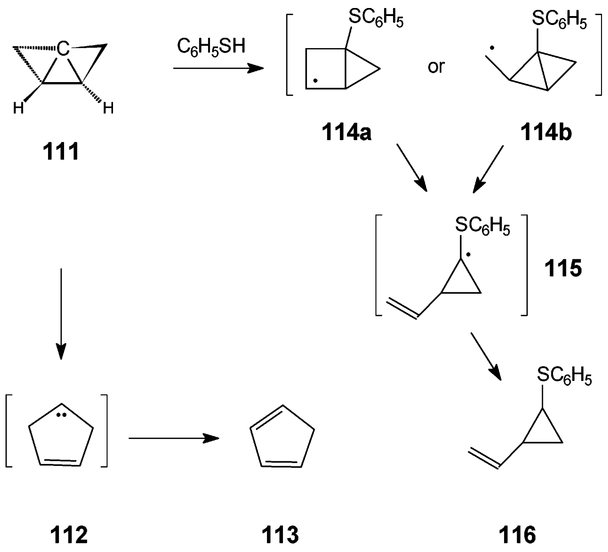
Beyond the interest in the structure of pyramidane **108a** the energy hypersurface of C_5H_4, which includes inter alia spiropentadiene **40**, was extensively studied.[96−101] According to these results pyramidane **108a** is a minimum but not the global minimum on the PES of C_5H_4. It has substantial barriers to isomerization and is 5−27 kcal/mol more stable than spiropentadiene **40** from where no transition state has been found for its exothermic isomerization into **108a**. The pyramidane structure is more stable than several structurally distinguishable carbenes, which could thermally isomerize to **108a** via low-lying transition states. It should be noted that such computational explorations refer to the gas phase. Computational results about other important features such as dimerizations, redox, and solvent-dependent reactions would be of additional value not only for experimentalists as general information about reactivities of such elusive structures.

Most recently the possible reaction pathways of **110a** were computationally evaluated.[103] This pyramidal structure would react via a very low lying transition state into a more stable carbene.

Since heats of combustion are lacking for compounds such as pyramidanes and even fenestranes, our knowledge of their heat content is exclusively based on computational results. In most cases structures with bond angles > 130° have total strain energies larger than the average carbon−carbon bond dissociation energy. This strain affects the whole structure, but it has been shown that there is clear tendency for the strain to increase with the planarizing distortions in the central $C(C)_4$ substructure.[104] Isolation of such highly strained hydrocarbons is heavily dependent on their kinetic stability, i.e., the lack of low-lying transition states. As mentioned above decomposition of methane into CH_2 and H_2 is a highly endothermic process, whereas fragmentation of planar methane is only slightly endothermic.[30] Dissociation of planar methane into methyl and a hydrogen atom was calculated to be slightly exothermic.[30]

Decomposition of a few saturated strained hydrocarbons has been investigated with respect to the mechanism.[105−107] Comparison of the homolytic cleavage of monocyclic hydrocarbons reveals that the strain release plays an important role for the differences in the heat of the ring-opening reactions. A few cases have been reported where the mode of decomposition or structural reorganization has been investigated for fenestranes and related compounds. Three examples are briefly discussed.

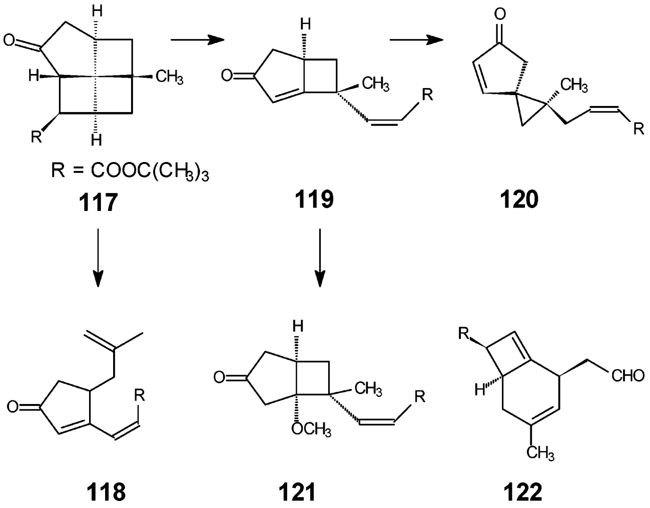
Scheme 5



Wiberg reported the synthesis of the tricylo[1.1.1.0^{1,3}]pentane **111** and its ready decomposition to cyclopentadiene **113** at temperatures below −50 °C (Scheme 5).[108,109] An ab initio calculation for the transformation of the tricyclic hydrocarbon **111** into the carbene **112** (considered to be an intermediate in the formation of cyclopentadiene **113**) showed it to be 33 kcal/mol lower in energy than **111**. In the presence of thiophenol **111** reacts via opening of a central or a peripheral C−C bond to **114a** or **114b**, respectively, and further to **115** and **116**.

Thermolysis of the fenestrane **117** was investigated by Agosta (Scheme 6).[110] The highly stereospecific fragmentation of the strained [4.4.4.5]fenestrane **117** at 100 °C to give **118** and **120** is really surprising. Formation of **118** is interpreted in terms of a symmetry-allowed thermal cycloreversion, stereoelectronically driven by the rigid bicyclo[2.2.0]hexane substructure and its thermal lability. There is evidence that **120** arises via **119**, the latter being formed by opening of the cyclobutane ring bearing the ester group and a subsequent acid-catalyzed ring contraction. Intermediate **119** is trapped in the presence of methanol to give **121**. In the absence of protons **118** is formed exclusively. Photolysis of **117** in methanol gave the *E*/*Z* isomers **121** and a small amount of **122**.

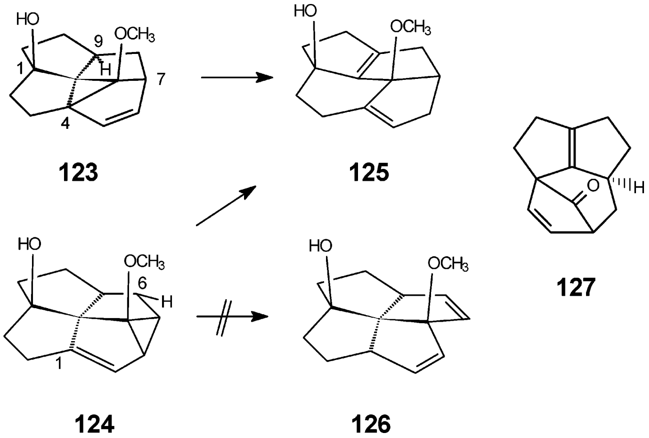
Scheme 6



Another example for control of the reaction pathways by the geometrical constraints was observed by us in the case of the two structurally related [3.5.5.5]- and [5.5.5.5]-

fenestranes **123** and **124** (Scheme 7; for the synthesis of these fenestranes, see below).[177]

Scheme 7



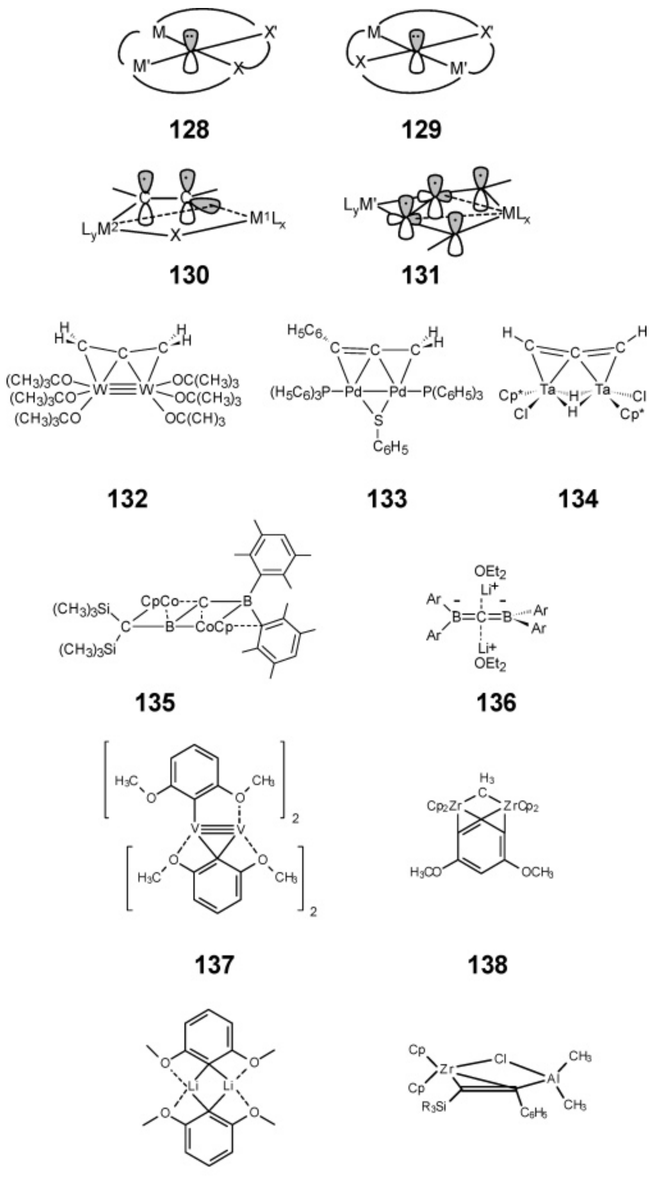
The two compounds, interrelated by a formal 1,3-sigmatropic shift in the vinyl-cyclopropane substructure, react upon thermolysis in toluene at 200 °C to the same compound **125**; formation of fenestrane **126** from **124** was not observed. This pseudopentadienyl rearrangement of both isomers to the same product is surprising. Although the distance between C(6)−H and the quaternary carbon atom of the bridgehead double bond in **124** is shorter than the corresponding distance C(9)−H/C(6) in **123** (2.91 vs 3.44 Å, respectively; AM1 results), the (vibrationally induced) distortion required for a concerted transfer of the hydrogen atom does not appear to be possible in **124**. Instead, thermal reaction of **124** appears to be initiated by a ‘forbidden’ 1,3-sigmatropic rearrangement to give **123** and proceeds further to **125**. In the more polar solvent DMSO the reaction follows a different pathway as both isomers fragment to the ketone **127**. This reaction may be interpreted in terms of a cylcopropylmethyl carbenium ion rearrangement with the subsequent loss of a methyl group from the methylketoxonium ion formed as a reaction intermediate.

4. Planar Tetracoordinate Carbon in Stable Metal Complexes

R. Hoffmann’s concept of stabilizing planar tetracoordinate carbon by σ-donating and π-accepting ligands is reminiscent of the MO interaction discussed for transition-metal complexes. According to the Dewar−Chatt−Duncanson model the ligands extend σ-donor bonds to the transition metal with the stability being further enhanced by back-bonding from the transition metal to the ligands via the π system.[112] With planar tetracoordinate carbon the bonding situation is reversed: metals including transition metals now being ligands provide σ-donor bonds and simultaneously provide the π-acceptor properties for back-bonding from the filled 2p AO at the carbon atom.

The basic arrangement for the planar carbon tetracoordinated by two metal ligands M and two additional ligands X gives rise to the two isomeric structures **128** and **129**, which may be denoted type 1 (Chart 12). As already mentioned in the context of the computational results the ligands are preferentially bonded to each other, forming a perimeter. A common feature of the type 2, depicted in **130** and **131**, is the presence of a carbon−carbon double bond which may be part of an aromatic ring and coordination in the σ plane at one of the two trigonal centers by two metal atoms.

Chart 12

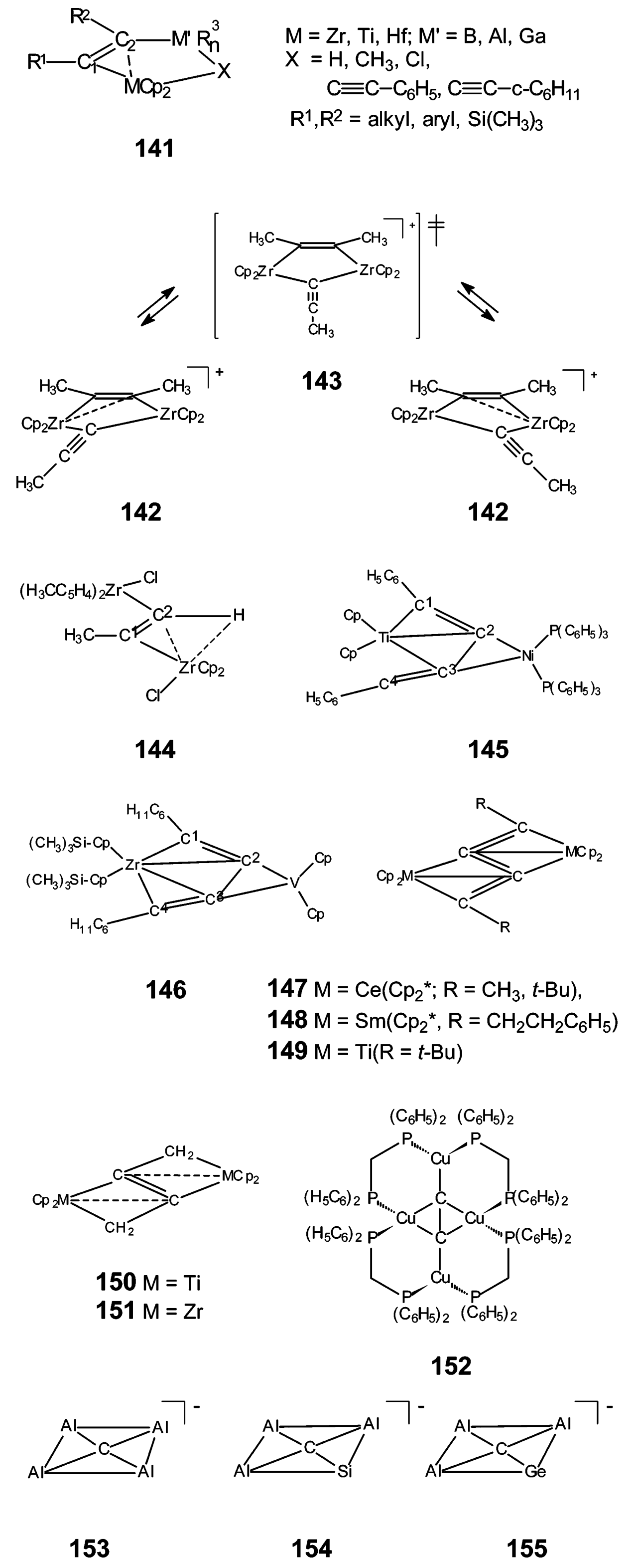


Structures **132**−**135** are representative examples for type 1 arrangements. The most salient feature in the di-tungsten−allene complex **132** is the geometry of the V-shaped C−C−C moiety which forms a plane with the two tungsten atoms.[113,114] In contrast to the orthogonal arrangement in free allene, the four allenes of complex **132** lie in one common plane. According to the MO scheme for the interaction of planar, bent H_2CCCH_2 with $W_2(OR)_6$ the allene acts as a four-electron donor to the W_2^{6+} center which back-donates four electrons.[115] The C−C bond distances in the μ-allene ligand are 1.46 Å, which are in the range of $C(sp^3)-C(sp^3)$ single bonds.

In the dinuclear palladium complex **133** the two palladiums, the three η^3-allenyl/propargyl carbons, the sulfur atom, and the two phosphorus atoms are located in the same plane.[116] The bonding between the almost linear allenyl fragment and the di-palladium ligand is discussed in terms of back-bonding emanating from the Pd−Pd dσ−dσ MO, leading to nucleophilic reactivity at the planar carbon.[117,118] In the di-tantal complex **134**, formally derived from allenylene ·C═C═C·, the C_3 fragment is coplanar with the two

Ta atoms. The bonding between the central carbon and the two Ta atoms is described in terms of a 3-center 2-electron bond and π bonds.[119] The only bona fide example for a complex containing planar tetracoordinate carbon in an arrangement related to the isomeric structure **129** is the μ-diborylcarbene dicobalt complex **135** reported by Siebert.[13] According to a detailed MO analysis of model complexes the planar tetracoordinate carbon is stabilized by the donating properties of the ligands in the σ plane and back-bonding from the carbon to the ligands in the π planes.[120] Finally, the contact ion pair **136** may be mentioned here. The aryl ligands (Ar = 2,3,5,6-tetramethylphenyl) are not orthogonal but twisted by 30°.[79]

Chart 13



M = Zr, Ti, Hf; M' = B, Al, Ga

X = H, CH_3, Cl, $C{\equiv}C{-}C_6H_5$, $C{\equiv}C{-}c{-}C_6H_{11}$

R^1,R^2 = alkyl, aryl, $Si(CH_3)_3$

147 M = Ce(Cp_2*; R = CH_3, *t*-Bu),

148 M = Sm(Cp_2*, R = $CH_2CH_2C_6H_5$)

149 M = Ti(R = *t*-Bu)

150 M = Ti

151 M = Zr

Prior to 1990, a few compounds containing a planar carbon tetracoordinated as in **130** had been described. Structures **137**−**140** are salient examples.[121−124] After the opening of an efficient pathway for preparation of type **130** compounds by Erker, a wealth of results for many compounds containing this structural feature have been established by him (Chart 13).[11,12,125,126] The judicious choice of group IVB together with IIIB elements, connected by a 3-center 2-electron bridge, leads to compounds with the composition depicted in **141**. The metal centers are coordinated to the vinylic, planar carbon forming another 3-center 2-electron bridge.

The di-zircona compound **142** shows dynamic behavior in solution at increased temperature on the NMR time scale. The metallocene subunits and the terminal methyl groups of the butyne moiety are equilibrated. This behavior is interpreted in terms of symmetric transition-state **143** containing two tricoordinated butyne carbon atoms with a barrier of $\Delta G\ddagger_{\mathrm{rearr}}$(190 K) = 9.5 ± 0.5 kcal/mol for this degenerate rearrangement. MO analysis of model compounds (where the Cp units are replaced by Cl) supports this interpretation.[126] Analyses of additional structures led to the suggestion that complexes such as **144** with its agostic interactions may also be considered as compounds containing tetracoordinate carbon.[11,127] Rosenthal and also Choukroun observed that reaction of Cp_2ZrR_2 (R = C≡C−R) with Cp_2Ti leads to monocyclic metallacycles which further react with $NiCp_2$ and VCp_2 moieties to give the bicyclic structures **145** and **146**, respectively.[128−131] In **146** the C2−C3 distance of 1.43 Å is characteristic of a C−C single bond in conjugated systems, whereas the C1−C2 and C3−C4 distances (mean value 1.337 Å) are in the range for a C=C double bond. Concomitantly the vanadium adopts a metallacyclopropane rather than a metallacylopropene structure. The distances from Zr to the central carbon atoms C2 and C3 are smaller than those in the Zr−Cp ligand. Complexes **147** and **148** (Cp* = $Cp(CH_3)_5$), described by Teuben and Evans, respectively, are formally derived from 1,4-disubstituted butadiynes and contain a zigzag form with a short central C−C bond (1.32 and 1.35 Å, respectively).[132,133] The two metal centers and the four carbon atoms are all in one plane, and thus, these compounds belong to the family of complexes containing in the center two adjacent planar tetracoordinate carbon atoms. The electron distribution in the complex **149** is different.[134−137] Here the length in the central C−C bond is 1.49 Å, reminiscent of a C−C single bond in a conjugated π system. The bond distances of the metal centers to the central carbon atoms are similar and thus evidence for the presence of planar tetracoordinate carbon atoms. Rosenthal et al. as well as Suzuki et al. described the $[(Cp_2)_2Ti]_2$ and the $[(Cp_2)_2Zr]_2$ complexes of butatriene, **150** and **151**, respectively.[136,137] In both complexes the central C−C bond is rather short (1.32 and 1.38 Å, respectively); the distances between the metal atoms and the central C−C double bond are similar. Supported by MO calculations, complex **150** may also be considered as a dimetalla-bicyclo[2.2.0]hex-1(4)-ene. Complex **152** is also a member of the structures containing planar tetracoordinate carbon. Two copper atoms are coordinated side-on to a dimetalated ethine.[138] Finally, the experimental results of Boldyrev are mentioned here.[56,57,59] Ions **153**−**155** were detected by anion photoelectron spectroscopy. In addition, complex $[Na^+(CAl_4)^{2-}]^-$ **52** was detected. Computational results were used to assign the structures given to these species (see section 2.5 for the corresponding MO results).

5. Recent Syntheses of Fenestranes

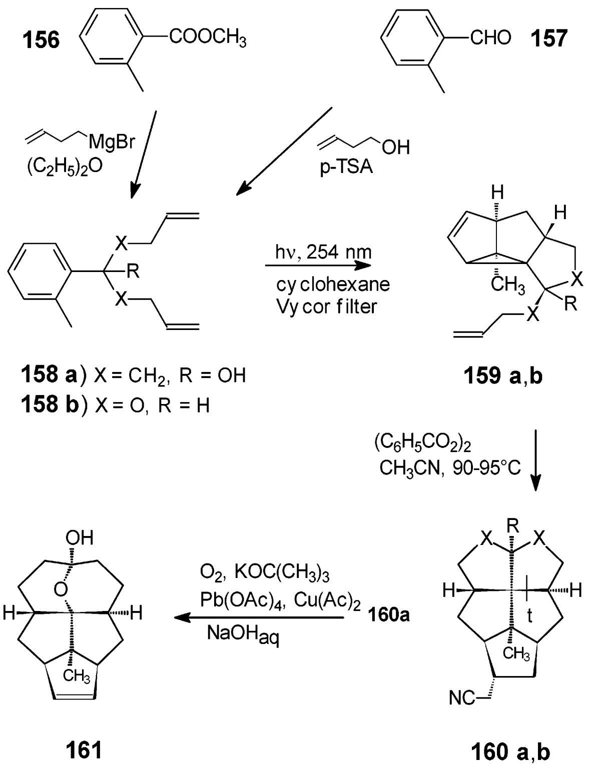
As mentioned above, fenestranes are useful for exploration of the deformation space between the tetrahedral and planar $C(C)_4$ structures. Beyond the question of their stability, strain and reactivity of such compounds are of interest for their use as scaffolds for a wide variety of advanced functionalities. Hitherto the main activity has been concerned with the development of efficient synthetic procedures, reducing the number of steps from up to 17 to a few transformations and increasing the yield. The early syntheses made use of aldol condensations, cyclodehydrations, transannular carbene insertions, and photoinduced [2+2]-cycloadditions as well as ring contractions, especially used for formation of fenestranes containing four-membered rings. More recently the efficiency was considerably enhanced—and the number of steps reduced—by making use of the intramolecular arene−olefin photocycloaddition and a subsequent cyclization cascade, specific cycloadditions, and transition-metal-induced cyclization−carbonylation reactions. The earlier syntheses have been reviewed by Agosta,[15] Kuck,[18,19]and this author.[9,17] Thus, the focus in this survey is on the most recent results including formation of stereoisomeric fenestranes. For easier interpretation of the stereochemical features Fischer projections are used throughout for depicting the configuration in the central $C(C)_4$ substructures.

5.1. *trans,cis,cis,cis*-[5.5.5.5]Fenestrane

Recently Wender developed a short, three-step synthesis of **160a** and **160b**, representing the first congeners of the stereoisomeric *t,c,c,c*-[5.5.5.5]fenestrane family.[87,88] He used the arene−alkene photocycloaddition[139−142] followed by a radical cyclization cascade for stereoselective formation of the two *t,c,c,c*-fenestranes (Scheme 8). The photoinduced arene−olefin reactions of **158a** or **158b**, easily prepared from **156** and **157**, respectively, give the tetracyclic linear triquinane intermediates **159a** and **159b** together with angular products (not shown) in ratios of 2:1 and 1:1. The reactive vinyl cyclopropane substructures are formed by a 1,3-cycloaddition followed by a 2,6-ring closure.[142] The radical-induced cascade reactions lead in a subtle stereoelectronic and stereocontrolled way to the fenestrane **160a** and the dioxafenestrane **160b**, respectively.

X-ray structure analysis of **161**, prepared from the noncrystalline **160a**, established the presence of a *trans*-bicyclo[3.3.0]octane substructure in this fenestrane.[88] According to semiempirical calculations the energy in **160a** and **160b** is ca. 11.2 and 20.4 kcal/mol, respectively, higher than in the corresponding all-*cis* isomers. A semiempirical estimate for the opposite bond angles in the unsubstituted *c,t,c,c*-[5.5.5.5]fenestrane indicated values of 118° and 126°.[9]

Scheme 8

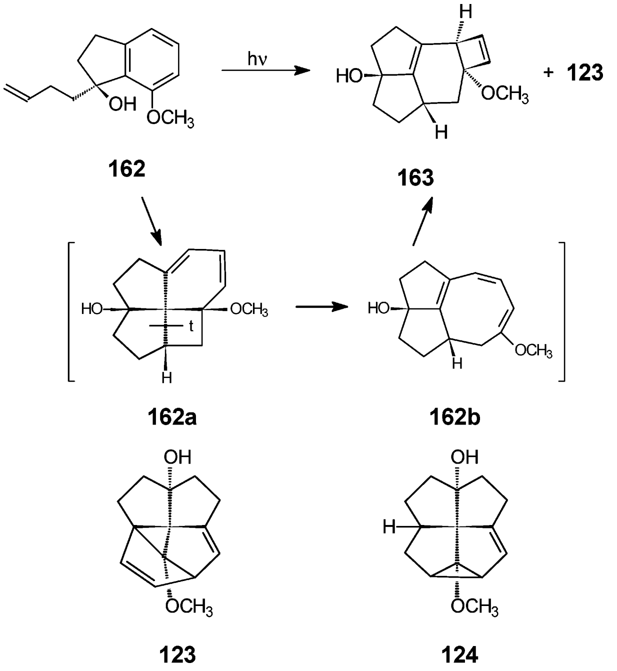


5.2. All-*cis* -[3.5.5.5]- and [5.5.5.5]-fenestrane

In our attempt to prepare fenestranes in a few steps earlier we successfully used the arene−alkene photocycloaddition of substituted phenylpentenyl compounds.[142] This led to formation of an intermediate bearing three of the four five-membered rings suitably annulated and substituents located appropriately for an additional ring closure. In further pursuit of this intriguing reaction we explored the photoreaction of the butenylindanol **162** (Scheme 9).

The all-*cis*-[3.5.5.5]fenestrane **123** containing an additional vinylene bridge and the all-*cis*-[5.5.5.5]fenestrane **124** were formed directly. However, the major photoproduct is **163**. Stereoselective formation of **163** is interpreted in terms of a [2+2] rather than a [3+2] photocycloaddition with the conformation of the double bond being appropriate for formation of the highly strained *t,c,c,c*-[4.5.5.6]fenestradiene **162a**. Symmetry allowed ring opening leads to **162b**, which upon further photoreaction gives stereoselectively **163**. It should be noted that a fenestrane could be obtained from

Scheme 9



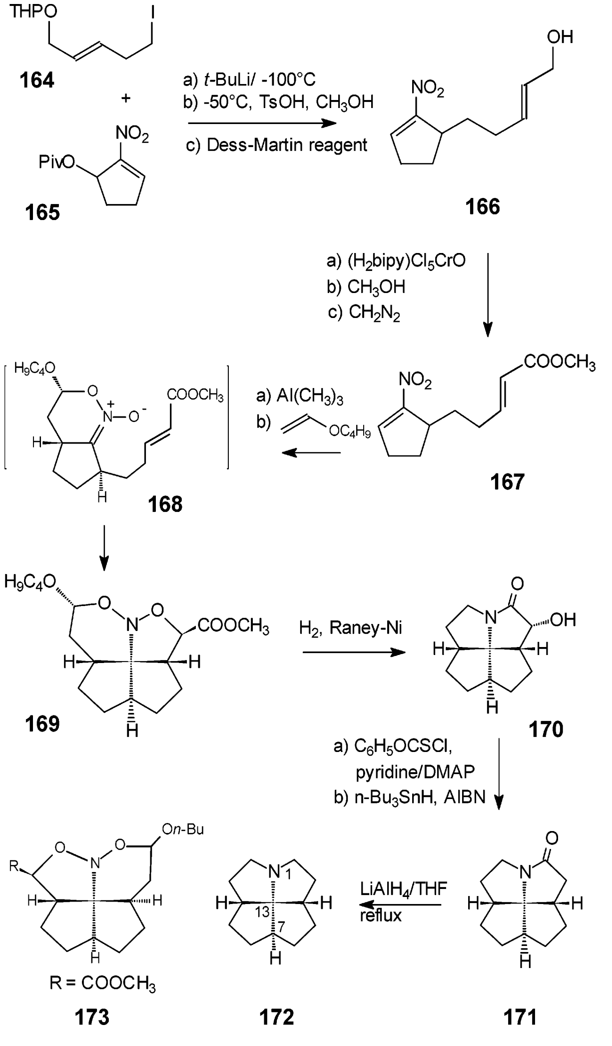
163 via opening of the cyclobutene substructure and a transannular insertion.

For further functionalization thermolysis of **123** and **124** was investigated (see above). The highly functionalized compound **123** is the only bona fide example of a [3.5.5.5]-fenestrane. Our own attempts to prepare a [3.*n*.3.*n*]fenestrane ($n = 5-8$), containing a spiro[2.2]pentane skeleton, remained incomplete.[143]

5.3. All-*cis*-[5.5.5.5]-1-azafenestrane

Hitherto only a few fenestranes with oxygen replacing methylene groups have been reported.[144] The most recent result is Wender's three-step synthesis of **160b** mentioned above.[87,88] The synthesis of aza-fenestranes has only recently been reported by Denmark.[94,95] The key reaction protocol is based on the tandem [4+2]/[3+2] cycloaddition of nitroalkenes. This transformation leads to highly functionalized nitrosoacetals, which give pyrolizidines upon catalytic hydrogenation. Retrosynthetic considerations led to the sequence of successful reactions (Scheme 10).

Scheme 10



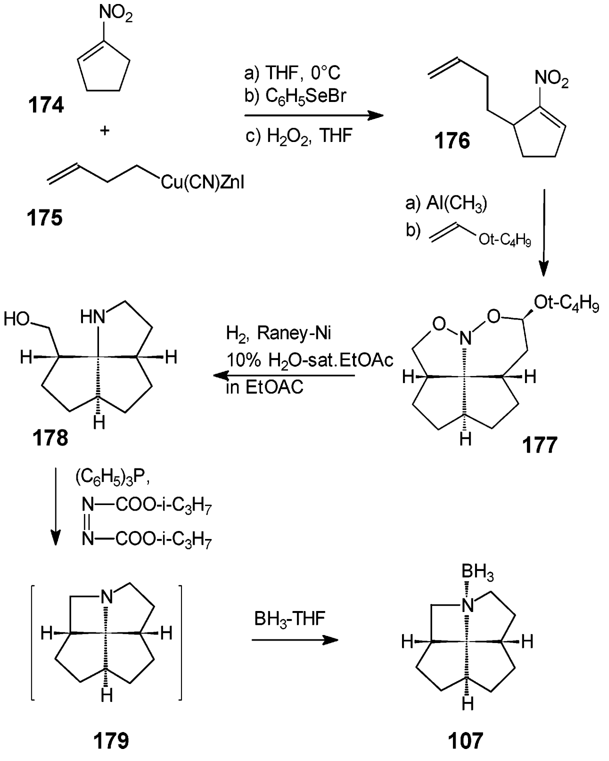
Reaction of the nitroalkene **167**, prepared from **164** and **165** via **166**, with butylvinyl ether and trimethylaluminum as a catalyst gave the [4+2] adduct **168** and, followed by the intramolecular [3+2] cycloaddition, directly the nitrosoacetal **169**. A diastereomer of nitronate **168** was obtained as a minor isomer from which the nitrosoacetal **173** was prepared. This compound is useful for preparation of a stereoisomeric [5.5.5.5]-1-azafenestrane. Hydrogenation of **169** and reductive removal of the hydroxy and carbonyl groups gave the target molecule **172** via **170** and **171**.

The spectroscopic data of **172** support its structure; X-ray structure analysis of **106**, the BH_3 adduct of **172**, revealed further details. The opposite bond angles surrounding the central carbon atom are 116.1° and 116.6°. They are similar to those observed in all-*cis*-[5.5.5.5]fenestranes.[17] Furthermore, the crystal structure of **106** reveals a torsional deformation. The dihedral angle B−N(1)−C(13)−C(7) = 11.6° and is similar to that found in electron diffraction analysis of the hydrocarbon all-*cis*-[5.5.5.5]fenestrane (12.4°).[84]

5.4. All-*cis*-[4.5.5.5]-1-azafenestrane

In a continuation of his efforts to prepare heterocyclic compounds Denmark reported very recently the synthesis of the all-*cis*-[4.5.5.5]-1-aza-fenestrane **179**.[95] Given the successful preparation of the homologue **172**, synthesis of **179** or a derivative thereof seemed to pose no problems (Scheme 11). However, minor changes in the substitution pattern led to severe obstacles. Synthesis of the substituted nitroolefin **176** required for the tandem [4+2]/[3+2] cycloaddition was performed from **174** and **175** as shown in Scheme 11. When *n*-butoxyethene was used for the cascade cycloaddition, a diatropic rearrangement was observed. Only when vinyl-*tert*-butyl ether was used was the desired tetracylic nitrosoacetal **177** obtained. Another rearrangement, undesirable for preparation of the fenestrane skeleton, occurred in the subsequent hydrogenation step. This problem could be solved by an intriguing choice of reaction conditions. Subsequent ring closure of **178** leads to the fenestrane **179**, which was in situ trapped as its BH_3 adduct **107**. This fenestrane could be obtained in five steps from the nitroolefin **174**.

Scheme 11

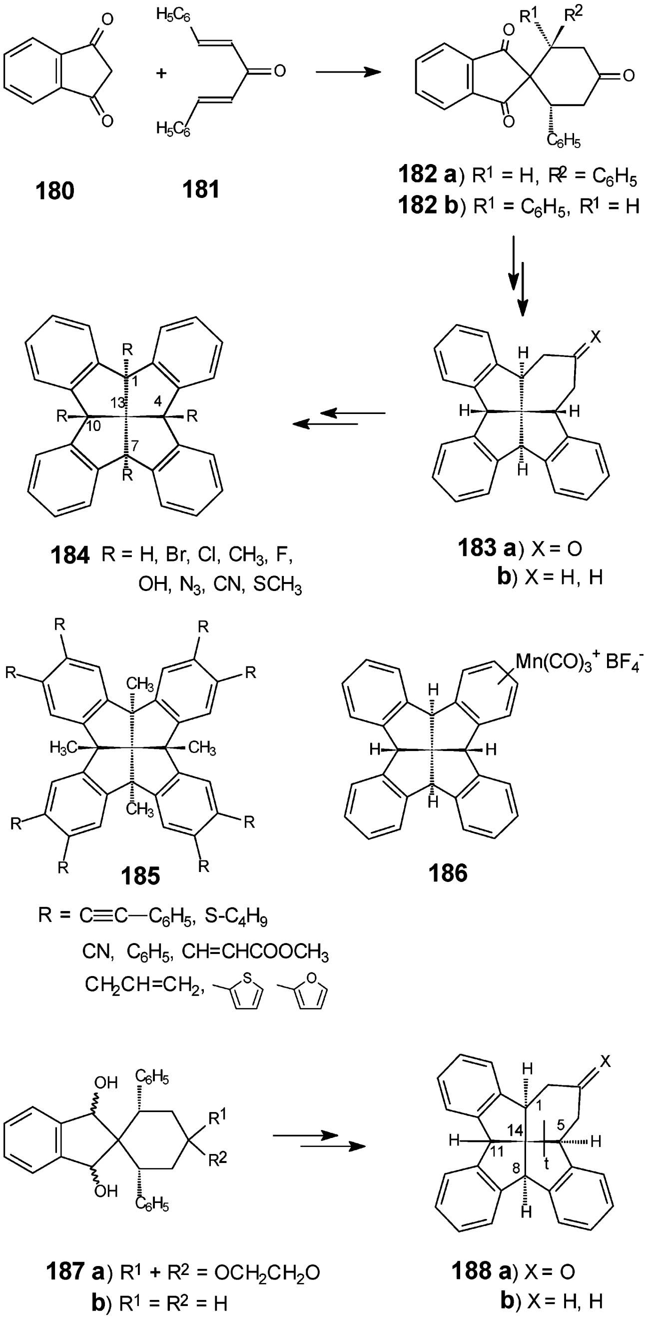


Structural features are apparent from X-ray analysis. The opposite bond angles in the two most populated crystal forms show bond angles of 119.8°/120.7° and 119.2°/121.2°, respectively. This supports the earlier observation that ring contraction leads to an opening of opposite bond angles in fenestranes.[9]

5.5. Benzannulated Fenestranes

As part of his general interest in polycyclic, indane-based hydrocarbons Kuck explored the synthetic entries into benzannulated fenestranes (Scheme 12).[18,19] Kinetic control of the condensation between the indanedione **180** and dibenzalacetone **181** gave **182a**. Reduction to the corresponding spirotriols followed by double cyclodehydration led to the tribenzo-all-*cis*-[5.5.5.6]fenestranone **183a** from which the parent tetrabenzo-all-*cis*-[5.5.5.5]fenestrane **184** (R = H) ("fenestrindan") was obtained by ring contraction and benzannulation.[145,146] This nine-step procedure provides **184** (R = H) with 12.7% overall yield. The ^{1}H NMR spectrum is interpreted in terms of an apparent D_{2d} symmetry as it exhibits a single resonance for the four brigdehead protons and a 4-fold degenerate AA′BB′ pattern for the eight arene protons. In the ^{13}C NMR spectrum only five lines are observed for the 29 carbon atoms. The X-ray structure reveals an S_4 rather than D_{2d} molecular symmetry. Two opposite bond angles around the central carbon were 116.2°, which are identical to those found in the electron diffraction structure of the unsubstituted all-*cis*-[5.5.5.5]fenestrane **91**. Each of the five-membered rings in **184** adopts an envelope-type conformation, similar to the structural features of parent tetracyclic hydrocarbon **91**.[84] In this way, eclipsed geometries in the central neopentane substructure are absent; the X-ray structure of **184** (R = H) shows a dihedral angle of 20.6°, e.g., for H(1)−C(1)−C(13)−C(7), whereas the electron diffraction of the unsubstituted all-*cis*-[5.5.5.5]fenestrane **91** gave 12.4° for the corresponding dihedral angle.[84] In these derivatives the dihedral and nonbridged C−C−C angles are increased, the latter ones to 121° (**184**, R = Br) and 118.6° (R = CH_3), as determined by X-ray structure analysis.[19] In addition, the in-plane interaction between the ortho hydrogens of the benzene rings is minimized. It may be mentioned that S_4 geometries are also found for fenestranes of type **184**, bearing more bulky bridgehead substituents as in **184** with R = Br.[19]

Scheme 12

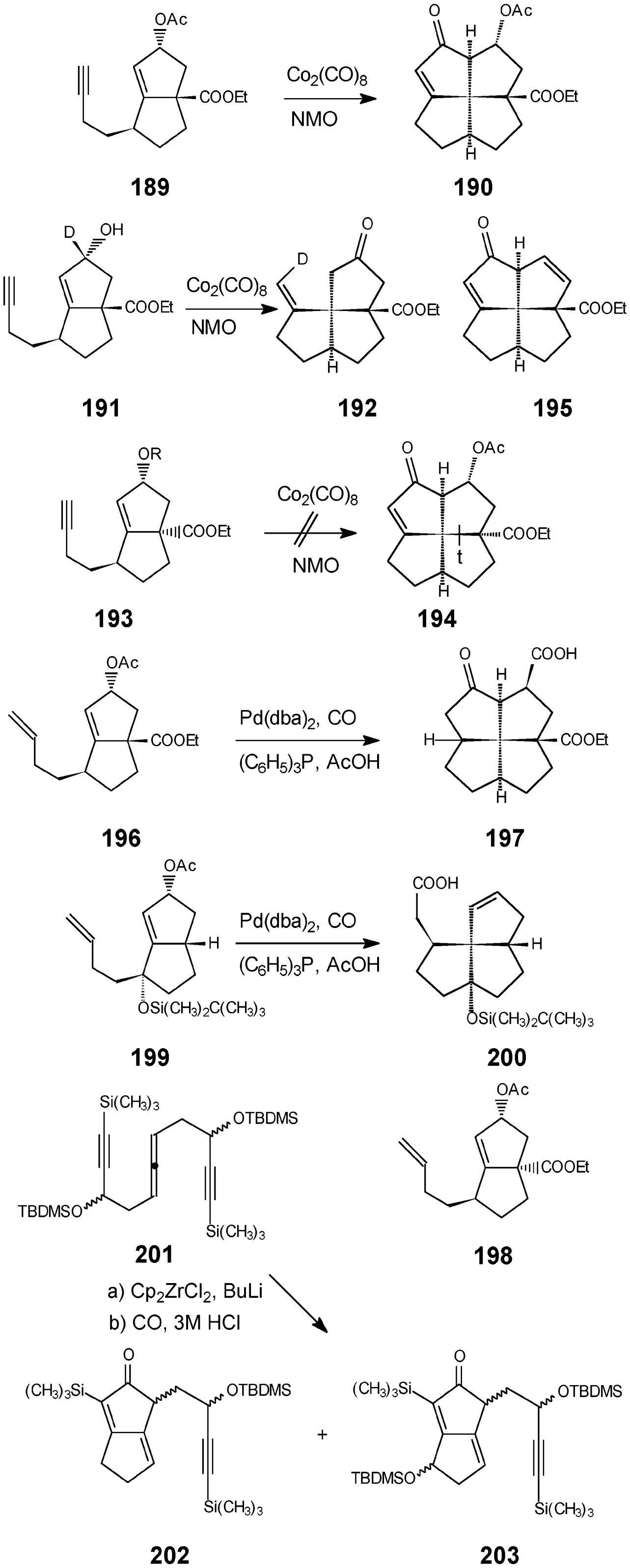


A variety of bridgehead-substituted derivatives of **184** (R = H), including doubly bridged compounds such as centrohexaindane, have been obtained via the tetrabromo derivative **184** (R = Br).[147−150] Efficient substitution in the peripheral benzene rings was achieved with methyl groups at the four bridgeheads of **184** (R = CH_3). Some examples are given with the general formula **185**.[151,152] The $Mn(CO)_3$ complex **186**, another functional derivative of **184** (R = H), has been reported.[153] It is apparent that the functional derivatives of the tetrabenzo-tetramethyl-all-*cis*-[5.5.5.5]-fenestrane **184** (R = CH_3) with its saddle-like structure may serve as a scaffold for a wide range of supramolecular compounds and devices.[154,155] Synthesis of the *c*,*c*,*c*,*t*-tribenzo[5.5.5.6]fenestranone **188a**, a stereoisomer of the all-*cis*-[5.5.5.6]fenestranone **183a**, was also reported by Kuck.[156,157] The *cis*-spirotriketone **182b**, the product of thermodynamic control in the double Michael reaction between **180** and **181**, was transformed into the dihydroxyketal **187a**, which gave via double cyclodehydration and hydrolysis the desired product **188a**. Alternatively, the dihydroxyspiro compound **187b** was directly transformed into the tribenzo-*c*,*c*,*c*,*t*-[5.5.5.6]fenestrane **188b**. NMR analysis of **188a** led to the conclusion that the six-membered ring adopts a boat conformation. This was confirmed by X-ray structure analysis of **188b**. As expected, the opposite bond angles in the central $C(C)_4$ fragment are larger than in the stereoisomeric all-*cis*-fenestrane **183b**. According to semiempirical calculations **188b** is more strained than **183b** by 11.3 kcal/mol. Specifically, bond angles of 120.8° and 115.5° are found in **188b** for C(5)−C(14)−C(11) and C(1)−C(14)−C8, respectively. Both compounds **188a** and **188b** are rather base sensitive and readily transformed into the stereoisomeric all-*cis*-**183a** and **183b**, respectively. H/D exchange reactions showed that in **188b** the proton at C(5) can be selectively replaced concomitant with inversion of the configuration.

5.6. Transition-Metal-Induced Formation of Fenestranes

Major advances in the synthesis of fenestranes and a plethora of related polycyclic hydrocarbons were achieved by the application of transition-metal-induced transformations (Scheme 13).[158−165] The most successful reaction for the efficient preparation of fenestranes is the Pauson−Khand reaction (PKR), where 1,6-en-ynes react with $Co_2(CO)_8$ in a [2+2+1] cyclization−carbonylation process to cyclopentenones.[166−168] Early results are due to Smit et al., who prepared functionalized oxa-all-*cis*-[4.5.5.5]fenestrenones.[144] Stimulated by these and other results the author of this review explored a wide range of transition-metal-induced reactions for the synthesis of fenestranes and discovered the first tandem Pauson−Khand reaction.[169,170] More recently, Chung reported a three-step one-pot synthesis of a functionalized all-*cis*-[5.5.5.5]fenestrane.[171] A selection of the recent results is described below.

Scheme 13



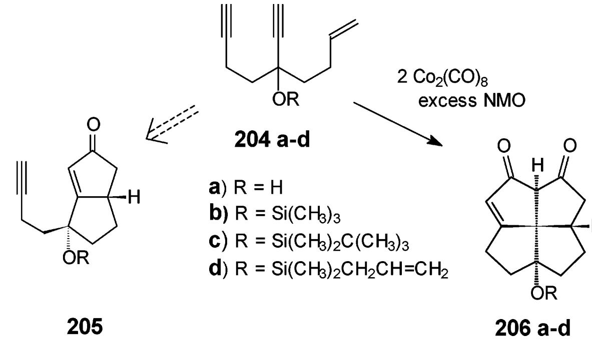
The *N*-methylmorpholino *N*-oxide-induced PKR of **189** with an *exo*-butynyl side chain gave the expected all-*cis*-[5.5.5.5]fenestrane **190** in 64% yield (Scheme 13).[172] Leaving the hydroxy group unprotected, reaction of **191** gives only the tricyclic product **192** instead of the expected fenestrane. The stereoselective transfer of deuterium may be interpreted as a metallo−ene reaction.[17] When the stereoisomeric enyne **193** with the butynyl side chain on the endo side was submitted to PKR conditions neither the metallo−ene nor the carbonylation−cyclization was observed. The PKR of **193b** would lead to a *c*,*t*,*c*,*c*-[5.5.5.5]fenestrane **194** with a trans-fused bicyclo[3.3.0]octane subunit and a strain of −12.4 kcal/mol (AM1) above that of **190**. A simple thermochemical estimate shows that the reaction between ethyne, ethene, and carbon monoxide in a [2+2+1] cycloaddition to form cyclopent-2-enone is exothermic by −40 kcal/mol. In view of this result the lack of reactivity on the endo side in **193** is remarkable.

The $Pd(dba)_2$-induced carbonylation−cyclization reaction of the diene **196** with an allylic acetoxy group also leads to a fenestrane.[173] Whereas the yield of **195** from **189** in the corresponding reaction is only modest, the 1,6-diene **196** reacts in the Pd-catalyzed reaction to the desired all-*cis*-[5.5.5.5]fenestrane **197** in good yield. As observed in the PK reaction, the isomer with the side chain on the endo side of the bicyclo[3.3.0]octane skeleton, **198**, does not undergo the Pd(0)-catalyzed cyclization−carbonylation reaction to the desired *c*,*t*,*c*,*c*-[5.5.5.5]fenestrane.

With the aim of preparing fenestranes with functionalities in different bridgehead positions the 1,6-diene, **199** (prepared by a PKR, see below) was submitted to the Pd(0)-catalyzed reaction. However, only the tricyclic product **200** was isolated. When the allene with two butynyl side chains **201** was submitted to the same reaction conditions, the bicyclic products **202** and **203** were obtained in moderate yield with low diastereoselectivity.[17] Thus, we concluded that the intramolecular PK reaction is the best choice for the synthesis of all-*cis*-fenestranes.

On the basis of retrosynthetic considerations we designed the ene−diynes **204** as suitable precursors for construction of the desired [5.5.5.5]fenestrane skeleton via two sequential PK reactions (Scheme 14). The first one leads to **205** as an intermediate where the carbonyl group should be modified; the second carbonylation−cyclization leads to a fenestrane as described for the transformation **189** → **190**. Much to our surprise the PK reaction of **204b** gave the fenestrane **206b** directly. The reaction proceeded well with **204b**, **204c**, and **204d**, all containing a protected hydroxy group but not with **204a**, and gave the highly functionalized fenestranes **206b**, **206c**, and **206d** in 24%, 22%, and 15% yield, respectively. Despite the modest yield of this procedure (17% over five steps for the synthesis of **206b**) it is one of the shorter routes to a [5.5.5.5]fenestrane with three functionalities in strategic

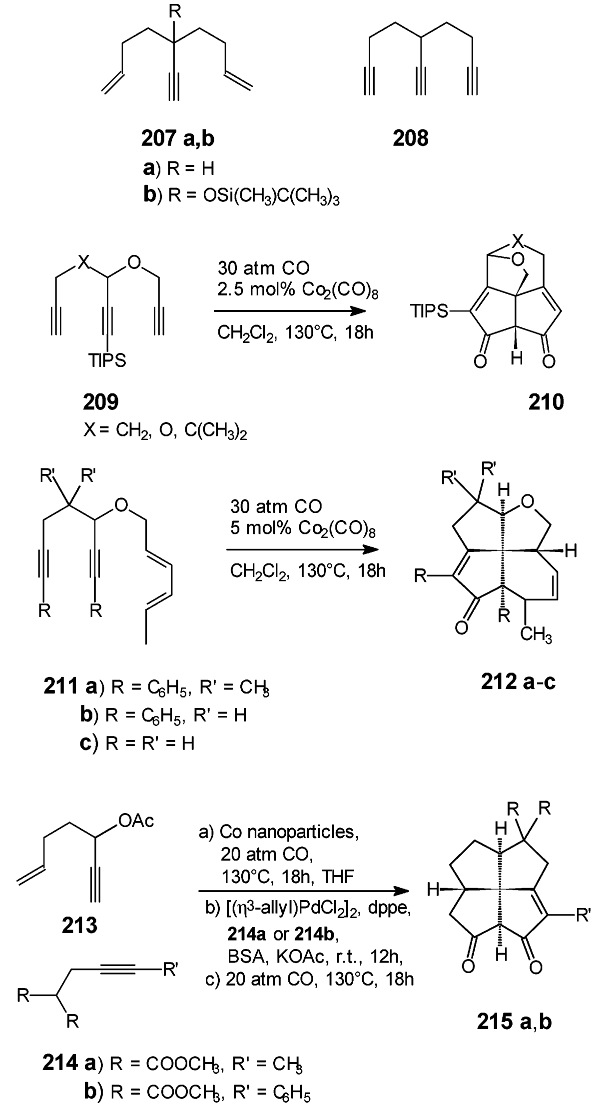
Scheme 14



positions. Mechanistic aspects of this unique tandem PK reaction have been discussed.[170]

In view of the successful synthesis of fenestranes from readily available di-enynes of type **207** and the tandem PK reactions of **204b**−**d**, Chung et al. surmised that triynes of type **208** might also lead to fenestranes via PK reactions.[174] Use of catalytic conditions for PK reactions was of particular interest. When the triynes **209** were submitted to catalytic PK reaction conditions, the tetracyclic compounds **210** rather than fenestranes were obtained (Scheme 15).[174] However, it should be noted that **210** (X = O) has the functionalities properly positioned for formation of fenestranes. In further pursuit of two sequential [2+2+1] carbonylation−cyclization reactions Chung found that dienediynes **211a**−**c** gave the [5.5.5.6]oxafenestranes **212a**−**c** in 51−84% yield.[175] Recently he reported the first three-step one-pot syntheses of [5.5.5.5]fenestranes from the readily available 1,6-enyne **213** and the alkynes **214a**,**b** as starting material.[176] The intriguing interplay of sequential reactions gives the highly functionalized [5.5.5.5]fenestranes **215a** and **215b** in 74% and 84% yield, respectively.

Scheme 15



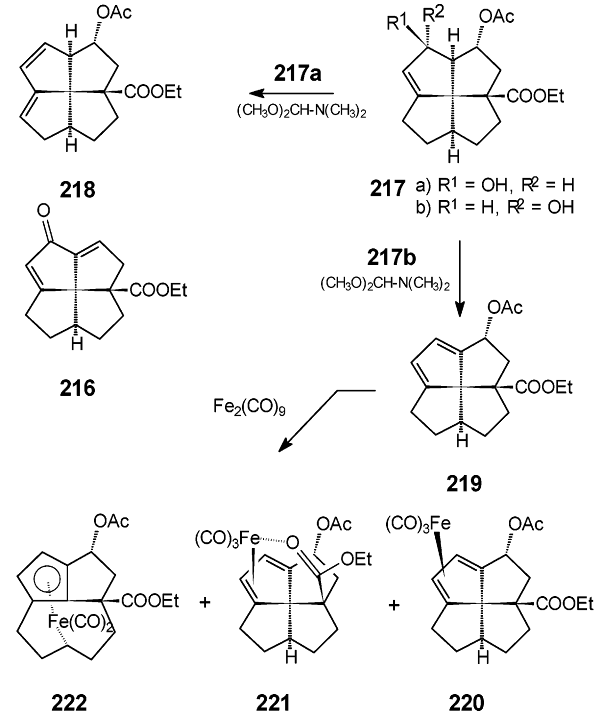
Use of Co nanoparticles in combination with other transition-metal complexes is the most exciting, recent development for the efficient, high-yield carbonylative transformation of readily available starting materials into complex molecules including the fenestranes.[177]

5.7. Enhanced Planarizing Distortions

As discussed above, opening of the opposite bond angles in [5.5.5.5]fenestranes can be enhanced by introduction of *trans*-bicyclo[3.3.0]octane subunits, ring contraction, and bridgehead double bonds.[9] Guided by semiempirical calculations, evaluation of the synthetic complexity, the experimental effort involved, and availability of appropriately functionalized fenestranes as starting material for specific transformations we explored a variety of concepts.[17] In the [5.5.5.5]fenestrane series thermolysis of **190** gave the dienone **216**, containing a bridgehead double bond. The calculated (AM1) opposite bond angles at the central carbon were 124° for the parent diene.[9] The intramolecular photoreaction of **206d** with an allyldimethylsilyl substituent on the endo side is well suited for the [2+2] photocycloaddition, but the reaction did not proceed to the expected *c*,*t*,*c*,*c*-[5.5.5.5]-fenestrane.[178]

Sigmatropic rearrangements of appropriate functionalities were envisaged as further methods for preparation of stereoisomeric [5.5.5.5]fenestranes. In a first attempt reaction of the stereoisomeric allylic alcohols **217a** and **217b** with *N*,*N*-dimethylformamide dimethylacetal was explored. In-

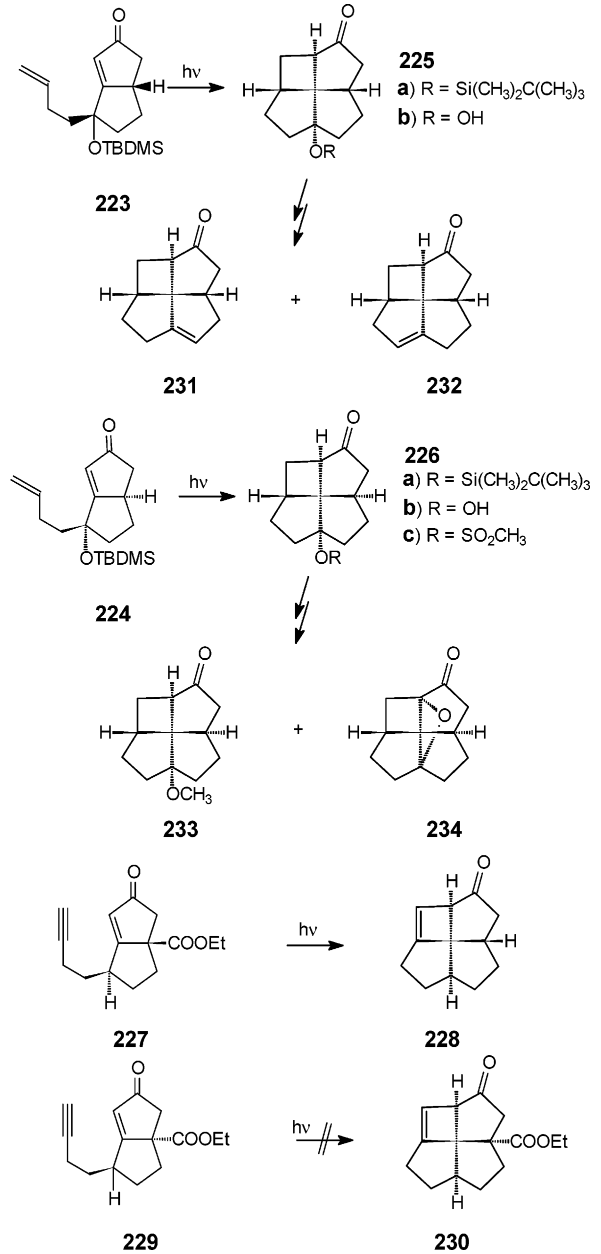
Scheme 16



stead of the expected [2,3]sigmatropic rearrangement,[179] which would lead to a bridgehead *N*,*N*-dimethylaminocarbonyl group, elimination took place in both isomers.[17] Whereas **217a** with an *exo*-hydroxy group gave diene **218**, **217b** with the *endo*-hydroxy group led selectively to diene **219**.This result is rather surprising in view of the ready Claisen rearrangement in the [4.5.5.5]fenestrane series, where a *c*,*t*,*c*,*c*-[4.5.5.5]fenestrane could be obtained.[92,180] The conjugated diene **219** is well suited for testing the formation and stability of an $Fe(CO)_3$ complex, envisaged as a possible intermediate en route to higher unsaturated fenestranes (Scheme 16).[181]

Complexation on the exo side, cis to the ester group, gave two π complexes **220** and **221**; the latter rearranges in solution to **220**. Reaction on the endo side leads to cleavage in the central $C(C)_4$ substructure with concomitant formation of the $CpFe(CO)_2$ complex **222**. This structure was established by X-ray analysis. These results show that masking of a diene moiety in a [5.5.5.5]fenestrane as an $Fe(CO)_3$ complex leads to rather unexpected results.

Scheme 17



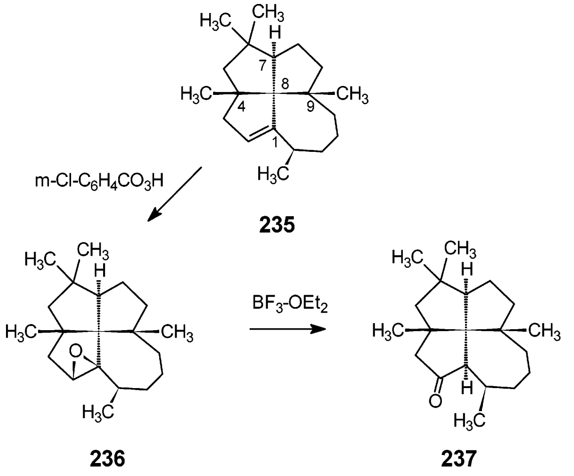
The PK reaction of the dienyne **204b** is well suited for formation of a mixture of the stereoisomeric bicyclooctenones **223** and **224** from which the stereoisomeric [4.5.5.5]-fenestranes **225** and **226** are obtained by photoinduced [2+2] cycloaddition (Scheme 17).[91,182] While photoreaction of **223** leading to all-*cis*-[4.5.5.5]fenestranes such as **225** is well established, novel reaction at the endo side of a bicyclo-[3.3.0]oct-1-en-3-one like **226** is remarkable and provides an efficient entry into the *c*,*t*,*c*,*c*-[4.5.5.5]fenestrane series.

Photoinduced [2+2] cycloaddition leading to stereoisomeric fenestranes is restricted to compounds such as **223** and **224**. Whereas photoreaction of **227** with an *exo*-alkyne side chain readily gives the expected [4.5.5.5]fenestrene **228**, the endo isomer **229** does not react to the corresponding stereoisomeric fenestrene **230**.[183] As mentioned above, the planarizing distortions in the central $C(C)_4$ substructure are enhanced by small rings, *trans*-bicyclic subunits, and bridgehead double bonds. In pursuit of these goals, formation of a bridgehead double bond in **225** and **226** was studied.[90] Whereas formation of the fenestrenones **231** and **232** occurred directly during preparation of the mesylate from **225b**, the corresponding stereoisomeric mesylate **226c** was isolated. Elimination reactions performed with **226c** gave products to which the structures **233** and **234** were tentatively assigned. According to our semiempirical results the *c*,*t*,*c*,*c*-[4.5.5.5]fenestrene with a bridgehead double bond should have bond angles of 138° and 131°. Thus, the question is still open of whether fenestranes with both bond angles larger than 130° can be prepared.

5.8. Laurenene—A Natural [5.5.5.7]Fenestrene

Beyond the synthetic, structural, and theoretical interest in the chemistry of fenestranes it is to be mentioned that Nature has provided us with laurenene **235**, a [5.5.5.7]-fenestrene even containing a bridgehead double bond (Scheme 18).[184−187] According to its X-ray structure the opposite bond angles are 117.9° and 118.9°. Epoxidation of **235** leads to **236**, a *c*,*c*,*c*,*t*-[5.5.5.7]fenestrane, which is readily converted into the ketone **237** with an all-*cis* fenestrane structure.[186]

Scheme 18



6. Concluding Remarks

Key concepts for the computational harnessing of planar tetracoordinate and hypercoordinate carbon are now known. The basic feature for stabilization is interaction of the planar carbon with four ligands which have σ-donating concomitant with π-accepting properties. This feature is reminiscent of stabilization of a metal center in complexes where low oxidation states of the metal are stabilized by σ-donating and π-accepting ligands. Incorporation of these electronic features into small rings and, furthermore, formation of aromatic ring systems[23−26,64−70] are important structural prerequisites for the computational realization of structures containing a planar tetracoordinate carbon.

Concepts that place a carbon atom in the center of a robust hydrocarbon cage with a lack of low-lying transition states for fragmentation led to further hypothetical structures containing a planar tetracoordinate carbon.

The internal compensation of charge generated by removal of two electrons from the formally nonbonding orbital of the planar carbon is an additional feature which led to a variety of important developments and results.

It has been found that CM_4 clusters with a perimeter of four appropriate metal atoms prefer a planar structure if 18 electrons are present. The first example of these compositions has been prepared in the gas phase, and there is evidence for their planar structure.[56,57,59]

Stabilization of planar tetracoordinate carbon by transition-metal complexes led to the preparation of many new compounds.

The structural landscape between the tetrahedral and planar carbon with the fenestranes as prototypical structures was explored computationally as well as experimentally. New fenestranes containing an inverted bridgehead substituent or heteroatoms were prepared. Transition-metal-induced carbonylation−cyclization reactions, particularly those of the Pauson−Khand type, now allow a variety of fenestranes to be prepared in a matter of steps. No fenestranes with opposite bond angles beyond 130° have been prepared yet.

The interplay of high-level computational explorations and synthetic efforts is an important prerequisite for development of this unique area of nonclassical carbon structures. Beyond the results discussed for carbon, they include other main-group elements such as Si and Ge in a planar tetracoordinate configuration. Theoretical and experimental results have been reported.[188−191] Intuition, rationalization, evaluation by MO methodology, experimentation, and verification will lead to further progress in the promising chemistry of planar tetracoordinate carbon.

7. Acknowledgment

The theoretical and experimental work in my group was performed over many years by dedicated co-workers, undergraduate and graduate students, and postdoctoral fellows, partially cited in the references. Success would not have been possible without their ideas, fundamental interest in science, stimulating discussions, experimental skills, and competent performance. Our endeavors have been generously supported over many years by the Swiss National Science Foundation.

8. References

(1) van't Hoff, J. H. *Arch. Neerl. Sci. Exactes Nat.* **1874**, *9*, 44.
(2) Le Bel, J. A. *Bull. Soc. Chim. Fr.* **1874**, *22*, 337.
(3) Helferich, B. Personal communication. Pfenninger, A.; Roesle, A.; Keese, R. *Helv. Chim. Acta* **1985**, *68*, 493; footnote 2.
(4) Wagner-Jauregg, T. Sterische Umlagerungen am asymmetrischen Kohlenstoffatom. In *Stereochemie*; Freudenberg, K., Ed.; Deuticke Verlag: Leipzig, 1933; Chapter VIII.
(5) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992.
(6) Woodward, R. B.; Hoffmann, R. *The conservation of orbital symmetry*; Verlag Chemie: Weinheim, 1970.
(7) Sorger, K.; Schleyer, P. v. R. *J. Mol. Struct. (THEOCHEM)* **1995**, *338*, 317.
(8) Radom, L.; Rasmussen, D. R. *Pure Appl. Chem.* **1998**, *70*, 1977.
(9) Luef, W.; Keese, R. *Advances in Strain in Organic Chemistry*, Halton, B., Ed.; JAI Press: Greewich, CT, 1993; Vol. 3, p 229.
(10) Minkin, V. I.; Minyaev, R. M.; Hoffmann, R. *Russ. Chem. Rev.* **2002**, *71*, 869 (*Usp. Khim.* **2002**, *71*, 989).
(11) Röttger, D.; Erker, G. *Angew. Chem.* **1997**, *109*, 840; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2372.
(12) Erker, G. *Chem. Soc. Rev.* **1999**, *28*, 307.
(13) Siebert, W.; Gunale, A. *Chem. Soc. Rev.* **1999**, *28*, 367.
(14) Choukroun, R.; Lorber, C. *Eur. J. Inorg. Chem.* **2005**, 4683.
(15) Venepalli, B. R.; Agosta, W. C. *Chem. Rev.* **1987**, *87*, 399.
(16) Agosta, W. C. In *The Chemistry of the Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1992; p 927.
(17) Thommen, M.; Keese, R. *Synlett* **1997**, 231.
(18) Kuck, D. *Top. Curr. Chem.* **1998**, *169*, 168.
(19) Kuck, D. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 4, p 81.
(20) Pople, J. A. *Angew. Chem.* **1999**, *111*, 2014; *Angew. Chem., Int. Ed.* **1999**, *38*, 1894.
(21) Foresman, J. B.; Frisch, E. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, 1996.
(22) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(23) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, J. J.; Hommes, N. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
(24) Schleyer, P. v. R.; Jiao, H. J.; Hommes, N. *J. Am. Chem. Soc.* **1997**, *119*, 12669.
(25) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.
(26) Boldyrev, A. I.; Wang, L. *Chem. Rev.* **2005**, *105*, 3716.
(27) Silvi, B.; Fourré, I.; Alikhani, M. E. *Monatsh. Chem.* **2005**, *136*, 855.
(28) Poater, J.; Duran, M.; Solà, M.; Silvi, B. *Chem. Rev.* **2005**, *105*, 3911.
(29) Minyaev, R. M.; Gribanova, T. N.; Starikov, A. G.; Gapurenko, O. A.; Minkin, V. I. *Dokl. Chem* **2005**, *404*, 193.
(30) Pepper, M. J. M.; Shavitt, I.; Schleyer, P. v. R.; Glukhotsev, M. N.; Janoscheck, R.; Quack, M. *J. Comput. Chem.* **1995**, *16*, 207.
(31) Yoshizawa, K.; Suzuki, A.; Yamabe, T. *J. Am. Chem. Soc.* **1999**, *121*, 5266.
(32) Yoshizawa, K.; Suzuki, A. *Chem. Phys.* **2001**, *271*, 41.
(33) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419.
(34) McGrath, M. P.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 3320.
(35) Lyons, J. E.; Rasmussen, D. R.; McGrath, M. P.; Nobes, R. H.; Radom, L. *Angew. Chem.* **1994**, *106*, 1722; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1667.
(36) Radom L.; Rasmussen, D. R. *Pure Appl. Chem.* **1998**, *70*, 1977.
(37) Rasmussen, D. R.; Radom, L. *Angew. Chem.* **1999**, *111*, 3051; *Angew. Chem., Int. Ed.* **1999**, *38*, 2876.
(38) Rasmussen, D. R.; Radom, L. *Chem.*−*Eur. J.* **2000**, *6*, 2470.
(39) Wang, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2002**, *124*, 11979.
(40) Gribanova, T. N.; Minyaev, R. M.; Minkin, V. I. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1780.
(41) Minyaev, R. M.; Gribanova, T. N.; Minkin, V. I.; Starikov, A. G.; Hoffmann, R. *J. Org. Chem.* **2005**, *70*, 6693.
(42) Wang, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2001**, *123*, 994.
(43) Wang, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2002**, *124*, 11979.
(44) Lammertsma, K.; Schleyer, P. v. R. *J. Phys. Chem.* **1988**, *92*, 881.
(45) Esteves, P. M.; Ferreira, N. B. P.; Corrêa, R. J. *J. Am. Chem. Soc.* **2005**, *127*, 8680.
(46) Priyakumar, U. D.; Reddy, A. S.; Sastry, G. N. *Tetrahedron Lett.* **2004**, *45*, 2495.
(47) Priyakumar, U.; Sastry G. N. *Tetrahedron Lett.* **2004**, *45*, 1515.
(48) Billups, W. E.; Haley, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 5084.
(49) Saini, R. K.; Litosh, V. A.; Daniels, A. D.; Billups, A. D. *Tetrahedron Lett.* **1999**, *40*, 6157.
(50) Merino, G.; Méndez-Rojas, M. A.; Vela, A. *J. Am. Chem. Soc.* **2003**, *125*, 5026.
(51) Merino, G.; Méndez-Rojas, M. A.; Beltrán, H. I.; Corminboeuf, C.; Heine, T.; Vela, A. *J. Am. Chem. Soc.* **2004**, *126*, 16160.
(52) Pancharatna, P. D.; Méndez-Rojas, M. A.; Merino, G.; Vela, A.; Hoffmann, R. *J. Am. Chem. Soc.* **2004**, *126*, 15309.
(53) Perez, N.; Heine, T.; Barthel, R.; Seifert, G.; Vela, A.; Méndez-Rojas, M. A.; Merino, G. *Org. Lett.* **2005**, *7*, 1509.
(54) Schleyer, P. v. R.; Boldyrev, A. I. *J. Chem. Soc., Chem. Commun.* **1991**, 1536.
(55) Zubarov, D. Y.; Boldyrev, A. I. *J. Chem. Phys.* **2005**, *122*, 144322.
(56) Li, X.; Wang, L.; Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1999**, *121*, 6033.
(57) Li, X.; Zhang, H.; Wang, L. S.; Geske, G. D.; Boldyrev, A. I. *Angew. Chem.* **2000**, *112*, 3776; *Angew. Chem., Int. Ed.* **2000**, *39*, 3630.

(58) Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1998**, *120*, 7967.
(59) Wang, L.; Boldyrev, A. I.; Li, X.; Simons, J. *J. Am. Chem. Soc.* **2000**, *122*, 7681.
(60) Boldyrev, A. I.; Wang, L. *J. Phys. Chem. A* **2001**, *105*, 10759.
(61) Geske, G. D.; Boldyrev, A. I. *Inorg. Chem.* **2002**, *41*, 2795.
(62) Su, M. *Inorg. Chem.* **2005**, *44*, 4829.
(63) Jemmis, E. D.; Parameswaran, P.; Phukan, A. K. *Mol. Phys.* **2005**, *103*, 897.
(64) Exner, K.; Schleyer, P. v. R. *Science* **2000**, *290*, 1937.
(65) Wang, Z.; Schleyer, P. v. R. *Science* **2001**, *292*, 2465.
(66) Erhardt, S.; Frenking, G.; Chen, Z.; Schleyer, P. v. R. *Angew. Chem.* **2005**, *117*, 1102; *Angew. Chem., Int. Ed.* **2005**, *44*, 1078.
(67) Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3433.
(68) Boldyrev, A. I.; Wang, L. *Chem. Rev.* **2005**, *105*, 3716.
(69) Gribanova, T. N.; Minyaev, R. M.; Minkin, V. I. *Mendeleev Commun.* **2001**, 169.
(70) Minyaev, R. M.; Gribanova, T. N.; Starikov, A. G.; Minkin, V. I. *Dokl. Chem.* **2002**, *382*, 41.
(71) Grimes, R. S. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G. Eds.; Pergamon: New York, 1995; Vol. 2, p 373.
(72) Ramachandran, B. M.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **2006**, *45*, 336.
(73) Kiani, F. A.; Hofmann, M. *Organometallics* **2006**, *25*, 485.
(74) Xie, Z. W. *Coord. Chem. Rev.* **2006**, *250*, 259.
(75) Zhai, H.; Alexandrova, A. N.; Birch, K. A.; Boldyrev, A. I.; Wang, L. *Angew. Chem.* **2003**, *115*, 6186; *Angew. Chem., Int. Ed.* **2003**, *42*, 6004.
(76) Gunale, A.; Pritzkow, H.; Siebert, D.; Steiner, D.; Berndt, A. *Angew. Chem.* **1995**, *107*, 1194; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1111.
(77) Gunale, A.; Steiner, D.; Schweikart, D.; Pritzkow, H.; Berndt, A.; Siebert, W. *Chem.—Eur. J.* **1998**, *4*, 44.
(78) Gunale, A.; Pritzkow, H.; Siebert, W.; Steiner, D.; Berndt, A.; Hyla-Krispin, I.; Gleiter, R. In *Advances in Boron Chemistry*; Siebert, W., Ed.; The Royal Society of Chemistry: Cambridge, 1997.
(79) Sahin, Y.; Hartmann, M.; Geiseler, G.; Schweikart, D.; Balzereit, C.; Frenking, G.; Massa, W.; Berndt, A. *Angew. Chem.* **2001**, *113*, 2725; *Angew. Chem., Int. Ed.* **2001**, *40*, 2662.
(80) Albright, T. T.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley & Sons: New York, 1985.
(81) Mitschka, R.; Cook, J. M.; Weiss, U. *J. Am. Chem. Soc.* **1978**, *100*, 3973
(82) Craig, R. E. R.; Craig, A. C.; Larsen, R. D.; Caughlan, C. N. *J. Org. Chem.* **1977**, *42*, 3188.
(83) Haas, G.; Prelog, V. *Helv.* **1969**, *52*, 1202.
(84) Brunvoll, J.; Guidetti-Grept, R.; Hargittai, I.; Keese, R. *Helv.* **1993**, *76*, 2838.
(85) Böhm, M. C.; Gleiter, R.; Schang, P. *Tetrahedron Lett.* **1979**, 2575.
(86) Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R. *Tetrahedron* **1981**, *37*, 921.
(87) Wender, P. A.; Dore, T. M.; deLong, M. A. *Tetrahedron Lett.* **1996**, *37*, 7687
(88) Wender, P. A.; deLong, M. A.; Wireko, F. C. *Acta Crystallogr.* **1997**, *C53*, 954.
(89) Keese, R.; Helbling, V.; Teng, Z.; Boss, C.; Hohenfeld, G.; Schnyder, A. *Recent Research and Development in Organic Chemistry*; Pandalai, S. G., Ed.; Transworld Research Network: Trivandrum, India, 1998; Vol. 2, p 463.
(90) Schmitz, A.; Prevot, L.; Thommen, M.; Eberle, M. K.; Bigler, P.; Keese, R. Manuscript in preparation.
(91) Thommen, M.; Keese, R.; Förtsch, M. *Acta Crystallogr.* **1996**, *C52*, 2051.
(92) Wang, J.; Thommen, M.; Keese, R. *Acta Crystallogr.* **1996**, *C52*, 2311.
(93) Rao, V. B.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 5732.
(94) Denmark, S. E.; Kramps, L. A.; Montgomery, J. I. *Angew. Chem.* **2002**, *114*, 4296; *Angew. Chem., Int. Ed.* **2002**, *41*, 4122.
(95) Denmark, S. E.; Montgomery, J. I. *Angew. Chem.* **2005**, *117*, 3798; *Angew. Chem., Int. Ed.* **2005**, *44*, 3732.
(96) Minkin, V. I.; Minyaev, R. M.; Orlova, G. V. *J. Mol. Struct. (THEOCHEM)* **1984**, *110*, 241.
(97) Balji, V.; Michl, J. *Pure Appl. Chem.* **1988**, *60*, 189.
(98) Lewars, E. *J. Mol Struct. (THEOCHEM)* **1998**, *423*, 173; **2000**, *507*, 165.
(99) Kenny, J. F.; Krueger, K. M.; Rienstra-Kiracofe, J. C.; Schaefer, H. F., III *J. Phys. Chem. A* **2001**, *105*, 7745.
(100) Minkin, V. I.; Minyaev, R. M. *Dokl. Chem* **2002**, *385*, 502.
(101) Minyaev, R. M.; Minkin, V. I.; Gribanova, T. N.; Starikov, A. G.; Hoffmann, R. *J. Org. Chem.* **2003**, *68*, 8588.
(102) Minyaev, R. M.; Minkin, V. I.; Gribanova, T. N.; Starikov, A. G.; Hoffmann, R. *J. Org. Chem.* **2003**, *68*, 8588.
(103) Mieusset, J.-L.; Brinker, U. H. *J. Org. Chem.* **2005**, *70*, 10572.
(104) Luef, W.; Keese, R. *J. Mol. Struct. (THEOCHEM)* **1992**, *257*, 353.
(105) O'Neal, H. F.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866 and 1968.
(106) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 5550.
(107) Genaux, (g) T.; Kern, F.; Walters, W. D. *J. Am. Chem. Soc.* **1953**, *75*, 6196.
(108) Wiberg, K. B.; McMurdie, N.; Mcclusky, J. V.; Hadad, C. M. *J. Am. Chem. Soc.* **1993**, *115*, 10653.
(109) Wiberg, K. B.; McCusky, J. V. *Tetrahedron Lett.* **1987**, *28*, 5411.
(110) Wolff, S.; Venepalli, R. B.; Gorge, C. F.; Agosta, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 6785.
(111) Zhang, C.; Bourgin, D.; Keese, R. *Tetrahedron* **1991**, *47*, 3059.
(112) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
(113) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Hampden-Smith, M. J.; Huffman, J. C.; Folting, K.; Ellis, P. D.; Huggins, B. A. *Angew. Chem.* **1989**, *101*, 1547; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1523.
(114) Chacon, S. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. *Organometallics* **1991**, *10*, 3722.
(115) Chisholm, M. H. *J. Chem. Soc., Dalton Trans.* **1996**, 1781.
(116) Ogoshi, S.; Tsutsumi, K.; Ooi, M.; Kurosawa, H. *J. Am. Chem. Soc.* **1995**, *117*, 10415.
(117) Ogoshi, S.; Nishida, T.; Tsutsumi, K.; Ooi, M.; Shinagawa, T.; Akasaka, T.; Yamane, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 3223.
(118) Kurosawa, H. *J. Organomet. Chem.* **2004**, *689*, 4511.
(119) Huang, J.-H.; Luci, J. J.; Lee, T.-Y.; Swenson, D. C.; Jensen, J. H.; Messerle, L. *J. Am. Chem. Soc.* **2003**, *125*, 1688.
(120) Hyla-Kryspin, I.; Gleiter, R.; Rohmer, M.-M.; Devemy, J.; Gunale, A.; Pritzkow, H.; Siebert, W. *Chem.—Eur. J.* **1997**, *3*, 294.
(121) Cotton, F. A.; Millar, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7886.
(122) Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397.
(123) Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802.
(124) Erker, G.; Frömberg, W.; Angermund, K.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372.
(125) Röttger, D.; Erker, G.; Fröhlich, R.; Grehl, M.; Silverio, S. J.; Hyla-Pryspin, I.; Gleiter, R. *J. Am Chem. Soc.* **1995**, *117*, 10503.
(126) Ahlers, W.; Erker, G.; Fröhlich, R.; Peuchert, U. *Chem. Ber./Recl.* **1997**, *130*, 1069.
(127) Menzel, M.; Steiner, D.; Winkler, H.-J.; Schwikart, D.; Mehle, S.; Fau S.; Frenking, G.; Massa, W.; Berndt, A. *Angew. Chem.* **1995**, *107*, 368; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 327.
(128) Pulst, Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem.* **1996**, *108*, 1175; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1122.
(129) Choukroun, R.; Cassoux, P. *Acc. Chem. Res.* **1999**, *32*, 494.
(130) Choukroun, R.; Donnadieu, B.; Zhao, J.-S.; Cassoux, P.; Lepetit, C.; Silvi, B. *Organometallics* **2000**, *19*, 1901.
(131) Choukroun, R.; Lorber, C. *Eur. J. Inorg. Chem.* **2005**, 4683.
(132) Heeres, H. J.; NIjhoff, J.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1993**, *12*, 2609.
(133) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618.
(134) Rosenthal, U.; Ohff, A.; Tillack, A.; Baumann, W.; Görls, H. *J. Organomet. Chem.* **1994**, *468*, C4.
(135) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Parameswaran, P.; Jemmis, E. D. *Chem. Commun.* **2004**, 2074.
(136) Rosenthal, U. *Angew. Chem.* **2004**, *116*, 3972; *Angew. Chem., Int. Ed.* **2004**, *43*, 3882.
(137) Suzuki, N.; Watanabe, T.; Iwasaki, M.; Chihara, T. *Organometallics* **2005**, *24*, 2065.
(138) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K.-K. *Angew. Chem.* **1996**, *108*, 1213; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1100.
(139) Wender, P. A.; Dore, T. M. Intra- and intermolecular Cycloadditions of Benzene Derivatives. In *Handbook of Organic Photochemistry and Photobiology*; Horspool, W. S., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; p 280.
(140) Wender, P. A.; Siggel, L.; Nuss, J. M. [3+2] and [5+2]Arene-alkene Photocycladditions. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: New York, 1991; Vol. 5, pp 645.
(141) Cornelisse, J. *Chem. Rev.* **1993**, *93*, 615.
(142) Mani, J.; Schüttel, S.; Zhang, C.; Bigler, P.; Müller, C.; Keese, R. *Helv. Chim. Acta* **1989**, *72*, 487.
(143) Grognuz, M. Ph.D. Thesis, University of Bern, 1988.
(144) Smit, v. 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. *Tetrahedron Lett.* **1991**, *32*, 2105.
(145) Kuck, D.; Bögge, H. *J. Am. Chem. Soc.* **1986**, *108*, 8107.

(146) Kuck, D. *Chem. Ber.* **1994**, *127*, 409.
(147) Kuck, D.; Schuster, A.; Krause, R. A. *J. Org. Chem.* **1991**, *56*, 3472.
(148) Kuck, D.; Schuster, A. *Angew. Chem.* **1988**, *10*0, 1222; *Angew. Chem., Int. Ed.* **1988**,
(149) Kuck, D.; Krause, R. A.; Gestmann, D.; Posteher, F.; Schuster, A. *Tetrahedron* **1998**, *54*, 5247.
(150) Tellenbröker, J.; Barth, D.; Neumann, B.; Stammler, H.-G.; Kuck, D. *Org. Biol. Chem.* **2005**, *3*, 570.
(151) Tellenbröker, J.; Kuck, D. *Eur. J. Org. Chem.* **2001**, 1483.
(152) Zhou, L.; Cao, X.-P.; Neumann, B.; Stammler, H.-G.; Kuck, D. *Synlett* **2005**, 2771.
(153) Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A.; Kuck, D.; Fusco, C.; Curci, R. *Organometallics* **2000**, *19*, 2233.
(154) Cao, X.-P.; Barth, D.; Kuck, D. *Eur. J. Org. Chem.* **2005**, 3482.
(155) Kuck, D. *Pure Appl. Chem.* **2006**, *78*, 749.
(156) Bredenkötter, B.; Barth, D.; Kuck, D. *Chem. Commun.* **1999**, 847.
(157) Bredenkötter, B.; Flörke, U.; Kuck, D. *Chem.—Eur. J.* **2001**, *7*, 3387.
(158) de Meijere, A., Ed. *Chem. Rev.* **2000**, *100* (8), 2739−3282.
(159) Kulinkovich, O. G.; de Meijere, A. *Chem. Rev.* **2000**, *100*, 2789.
(160) Yet, L. *Chem. Rev.* **2000**, *100*, 2963.
(161) Tsuji, J. *Transition Metal Reagents and Catalysts*; Wiley & Sons: Sussex, 2000.
(162) Beller, M., Bolm, C., Eds.; *Transition Metals for Organic Synthesis*; Wiley-VCH: Weinheim, 1998.
(163) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127.
(164) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285.
(165) Hartwig, J. F. In *Comprehensive Coordination Chemistry II*; Mc-Cleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford U.K., 2004; Vol. 9, p 369.
(166) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc., Chem. Commun.* **1971**, 36.
(167) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem Soc., Perkin Trans. 1* **1973**, 977.
(168) Boñaga, L. V. R.; Krafft, M. E. *Tetrahedron* **2004**, *60*, 9795.
(169) van der Waals, A.; Keese, R. *J. Chem. Soc., Chem. Commun.* **1992**, 570.
(170) Thommen, M.; Veretenov, A. L.; Guidetti-Grept, R.; Keese, R. *Helv. Chim. Acta* **1996**, *79*, 461.
(171) Son, S. U.; Park, K. H.; Chung, Y. K. *J. Am. Chem. Soc.* **2002**, *124*, 6838.
(172) Thommen, M.; Gerber, P.; Keese, R. *Chimia* **1991**, *45*, 21.
(173) Keese, R.; Guidetti-Grept, R.; Herzog, B. *Tetrahedron Lett.* **1992**, *33*, 1207.
(174) Son, S. U.; Yoon, Y. A.; Choi, D. S.; Park, J. K.; Kim, B. M.; Chung, Y. K. *Org. Lett.* **2001**, *3*, 1065.
(175) Kim, D. H.; Son, S. U.; Chung, Y. K.; Lee, S.-G. *Chem. Commun.* **2002**, 56.
(176) Son, U. K.; Park, K. K. H.; Chung, Y. K. *J. Am. Chem. Soc.* **2002**, *124*, 6838.
(177) Park, K. H.; Chung, Y. K. *Synlett* **2005**, 545.
(178) Thommen, M. Ph.D. Thesis, University of Bern, 1995.
(179) Abdulla, R. F.; Brinkmeyer, R. S. *Tetrahedron* **1979**, *35*, 1675.
(180) Grieco, P. A.; Brandes, E. B.; McCann, S.; Clark, J. D. *J. Org. Chem.* **1989**, *54*, 5849.
(181) Wang, J.; Guidetti-Grept, R.; Keese, R.; Stoeckli-Evans, H. *Helv. Chim. Acta* **1997**, *80*, 1169.
(182) Keese, R. *Angew. Chem.* **1992**, *104*, 307; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 344.
(183) Gerber, P.; Keese, R. *Tetrahedron Lett.* **1992**, *33*, 3987.
(184) Weavers, R. T. *J. Org. Chem.* **2001**, *66*, 6453.
(185) Chin, A. F. O.; Clarke, D. B.; Hinkley, S. F. R.; Nigel, B. P.; Weavers, R. T. *Aust. J. Chem.* **2001**, *54*, 205.
(186) Corbett, R. E.; Couldwell, C. M.; Lauren, D. R.; Weavers, R. T. *J. Chem. Soc., Perkin Trans. I* **1979**, 1791.
(187) Corbett, R. E.; Lauren, D. R.; Weavers, R. T. *J. Chem. Soc., Perkin Trans. I* **1979**, 1774.
(188) Boldyrev, A. I.; Wang, L.-S. *Angew. Chem.* **2000**, *112*, 3445; *Angew. Chem., Int. Ed.* **2000**, *39*, 3007.
(189) Boldyrev, A. I.; Schleyer, P. v. R.; Keese, R. *Mendeleev Commun.* **1992**, 93.
(190) Rong, G.; Keese, R.; Stoeckli-Evans, H. *Eur. J. Inorg. Chem.* **1998**, 1967.
(191) Ding, B.; Keese, R.; Stoeckli-Evans, H. *Angew. Chem.* **1999**, *111*, 387; *Angew. Chem., Int. Ed.* **1999**, *38*, 375.

CR050545H