

Theoretical Investigation and Synthesis Strategy of ‘hypervalent’ Carbon

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Abstract: *Hypervalent* compounds using main group elements are often used as reagents in the variety of interesting reactions in chemistry, such as in the total synthesis of some important natural products and/or drugs, as molecular switch, as oxidizing agents, in the synthesis of novel polymers, in rearrangement reactions, in oxidative cleavage reactions, in activation of small molecules (such as H₂, O₂, O₃, P₄...) etc. However, although *hypervalent* compounds of main group elements are well known, there are a few examples in the literature about DFT-calculation and synthesis strategy of *hypervalent* carbon compounds. Some scientists are still of the opinion that carbon atom does not have the ability to form hypervalent carbon bonds. Therefore, they argue that *multiple* bonded (more than 4 bond) carbon atoms should be termed “*hypercoordinated*”. The fact is that both “*hypervalent*” carbon compounds and “*hypercoordinated*” carbon compounds existed. However, there are certain requirements for a *multiple* bonded carbon compound to be called “*hypervalent*”. The most important requirements are the bond length, the existence of 3c–4e bonding mode and the bound ligand to carbon. This review discusses the conditions for the *hypervalence* and summarizes, analyzes the established synthesis strategy and some important DFT-calculation of *hypervalent* carbon compounds.

Keywords: *Hypervalent* Synthesis, *hypervalent* Chemistry, *hypercoordinated* Carbon, *hypervalent* Carbon

1. Introduction

‘Hyper’ is a greek word and means “too much” or “over”. *Hypervalent* has the meaning that the central atom of the compound has more than eight electrons in its valence shell. Scientists are convinced that most of the produced *multiple bonded* (more than four bonds) carbon compounds have *hypervalent* character. They believe that the bond lengths for such compounds are unusually long and cannot be called covalent bonds and have similar *hypervalent* bonding and chemical properties as the other typical *hypervalent* compounds in group 14. Therefore, it is important to the arguments of the proponents of the thesis of “*hypervalent carbon*”. In this review, both theoretically calculated, and experimentally produced *hypervalent* carbon compounds have been studied and analyzed in detail.

Hypervalence is the deviation from the valence theory or octet rule, according to which the outer shell of an atom can hold more electrons than the eight possible electrons according to the noble gas configuration of s and p orbitals.

Hypervalent as a word was first introduced in 1969 by Jeremy Musher to describe the heavy metal bonds (period 3 and down). [1-4]

Historically, in the 1930s, on the basis of parachor measurements, Sugden et al. tried to explain the phenomenal for the existence of 2c–1e covalent bonds. [5] They showed how they could be used, in conjunction with traditional 2c–1e covalent bonds, to explain the bonding in *hypervalent* compound. They want to explain the bonding in *hypervalent* compound without extending the scope of the octet rule. However, their suggestions were not widely accepted. [6] In the late 40s and early 50s the bonding of *hypervalent* compounds was explained for the first time by Rundle [7] and Pimentel [8] via MO theory and their introduction of the so-called 3c–4e bond of which only two of the four electrons are actually bonding and correspond to two collinear 2c–1e bonds. The remaining two electrons correspond to *non-bonding* or weakly *anti-bonding* electrons concentrated on the outer periphery of the molecule. In the 1960s and 1970s an extensive literature developed. Based on empirical bond

length and bond angle correlations, which argued for octet expansion, not only in the case of *hypervalent* species, but also for purposes of invoking multiple bond character, via backbonding, in such apparently normal octet species as $\text{N}(\text{SiH}_3)_3$, S_4N_4 , and ClO_4 . [9, 10]. At about the same time, quantitative MO calculations on *hypervalent* species began to appear that tended to support the conclusion and to largely confirm the Rundle–Pimentel picture of the bonding in these compounds, which is largely accepted. Nowadays, the *hypervalent* chemists try to understand these compounds with the 3c–4e bond model. The following filling of the molecular orbitals, shown in figure 1, occurs in a *hypervalent* central atom. In this concept, the bonding σ orbital is first occupied with two electrons. The other two electrons are occupied with "n" in non-binding orbital. The anti-binding orbital " σ^* " remains empty. The HOMO orbital is the non-binding orbital and the LUMO orbital of the molecule is the anti-binding orbital. These orbitals belong to three atomic centers and are occupied by a total of 4 electrons. Hence three centers are called four electron bonds. Such compounds have very interesting properties, both chemically and physically.

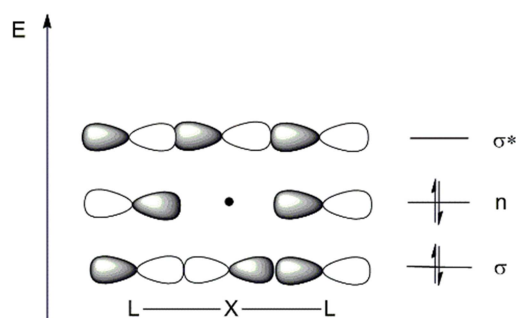


Figure 1. Occupation of the molecule orbitals of the 3c–4e bonds.

Such *hypervalent* compounds are named differently. N–X–L nomenclature, introduced collaboratively by the research groups of Martin, Arduengo, and Kochi in 1980 [11] is often used to classify *hypervalent* compounds of main group elements, where:

- 1) N represents the number of valence electrons
- 2) X is the chemical symbol of the central atom
- 3) L the number of ligands to the central atom

The synthesis strategy of *hypervalent* carbon compounds is completely different from the synthesis strategy of the other main *hypervalent* elements. Martin ligands are certainly one of famous ligands for the synthesis of *hypervalent* main group elements (Si, Sn, P, S, Br, I) (figure 2). [12]

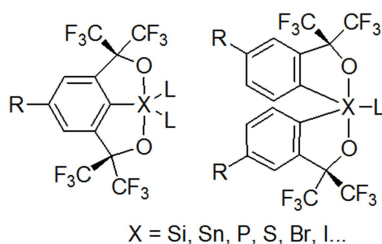


Figure 2. Martin Ligands for the production of *hypervalent* main group elements (Si, P, S, Br and I).

As has been described, the *hypervalent* compounds have special physical and chemical properties that can be used in many ways in the synthesis. As reagents and/or oxidizing agents, the *hypervalent* compounds enable unusual reactions to obtain the unusual products. [13–32] They are often used in the total synthesis of natural substances and/or in pharmaceutical products. With these, many new reactions can be made possible and thus interesting pharmaceuticals and/or chemical building blocks can be synthesized. Such *hypervalent* compounds are even used in material sciences and in the development of novel polymers. [33] It is therefore very important to study such compounds / reagents in detail, to stabilize them and thereby make them manageable in order to develop novel reactions / methods and to discover new applications in technology.

Ironically, although *hypervalent* compounds of the main groups except for carbon have received so much attention from inorganic chemists in recent years, the *hypervalent* carbon compounds have not received as much attention from organic chemists as it should have been since their discovery. Therefore, only a handful synthetic strategy and thus handful *hypervalent* carbon compounds are known in the literature. Therefore, no application of such *hypervalent* carbon compounds in chemical and/or pharmaceutical industries has taken place up to now. In this review, the *hypervalent* carbon compounds and their chemical and physical properties invented so far, are going to be discussed.

2. The Discussion Goes Still on: Is Carbon Atom Able to Form Any *hypervalent* Compounds

Here must be said that there are still strong divided opinions among scientists. Some scientists believe that carbon is not capable of forming *hypervalent* compounds. Since all carbon atoms always follows the octet rules. The compounds in which the central carbon atom has more than 4 bonds must therefore be called *hypercoordinated* compounds (or *multiple bonded* compounds). The term and concept of hypervalency of carbon compounds still fall under criticism. In 1984, in response to this general controversy, Schleyer et. al proposed the replacement of 'hypervalency' with use of the term '*hypercoordination*' because this term does not imply any mode of chemical bonding and the question could thus be avoided altogether. [1] According to Gillespie and Silvi is that it should be referred to *multiple bonded* carbon compounds as hypercoordinated carbon (or hypercarbon for short). [38] Olah et al. have added to this hypothesis that the previously known multi-bonded species should be referred to as 2c–2e, 2c–4e, 2c–6e, or 3c–2e bonds. They are of the opinion that all carbon compounds obey the octet rule. Hypervalent compounds, on the other hand, are those compounds that do not obey the octet rule and have more electrons in their valence shells. [34] With only four bond pairs, carbon atoms cannot bond simultaneously to more than four neighboring atoms using only two-center electron pair

bonds. If attached to more than four neighboring atoms, they must resort to some form of *multicenter σ bonding*, in which the bonding power of a pair of electrons is spread over more than two atoms. All carbon atoms with coordination numbers greater than four are therefore necessarily hypercoordinated. In CH_5^+ ion, for example, a 3c–2e bond can be calculated for the bonding between the carbon atom and the two hydrogen atoms furthest from the carbon atom, as represented in figure 3. [34]

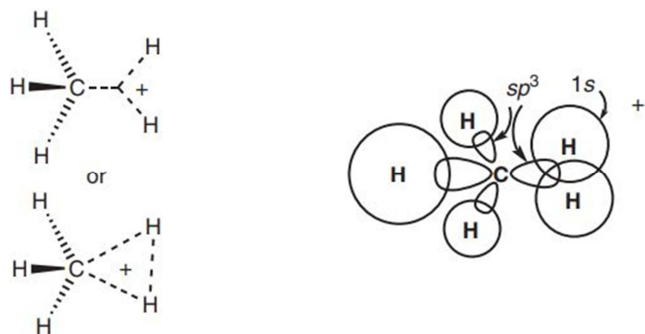


Figure 3. Description of hypercoordination of carbon using molecule orbital model. [34]

However, most of the scientists are convinced that *hypervalent* carbon compounds exist. The first '*hypervalent*' carbon compounds were synthesized and characterized in 1979 by Forbus et. al., this compounds were discussed about their *hypervalent* characters in the manuscript. [37] They established also the needed "conditions" to be called as *hypervalent* compounds. These conditions are discussed down. In summary, *hypervalent* properly refers to 3c–4e bonding. There are several examples of hypervalent carbons in this review that have 3c–4e bond character. [35, 36] A handful multiple bonded carbon compounds could be also synthesized and characterized using spectroscopy and X-ray analysis by Akiba et al. They believed that such synthesized compounds should be termed also as "*hypervalent compounds*". According to their interpretation, the synthesized compounds prove 3c–4e bond characters. The bond lengths of such synthesized compounds are longer than usual simple covalent bonds and shorter than the Van der Waals bonds; therefore they should be called as *hypervalent* compounds. Also such synthesized compounds possess similar chemical properties to the classical hypervalent compounds known in the literature. [35, 36]

In fact, both types of carbon compounds exist in the literature, both *hypervalent* carbon compounds, which resemble all the Forbes conditions of common *hypervalent* main group compounds, and '*hypercoordinated*' carbon compounds, which consist of *multiple* bonds and do not meet the conditions. In this review are going to be discussed both.

3. Pentacoordinated *hypervalent* Carbon

Historically, the first *hypervalent* compound was established relatively late in 1979. However, these

compounds were not defined as *hypervalent*. Forbus et. al. have shown by NMR studies that compounds 5-7 are pentacoordinated and the geometrical structure resembles the $\text{S}_{\text{N}}2$ transition state of the species. They explained the stabilization of the benzene ring by the definition of *bis-ipso aromaticity* 5-7. The compounds were presented in four synthesis steps. 1,8-dichloroanthracene-9,10-dione 1 was taken as the starting material for the synthesis of compounds 5-7. Evidence is presented for a bis-sulfonium structure containing a *hypervalent* trigonal bipyramidal (TBP) carbon atom. The thio-substituted 9,10-dione product was synthesized by Ullman coupling using *para*-alkylthiophenol copper 2 reagent. Then phenyl group was added at 9th position by Grignard reaction using phenyl magnesium bromide. Subsequently, the other carbonyl group reacted with 2,6-dimethoxy-4-alkylphenyllithium, whereby the compound 4 was formed. Compounds 5-7 were characterized by ^1H -NMR screening at -80°C , while in strong acids such as liquid sulfur dioxide, sulfuryl chlorofluoride or trifluoro sulfonic acid was synthesized. These compounds are sensitive to moisture and react to compound 8 in the presence of water. [37] They found that the chemical shift of ^1H -NMR of compounds 5 is different from ^1H -NMR of compound 8. The characteristic peaks of compound 5 in ^1H -NMR, $\delta = 8.6$ ppm, appear a triplet, while for compound 8 for the same hydrogen, a multiplet peak appears at $\delta = 7.56\text{--}7.45$ ppm (figure 4).

Although *hypervalent* iodine reagents were discovered a long time ago and (dichloroiodo)benzene [65] as the first member of this class was prepared by Willgerodt in 1886, the first manufactured, isolated and characterized *hypervalent* carbon compound was used very late, in 1979.

Structural features common to these compounds, which stabilize the TBP (trigonal bipyramidal) geometry sufficiently to enable direct observation, were used as the basis for what Forbus et al. described as followed: [37]

- Electronegative axial ligands (e.g. sulfonium-sulfur atoms),
- Multidentate ligands that bond to the equatorial positions of the trigonal bipyramidal structure (TBP),
- The multidentate ligands should be tridentate to stabilize TBP relative to tetrahedral carbon,
- The equatorial ligands should be relatively electropositive ligands that reduce the effective electronegativity of the central carbon atom,
- A strain-free electron acceptor that is stabilized by resonance or by the *I*-effect and is a bidentate equatorial chelating ligand that accepts electrons from the axial electron-rich three-center-four-electron bond and thereby stabilizes the entire complex.

Forbus et al. developed descriptions for the formation of stable *hypervalent* carbon compounds, which were later refined by various researchers and thereby various ligands were developed that enable the *hypervalent* main group elements (such as Martin ligands, see figure 2).

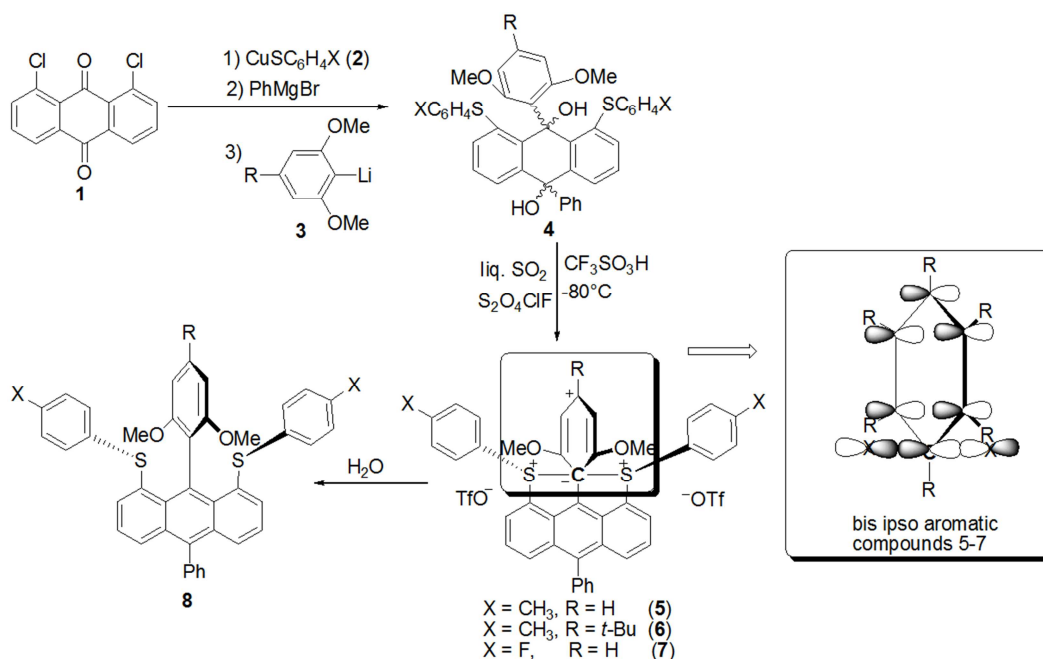


Figure 4. The first successful synthesis for 10-C-5 hypervalent carbon compounds.

However, the first theoretically calculated *hypervalent* organometallic compounds were the penta-, hexa-, heptacoordinated *hypervalent* lithium-carbon compounds. Schleyer et al. first theoretically calculated the dissociation energy, the geometric structure, and the bond length of the pentacoordinated carbon CLi_5 and hexacoordinated CLi_6 . [39-42] In the opinion of Schleyer, CLi_5 has a trigonal bipyramidal structure, which corresponds to a D_{3h} symmetry. The *hypervalent* electrons (ninth and tenth) fill totally symmetrical molecular orbitals, which have a_1 symmetry and lithium-lithium binding characters. A simple interpretation

assigns only an octet of electrons to the central atom, and any additional electrons to the surrounding lithium cage. Dissociation energy of hyperlithiated neutral molecules were calculated $\Delta G_{(\text{CLi}_5)} = +54.1$ kcal/mol basic setting 3-21G/3-21G level. It is calculated from the energy addition of CLi_4 and one Lithium atom. The dissociation energy of CLi_6 starting from $\text{CLi}_5 + \text{Li}$ was calculated as +14.2 kcal/mol. [39-42] After that, in 1998 the dissociation energy and the atomization energy were calculated by Zhizhong et al. with different basic settings PHF, PMP2, PMP4 and BLYP-DFT methods and different values were obtained. [43]

Table 1. Total energy and zero point energy of CLi_5 , CLi_6 and related species with the 6-31G* basis set (units: Hartrees). ^aNIF: number of imaginary frequencies. ^bE,Z,T = Total energy without zero point energy, zero point energy, energy with zero point energy scaled by 0.94. ^cThe energy of PUHF, PMP2, PMP4.

| | | HF//HF | MP2//MP2 | MP4 (SDTQ)//MP2 | BLYP//BLYP | NIF ^a |
|----------------------------|----------------|-------------------------|-------------|-------------------------|-------------|------------------|
| CLi_5 D_{3h} | E ^b | -75.053357 ^c | -75.2197550 | -75.249705 ^c | -75.6062184 | 0/0/*/0 |
| | Z | 0.008658 | 0.011041 | 0.01141 ^d | 0.009628 | |
| | T | -75.045218 | -75.209376 | -75.238980 | -75.597168 | |
| CLi_6 O_h | E | -82.4842183 | -82.7482033 | -82.7751740 | -83.158755 | 0/0/*/0 |
| | Z | 0.012591 | 0.011674 | 0.011674 ^d | 0.0121158 | |
| | T | -82.472383 | -82.737229 | -82.764200 | -83.147326 | |

In the dissociation energy to the tetrahedron and Li_2 , there was not such a large deviation compared to the experimentally determined value. The best calculation with regard to DFT-Basis-set was successful with 3-21G* and BLYP-basis-set function. For example, the dissociation energy of CLi_6 to CLi_4 and Li_2 were calculated theoretically 64.35 kcal/mol and 65.2 kcal/mol respectively, and were determined experimentally

65.8 ± 2.6 kcal/mol. However, when they calculated the atomization energy of these compounds, there was a big difference. The theoretically calculated value of the atomization energy of 1 molecule CLi_6 to 1 carbon atom and 6 Lithium atoms were determined to be 272.63 kcal/mol using "BLYP" function and the experimentally determined value was 365.7 kcal/mol (table 2). [44]

Table 2. Dissociation energy and atomization energy of CLi_5 , CLi_6 and related species (kcal/mol).

| | HF//HF | MP2//MP2 | MP4//MP2 | BLYP//BLYP | Experimental | 3-21G* |
|----------------------------------------------------------------------|--------|----------|----------|------------|--------------|-------------------|
| $\text{CLi}_6 (O_h) \rightarrow \text{CLi}_4 (T_d) + \text{Li}_2$ | 59.44 | 68.11 | 64.39 | 64.35 | 65.8±2.6 | 65.2 ^a |
| $\text{CLi}_6 (O_h) \rightarrow \text{CLi}_5 (T_d) + \text{Li}$ | -2.64 | 60.54 | 58.89 | 43.94 | | 14.2 ^a |
| $\text{CLi}_5 (D_{3h}) \rightarrow \text{CLi}_3 (T_d) + \text{Li}_2$ | 80.85 | 80.17 | 86.45 | 70.46 | | 61.6 ^a |

| | HF//HF | MP2//MP2 | MP4//MP2 | BLYP//BLYP | Experimental | 3-21G* |
|--------------------------------------------------------------------|--------------------|--------------------|--------------------|------------|--------------|-------------------|
| $\text{CLi}_5 (D_{3h}) \rightarrow \text{CLi}_4 (T_d) + \text{Li}$ | 64.21 ^b | 21.36 ^b | 24.88 ^b | 40.23 | | 54.1 ^a |
| $\text{CLi}_6 (O_h) \rightarrow \text{C} + 6\text{Li}$ | 127.57 | 261.06 | 267.03 | 272.63 | 365.7±8 | |
| $\text{CLi}_5 (D_{3h}) \rightarrow \text{C} + 5\text{Li}$ | 130.21 | 200.51 | 205.68 | 228.69 | | |

When the bond lengths were calculated in Angstroms, it was found that the bond lengths of the C-Li bonds are much shorter than a van der Waals radius (3.25 Å). Therefore, it was assumed that the compound is *hypervalent* and that the C-Li bond has 3c-4e bond character. [45]

Table 3. The optimized geometries of CLi_5 , CLi_6 and related species. Bond lengths are in angstroms, bond angles in degrees. [45]

| | | $r[\text{C-Li(a)}]$ | $r[\text{C-Li(e)}]$ | $r[\text{Li(a)-Li(e)}]$ | $r[\text{Li(a)-Li(e)}]$ | Li(a)-C-Li(a) | Li(a)-C-Li(a) |
|----------------------------|------|---------------------|---------------------|-------------------------|-------------------------|------------------------|------------------------|
| CLi_5 D_{3h} | HF | 2.070 | 2.043 | 2.908 | 3.538 | 180.0 | 120.0 |
| | MP2 | 2.004 | 1.959 | 2.802 | 3.393 | 180.0 | 120.0 |
| | BLYP | 1.999 | 1.967 | 2.804 | 3.406 | 180.0 | 120.0 |
| CLi_6 O_h | HF | 2.045 | 2.892 | 2.892 | 2.892 | 180.0 | 90.0 |
| | MP2 | 2.085 | 2.949 | 2.949 | 2.949 | 180.0 | 90.0 |
| | BLYP | 2.024 | 2.862 | 2.862 | 2.862 | 180.0 | 90.0 |

After that, Grimley et. al. published the evidence of CLi_6 , which was formed in gas phase over solid Li_2C_2 and was identified by Knudsen-Effusion mass spectrometry. [45] It was confirmed, that the dissociation reaction mentioned is significantly endothermic, indicating that carbon can expand its octet of electrons to form this relatively stable molecules (figure 5). [46]

CLi_n was detected by Mass Spectroscopy by Lievens et al. and calculated their structure by DFT, whereby they found and noticed in the manuscript, when the number of lithium surrounded to carbon atom is smaller than 8 ($n \leq 8$), the cluster should be named as '*hypervalent compounds*'. In case, $n=6$ an octahedral structure of CLi_6 was also calculated. By using of laser vaporization CLi_n cluster produced and

their ionization potential was measured by threshold photoionization spectroscopy (figure 6). [47]

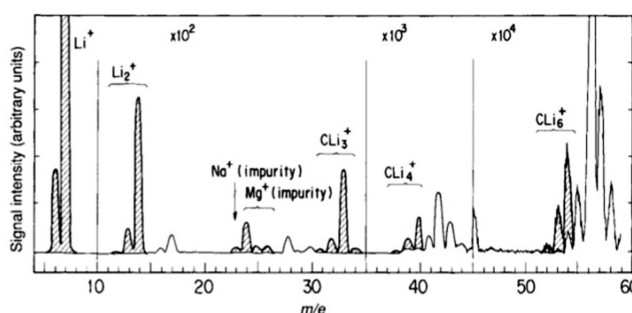


Figure 5. Knudsen-Effusion mass spectrometry of CLi_6 .

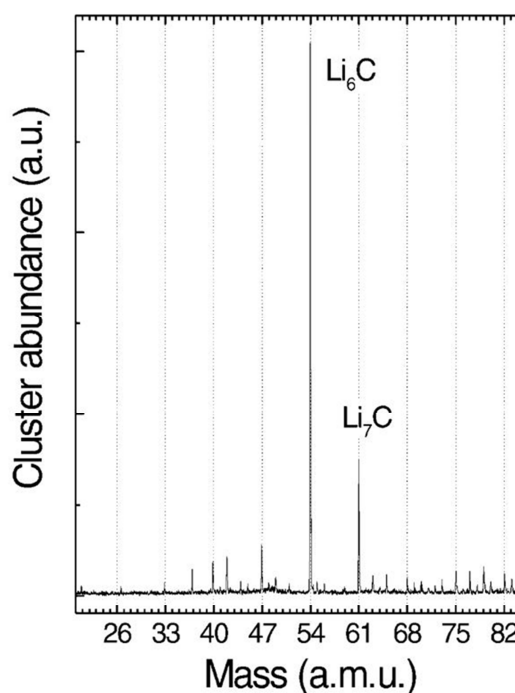
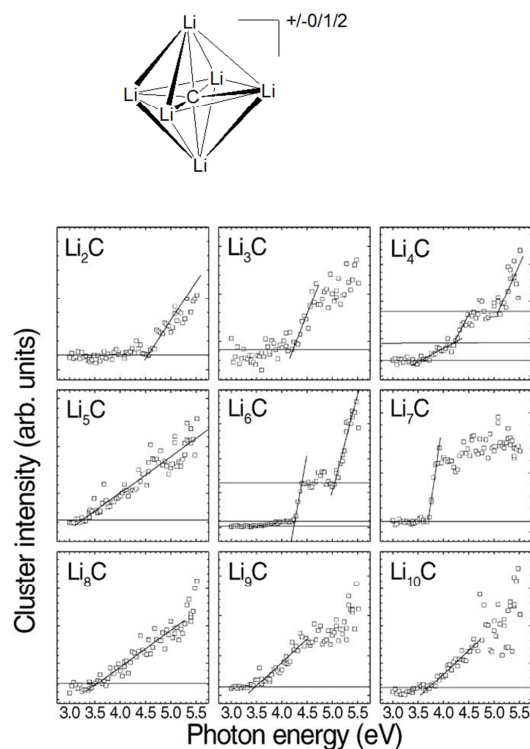


Figure 6. Time-of-flight mass spectrum and photoionization efficiency curves for Li_nC ($n = 2-10$). [47].

Generally, photoionization refers to a process in which highly energetic radiation with wavelengths of <100 nm was absorbed by removing electrons from atoms, resulting in ionized atoms. According to the graphics, shown in figure 6, Li_6C has two steep climbs at 4.25 eV. Another steep increase of the cluster yield begins at 5.05 eV. Also, a very small ionization probability is noticed below the threshold at 4.25 eV. Similar behavior can be detected for Li_4C . These might correspond to Franck–Condon limited ionization into an ionic structure very different from the ground state, but this is not predicted by theory. In addition, the mass spectrometric measurement in figure 6 confirmed the presence of CLi_6 and CLi_7 .

Another theoretical calculation was also made by Gutsev et. al. for the pentacoordinated *hypervalent* carbon halides (such as CF_5 , CF_4Cl , CCl_5 , CCl_4F , CBr_5). The geometrical and electronic structure of these neutral pentacoordinated carbon halogenides were studied and their singly charged negative ions have been studied within the framework of the DFT approach. According to the results of the calculations, all the neutrals considered possess the ground state configurations of the adduct CX_4Y (C_{3v}) type, which are weakly stable towards the decay channel $\text{CX}_4 + \text{Y}$, except for the CCl_4F adduct. [48]

Hyparenes are another type of compound classes, whose geometric structure and minimum energy were determined and calculated theoretically. On the basis of another DFT calculation it was shown that pentacoordinated carbon compounds can exist in planar form through multiple bonds

of carbon and boron called “hyparenes”. In their calculation they exchanged the units $-\text{C}_3\text{B}_3-$, $-\text{C}_2\text{B}_4-$ and $-\text{CB}_5-$ with $-(\text{CH})_3-$ units in both aromatic and non-aromatic systems and repeated the calculation. Hyparenes can have both aromatic and non-aromatic characters. The bond has part sigma and part pi character. These multicenter compounds were called in the manuscript as *hypercoordinated* carbon compound, although the authors justified that these compounds did not violate the octet rule (figures 7, 9 and 10). [49]

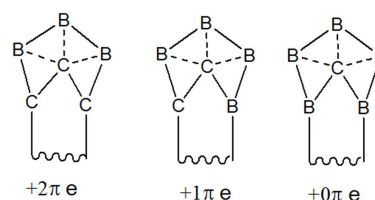


Figure 7. Theoretically calculated “Hyparenes” compounds with the central pentacoordinated planar carbon atoms.

Exner et. al. have calculated other classes of hyparene and studied their stability with planar hexacoordinate carbon atoms. They carried out the calculation for CB_6^{2-} , for CB_6H_2 isomers and for three C_3B_4 minima. These compounds are aromatic and have six π electrons. According to Exner et. al., these planar structures do not violate the octet rule and thus the authors have tried to explain this species with *hypercoordination* theory (figure 8). [50]

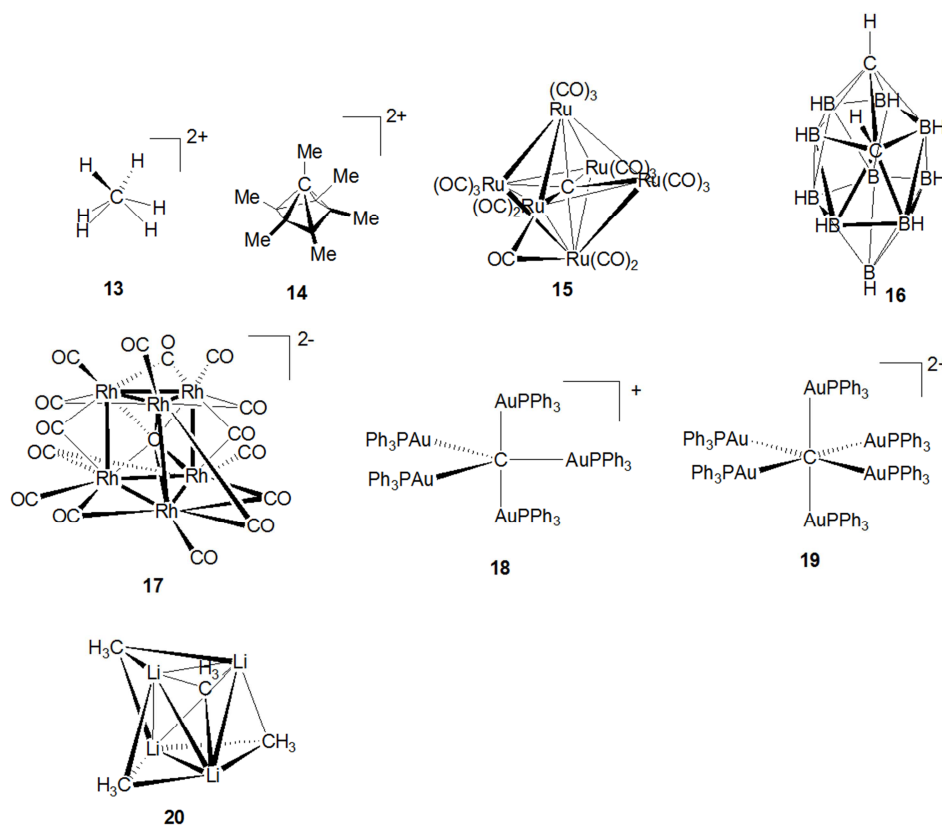


Figure 8. Synthetically prepared hypercoordinated carbon compounds with the central hexacoordinated octahedral carbon atom.

Hogeveen's dication 14 was prepared starting from material 20 with the displacement of the strong acid.

Compound 14 was presented as a *hypercoordinated* compound in the article (figure 9). [51]

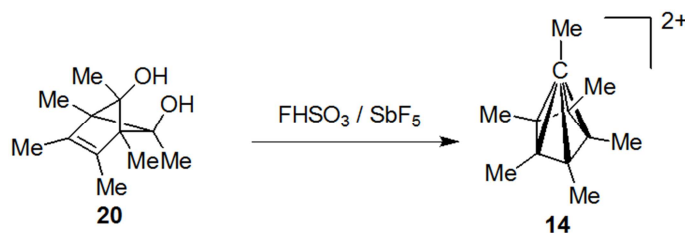


Figure 9. Synthesis of Hogeveen's dication.

The compound $\text{Ru}_6\text{C}(\text{CO})_{17}$ 15 was prepared by heating $\text{Ru}_3(\text{CO})_{12}$ in *n*-octane or *n*-nonane. [52, 53]. Whether the carbon compound is *hypervalent* or *hypercoordinated*, was not reported in the two articles.

Carboranes are boranes in which one or more boron atoms have been replaced by carbon atoms, for example the air-stable *para*- $\text{B}_{10}\text{C}_2\text{H}_{12}$ 16. [54] Such complexes, of which a very large number have already been characterized, are often good catalysts, for example for the hydrogenation reaction. Fluorinated carboranoic acid (formula $\text{H}(\text{CHB}_{11}\text{F}_{11})$) is the strongest superacid produced to date. It is even able to protonate *iso*-butane at room temperature. [55]

Dodecacarbonyltetrahodium $\text{Rh}_4(\text{CO})_{12}$ was added to a solution of sodium hydroxide in methanol under carbon monoxide. Thereafter, chloroform was added to the solution. After adding excess dry ice and removing the solvent, water was added. Structure 17 was obtained as crystalline. [56] The compound was prepared from $\text{CH}_2[\text{B}(\text{OCH}_3)_2]_2$ 21 and strong bases such as hexamethyl phosphine amide (HMPA) and Ph_3PAuCl 22 in the presence of cesium fluoride. In the reference, compound 18 is not referred to as *hypervalent* but as *hypercoordinated compound*. The Au-C is described as particularly electron-poor. Therefore, according to the authors of the manuscript, this compound is not *hypervalent* (figure 10). [57]

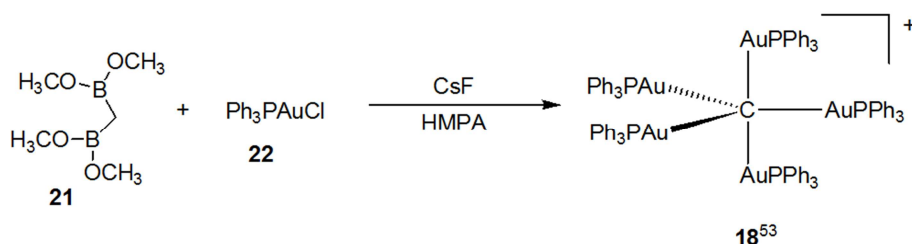


Figure 10. Synthesis of pentacoordinated gold carbon compound 18.

Additionally, compound 19 was synthesized starting from trimethylsilyldiazomethane ($\text{Me}_3\text{SiCHN}_2$) with tris[(triphenylphosphane)-gold(I)oxoniumtetrafluoroborate

$[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}^+\text{BF}_4^-$ in dichloromethane. Compound 19 was prepared in 64% yield. Like compound 18, compound 19 was not described as *hypervalent* but as *hypercoordinated* (figure 11). [58]

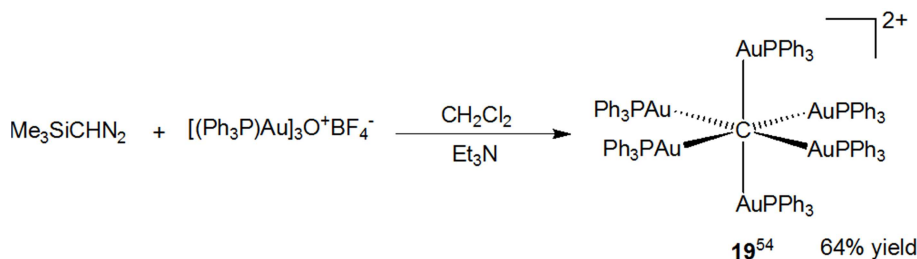


Figure 11. Synthesis of compound 19.

The existence of CH_5^+ was later confirmed by the manuscript of Asvany et. al. Infrared experiments with bare CH_5^+ have shown that the CH_5^+ consists of a CH_3 and H_2 units. They discovered a dynamic mechanism that happens between CH_3 tripod positions and the three-center bonded H_2 moiety, which eventually leads to full hydrogen scrambling. [59] However, it was not mentioned here whether the carbon has a *hypervalent* or a *hypercoordinated* character. However,

the experimental values obtained support the theory proposed (see figure 1 and figure 3). [59]

Galindo et al. have summarized a number of the structures that have been theoretically calculated up to now. The study includes the geometrical structures possessed by the central planar pentacoordinated carbon atom (ppC). The first theoretically calculated compound was CAI_5^+ , which has D_{5h} symmetry. This was followed by a number of compounds

that can be obtained by replacing heteroatoms. Complex ppC compounds have also been proposed, which can be metallocenes, 2D materials, and heteratom-based fullerenes. The theoretical calculations suggested a total of 104 possible structures (including compounds 19-59). The general design principles for planar tetracoordinated carbon (ptC)-centered candidate structures include delocalization of the central lone C $2p_z$ electron pair, which ensures an 18 valence electron

number and enables strong electron delocalization. This stabilizes the ptC structure. Galindo et. al. however, have not made any statements about the possible *hypervalent* carbon. They have declared the carbon atom should be *hypercoordinated*. However, none of these structures has been proven experimentally. The possible compounds with their possible structures are listed below (figure 12) [50]:

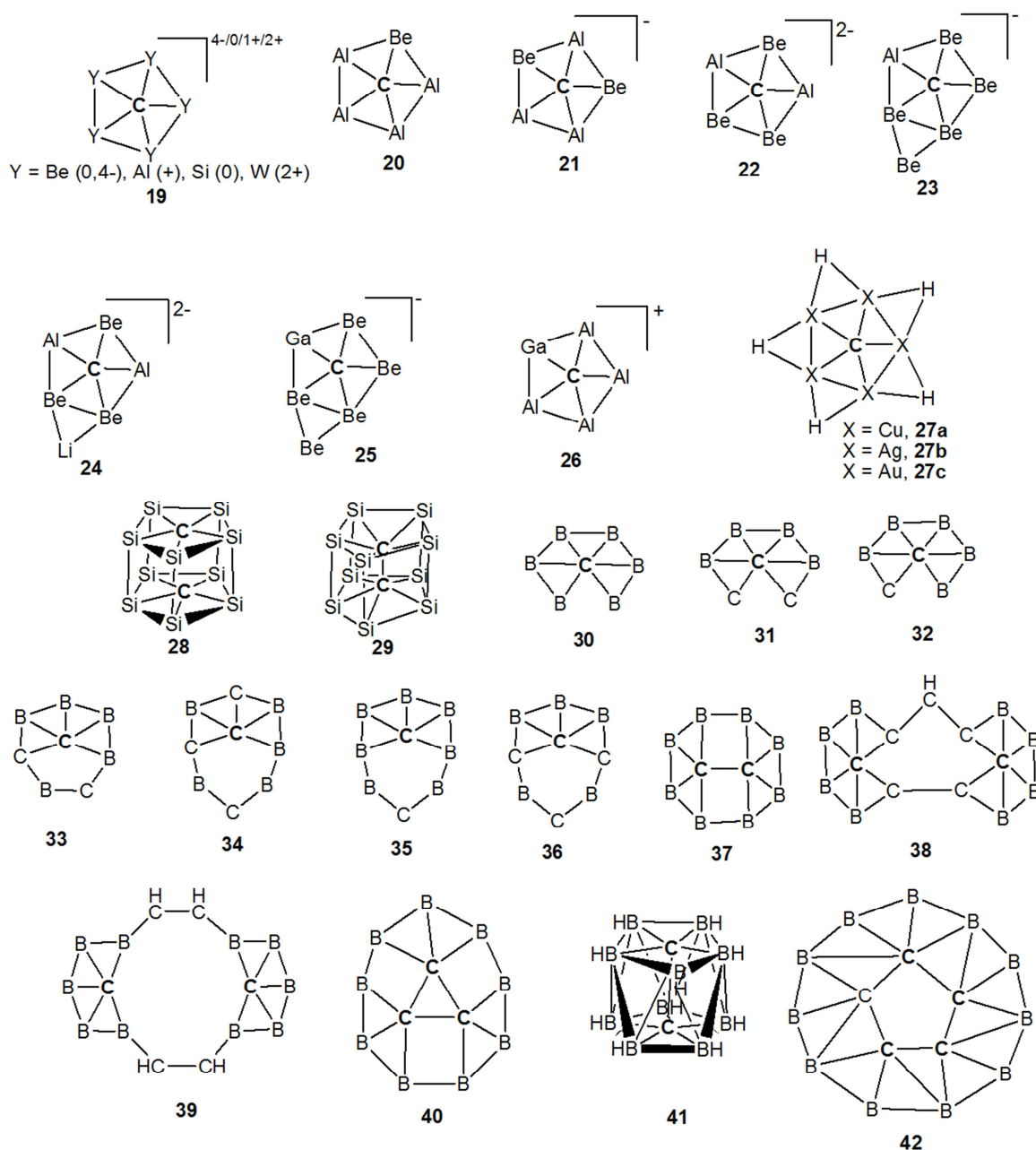


Figure 12. All theoretically calculated pentacoordinated planar carbon compounds with minimum energy.

The potential energy surfaces of a series of clusters with formula CBe_5Li_n ($n=1-5$) are systematically explored. The computations show that the lithium cations preserve the CBe_5^{4-} pentagon, such that the global minimum structure for these series of clusters has a planar pentacoordinate carbon (ppC). The systems are primarily connected by a network of

multicenter σ -bonds, in which C atom acts as σ -acceptor and this acceptance of charge is balanced by the donation of the $2p_z$ electrons to the π -cloud. The induced magnetic field analysis suggests that the clusters with formula CBe_5Li_n ($n=1-5$) are fully delocalized. The fact that these ppC-containing clusters are the lowest-energy forms on the

corresponding potential energy surfaces raises expectations that these species can be prepared experimentally in the gas phase (figure 13). [61]

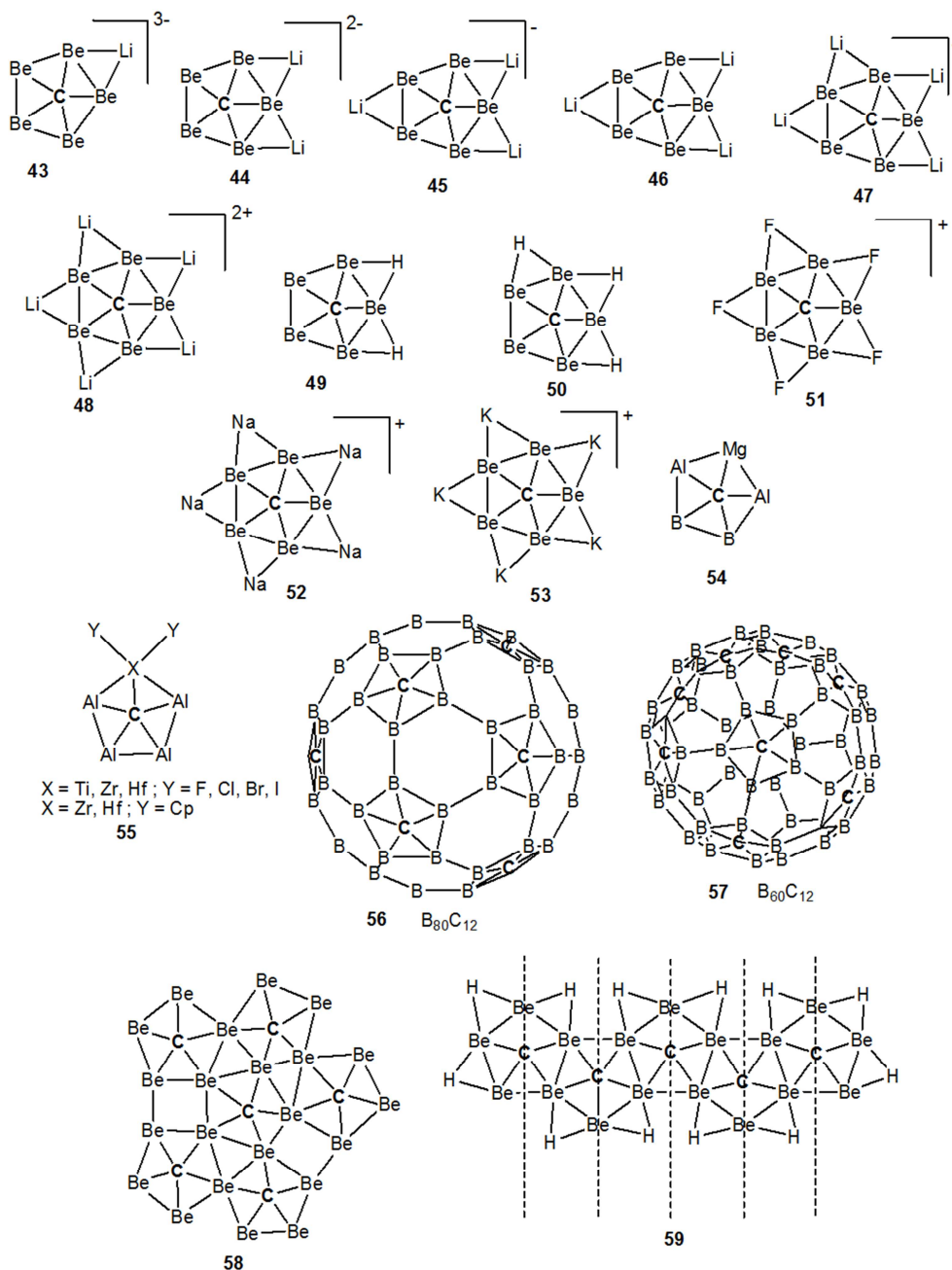


Figure 13. All theoretically calculated pentacoordinated planar carbon compounds with minimum energy.

Guo et. al. have computationally designed two ternary C–Be–Li clusters, C_{2v} CBe_4Li_4 and D_{4h} $CBe_4Li_4^{2-}$. They are perfectly planar, featuring planar pentacoordinate and tetracoordinate carbons (ppC and ptC), respectively. Both species show 2π and 6σ delocalization around the central carbon atom, suggesting that double π/σ aromaticity (rather than the 18-electron rule) governs such exotic ppC or ptC clusters. [62] Although the first proposed compound, the ligand of which consists of methyl groups, was $C(CH_3)^{5+}$, no theoretical calculation was carried out until 2014 as to whether it could be produced in laboratory conditions.

According to the DFT calculation by Schleyer et. al., the compound can possibly be made close to 0 K. [63-67]

Akiba et al. also synthesized a few *hypervalent* carbon compounds based on the synthesis strategy of Forbus et al. They were able to synthesize the *hypervalent* carbon compound 65, which was prepared starting from compound 1,8-dihydroxyanthracene-9,10-dione 60, which can be obtained commercially and then this compound was methylated using a strong methylation reagent (such as dimethyl sulfate). Thereafter, tin chloride was used to reduce to the corresponding alcohol (4,5-dimethoxyanthracen-10-ol

62). Compound 63 reacts further through the Heck reaction to form the corresponding ester 64. With trimethyloxonium tetrafluoroborate, a methoxy group attacks the carbonyl ester to produce the *hypervalent* carbon compound 65. Akiba et al.

have also succeeded in determining a crystal structure using X-ray structure analysis. $^1\text{H-NMR}$ (400 MHz) spectroscopy clearly shows the chemical shift of the hydrogen between compounds 64 and 65 (figure 14).

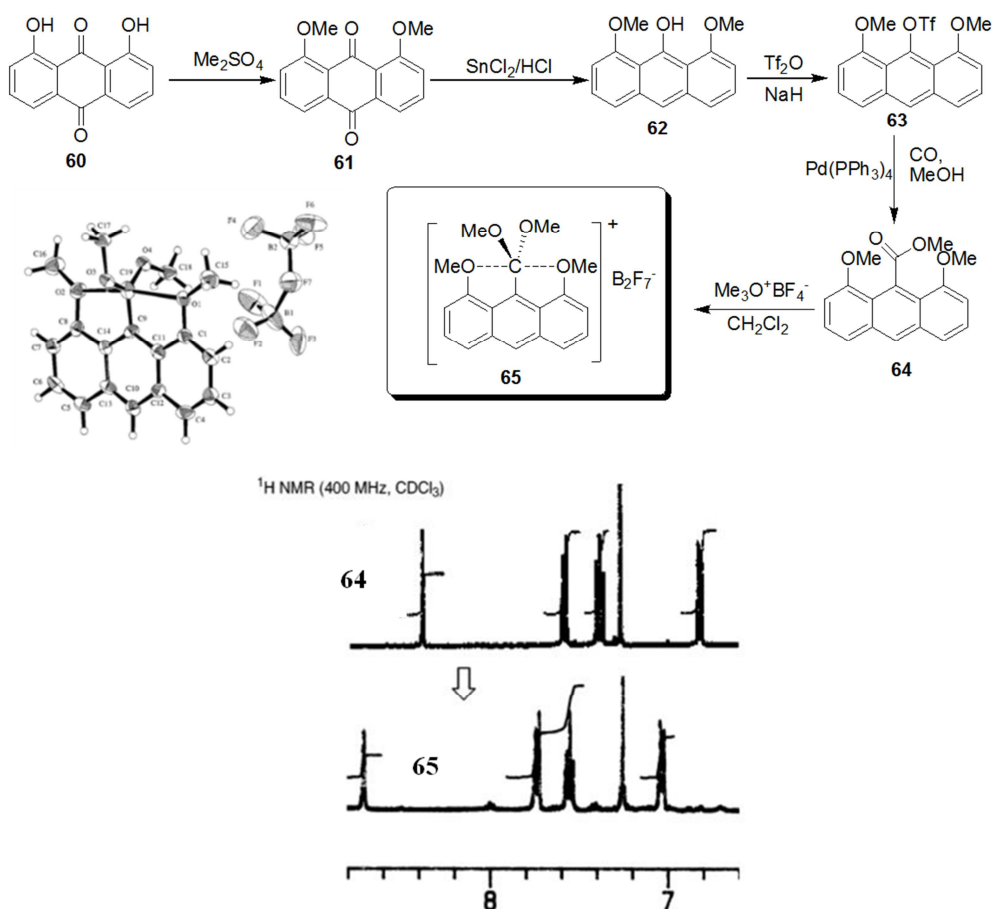
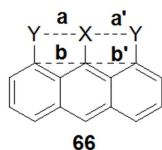


Figure 14. Synthesis of hypervalent carbon compound 65 and its $^1\text{H-NMR}$ spectrum compared to non-hypervalent carbon compound 64.

Table 4. Determination of bond length and the distance between two α -phenyl carbon atoms.



| Compounds | a | a' | b | b' |
|-------------------------------------------------|--------|--------|-------|-------|
| X = Y = Br | 3.2658 | 3.2738 | 2.564 | 2.567 |
| X = OTf, Y = OMe | 2.572 | 2.571 | 2.554 | 2.545 |
| X = CN, Y = OMe | 2.530 | 2.531 | 2.538 | 2.542 |
| X = C ⁺ (OMe) ₂ , Y = OMe | 2.45 | 2.43 | 2.49 | 2.52 |

The distances b-b' and bond distances a-a', shown in table 4, published using X-ray crystal structure analysis: Akiba et al. calculated the distance a-a' and b-b' using different ligands. A 3c-4e axial bond is created along a-a', therefore they considered it important to determine this distance theoretically. They assumed by using X = Y = Br that there is no bond along the a-a', because of bond length (more than 3.0 Å). They calculated using different groups, which contained a partial electropositive carbon that the distance a-

a' became shorter. The shortest distance was calculated for group C⁺(OMe)₂ (Table 4).

Akiba *et al.* synthesized a series of hypervalent carbon compounds with different sulfur ligands and studied the effect of sulfur ligands on the stability of hypervalent carbon compounds (figure 15). The hypervalent carbon compounds bearing different sulfur ligands were prepared from the substitution of 2-bromo-1,3-bis(bromomethyl)benzene 67 with sulfur nucleophiles. Compound 70 was prepared in good yield by the formation of lithium benzene derivatives and their addition to aryl aryl ketones. Then, with the addition of strong acid (e.g. hypochloric acid), compound 71 was prepared. This compound is stabilized by the exchange of axial sulfur ligands 71 and 73, which are in equilibrium. The transition state hypervalent carbon compound 72 and its existence was confirmed by the NMR study [68].

Various carbon compounds bearing a 1,8-disubstituted anthracene skeleton were synthesized and characterized by X-ray analysis (figure 16). They discovered two types of structures based on the kinds of substituents. The first one has the sp² carbon atom and the two weak axial interactions, which is symmetrical and a loose pentacoordinate structure.

The next one has the sp^3 central atom, which is an unsymmetrical tetracoordinate structure. The existence of *hypervalent interaction* has been proved on the basis of these atoms in molecules theory, experimental electron distribution analysis and a comparison among the structures of tight and loose pentacoordinate species. To prepare an anionic *hypervalent* pentacoordinate carbon compound, they synthesized a novel ligand, which is substituted with two deprotectable methoxymethyl groups as a trianion equivalent. The synthesis strategy was as followed: first, bromine of commercially available compound 1,8-dibromo-9-methoxyanthracene 75 was substituted at the 8th position with hydroxy group using reagent 74 to obtain the compound 76. Then this hydroxyl group was protected with a methoxymethylene group. The substitution of bromine with another hydroxyl group on the 1st position was the same as before, but here air oxygen was used instead of sulfoxides. The substitution of the methoxy group of the compound 78 with the bromine group took place with LDBB and 1,2-

dibromotetrafluoroethane. This was followed by the addition of anthracenyl anion, which was generated by *n*-BuLi, to the carbonyl carbon of hexafluoroacetone, the sp^3 hybridized carbon compound 80 being formed first. When working up this reaction, the reaction mixture is washed with HCl_{aq} offset. The MOM group was afterward removed and the hydroxy group was deprotected. Akiba et al. first tested the methyl group instead of the MOM group in order to protect the hydroxy group. However, they could not remove the methyl group after bromination, successfully. The *pentacoordinated hypervalent* compound 81, which has trigonal bipyramidal structure, was then finally synthesized using potassium hydride in diethyl ether by formation of hydrogen gas. The two trifluoro methyl substituents of compound 81 are strong σ -electron-withdrawing groups, which could stabilize the hypervalent axial bonds of trigonal bipyramidal structure of compound 81. The additional stability of the pentacoordinated *hypervalent* compound 81 gave the crown ether, such as 18 crown 6 (figure 16). [68]

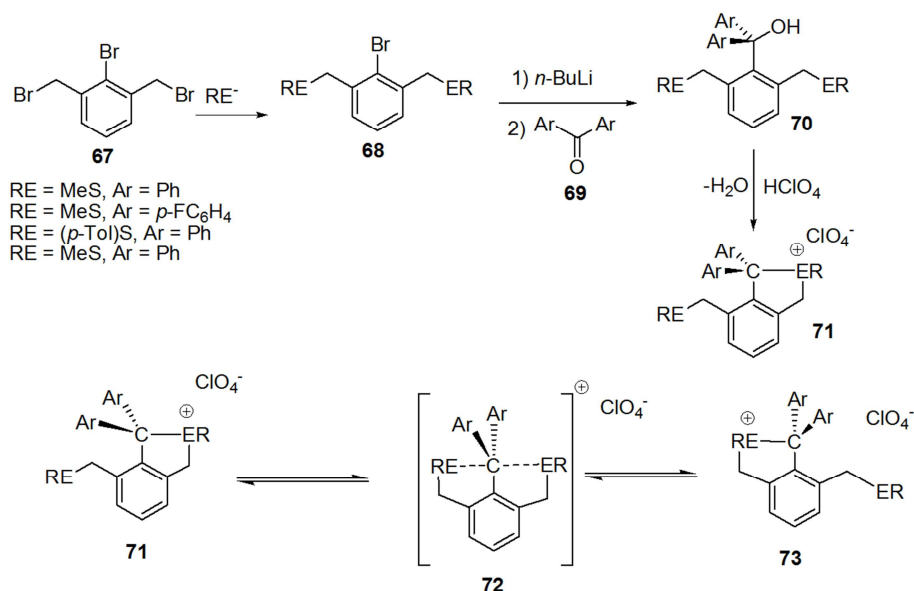


Figure 15. Synthesis of hypervalent carbon compounds.

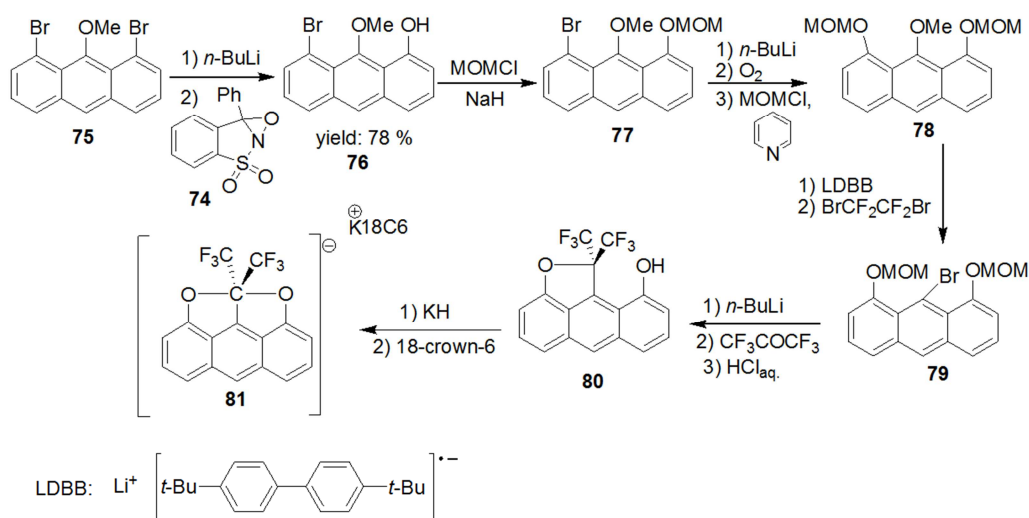


Figure 16. Synthesis of hypervalent carbon compound 81, starting from 1,8-dibromo-9-methoxyanthracene 75.

Other possible synthesis of pentacoordinated *hypervalent* compounds were synthesized by following strategy:

Akiba et al. synthesized and isolated the carbocations (86a and 86b) bearing a 2,6-bis(p-tolyloxymethyl)benzene as a flexible ligand. The synthesis strategy of 86a and 86b are shown in figure 14. They synthesized first compound 83 starting from commercially available compound 82 using NBS as source for bromine and BPO (benzoyl peroxide) as a radical starter. This reaction proceeds under radical reaction mechanism to substitute the methyl group with bromine. The visible light was used to form a radical using BPO. By the substitution of methylenebromine group using p-

methylphenol forms the compound 84. *In situ* was lithium-substituted compound 84 synthesized by addition of *n*-BuLi. Thereafter, carbonyl compound (*para*-substituted diphenyl ketone) added to the reaction mixture to form compound 85. By using strong acids, such as hydroperchlorate or tetrafluoro hydroboronic acid could be obtained compounds 86a-b. The pentacoordinated *hypervalent* compounds 86a-b were somewhat unstable at room temperature in solution but the dark green color persisted up to 0°C for several hours. They were also successful to obtain the X-ray crystal structure, which is shown in figure 11 as ORTEP drawing of a single molecule of 86b-ClO₄ (figure 17). [69]

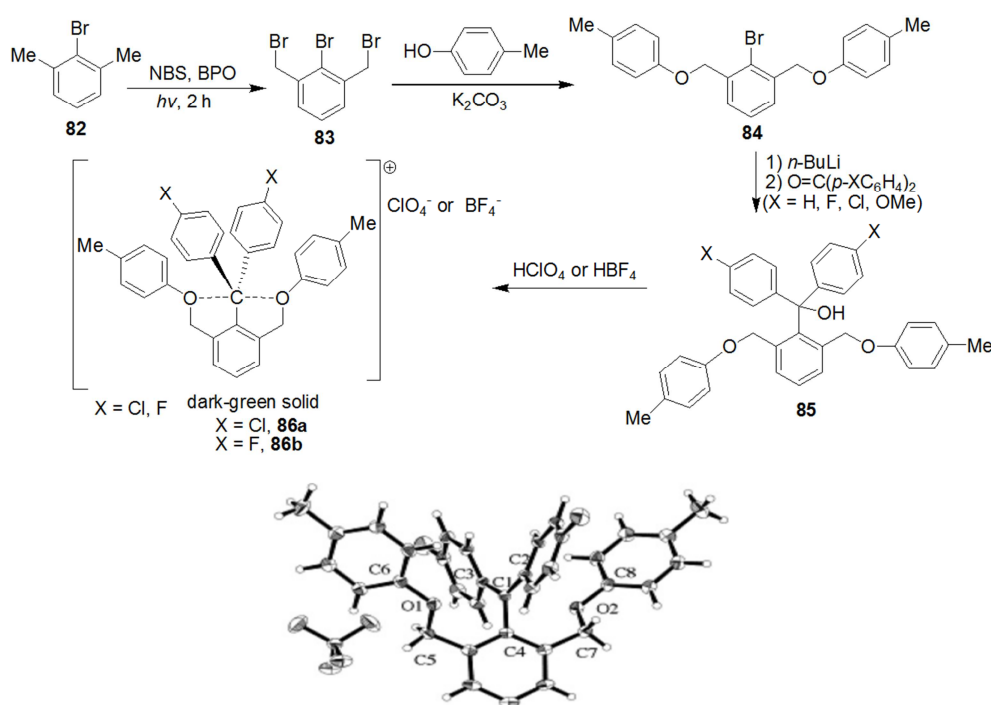
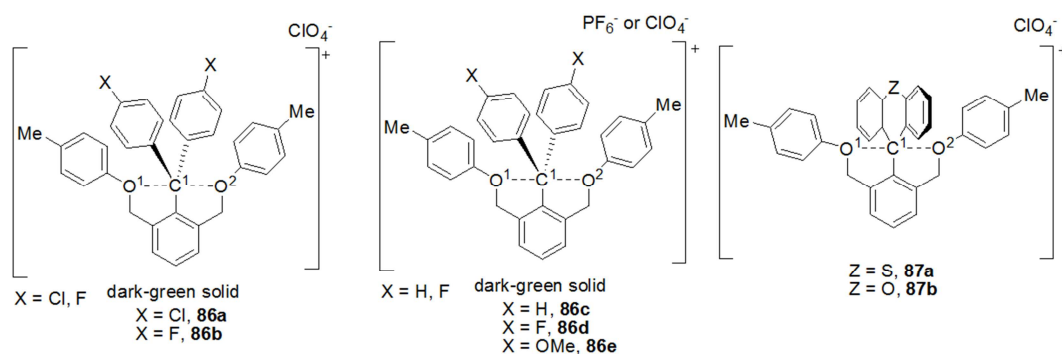


Figure 17. Synthesis of a new tridentate ligand precursor, 1-bromo-2,6-bis(p-tolyloxymethyl)benzene, and its application to the synthesis of hypervalent carbon compounds.

In Table 5, it is clearly observed that in the case of electron-withdrawing substituents (such as X = Cl, F), the bond length was determined shorter and more stable by using X-ray analysis. Therefore, it has more *hypervalent* character compared to the substituents that are electron-

donating (such as X = OMe, Z = S or Z = O) (table 5). For example, it has little interaction like a normal Van der Waals interaction because the bond length was obtained 3.026 Å, when Z = O.

Table 5. Bond length in angstrom and bond angle of 86a-e and 87a-b obtained by X-ray analysis.



| bond length (Å) | X = Cl 86a | X = F 86b | X = H 86c | X = F 86d | X = OMe 86e | Z = S 87a | Z = O 87b |
|--------------------------------|---------------|--------------|--------------|--------------|----------------|----------------|--------------|
| C ¹ -O ¹ | 2.671 | 2.690 | 2.705 | 2.718 | 2.77 | 2.776 2.617 | 3.026 |
| C ¹ -O ² | 2.682 | 2.690 | 2.705 | 2.718 | 2.78 | 2.855 2.827 | 4.23 |
| bond angle (°) | 161.9 | 162.3 | 158.9 | 160.4 | 159.1 | 155.7 165.0 | - |

The existence of *hypervalent* carbon of the compound 86b at -45 °C was also proven experimentally by ¹³C NMR spectroscopy (figure 18). ¹³C-NMR clearly shows that doublets (132 ppm and 141 ppm) are formed at -45°C, while

at room temperature at 132 ppm and at 141 ppm a singlet for equatorial carbons was observed. This doublet comes about by coupling with the central carbon atom, which at low temp. begins to make fivefold bond.

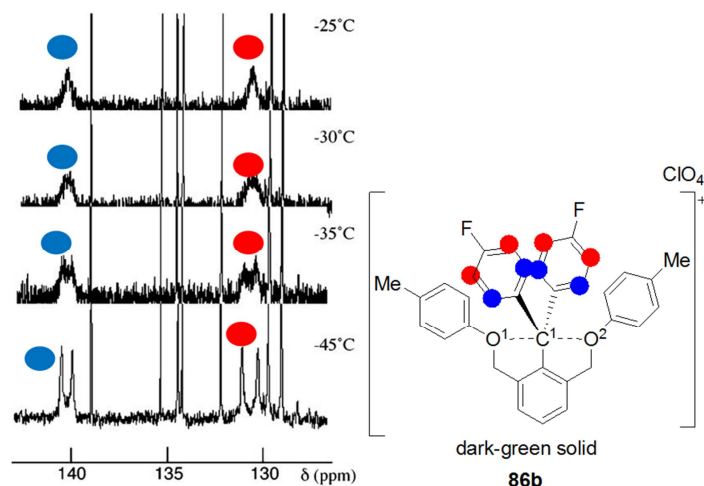
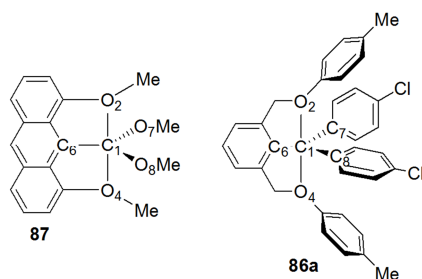


Figure 18. Variable-temperature ¹³C NMR (CD₂Cl₂) spectra of 86b.

After that geometry optimizations of compounds 86a and 87 were carried out by the DFT calculations with the B3LYP hybrid functional by using Gaussian 03 program [70], the Bond-EDA was calculated by Gamess program package [71].

Table 6. The calculations of bond length in Angstrom, bond angle and dihedral angle of compounds 86a and 87 compared to experimental value.



| 87 | 86a | | | |
|-------------------------------------------------------------|---------------|--------------|----------------|--------------|
| | Calculated | Experimental | Calculated | Experimental |
| <i>Bond length (Å)</i> | | | | |
| C ₁ -C ₆ | 1.489 (+0.01) | 1.48 | 1.489 (+0.006) | 1.483 |
| C ₁ -C ₇ | | | 1.443 (+0.010) | 1.433 |
| C ₁ -C ₈ | | | 1.443 (+0.009) | 1.434 |
| C ₁ -O ₇ | 1.285 | 1.26 | | |
| <i>Angle (°)</i> | | | | |
| C ₇ C ₁ C ₈ | | | 122.3 (-1.1) | 123.4 |
| O ₇ C ₁ O ₈ | 117.2 (-0.7) | 117.9 | | |
| O ₂ C ₁ C ₈ | | | 97.1 (+0.9) | 96.2 |
| O ₂ C ₁ O ₈ | 89.0 (+0.2) | 88.8 | | |
| O ₂ C ₁ O ₄ | 168.0 (-0.7) | 168.7 | 160.8 (-1.1) | 161.9 |
| <i>Dihedral angle (°)</i> | | | | |
| O ₂ C ₁ C ₆ C ₈ | | | 92.9 | |
| O ₂ C ₁ C ₆ C ₈ | 85.7 | | | |
| O ₂ C ₆ C ₁ O ₄ | 188.7 | | 180.0 | |

Here, in table 6, it can also be clearly observed that the calculated bond lengths are almost identical to the experimentally determined bond lengths (see tables 5 and 6). There is a 7° difference in the bond angle of $O_2-C_1-O_4$ between the calculated and experimentally determined value. With the dihedral angle of $O_2-C_6C_1-O_4$ there is an 8° difference between the experimentally measured and theoretically calculated value (table 6).

Table 7. Bond energy of 86a, 87, 111a-113a and 111b-113b.

| | 87 | 86a | 111a-113a | 111b-113b |
|--------------------------------|--------|--------|-----------|-----------|
| C ₁ -O ₂ | -24.8 | -11.5 | -18.1 | -26.9 |
| C ₁ -O ₃ | | | -18.1 | -26.9 |
| C ₁ -O ₄ | -24.8 | -11.4 | -17.7 | -26.9 |
| C ₁ -O ₅ | | | -17.7 | -26.9 |
| C ₁ -C ₆ | -129.2 | -136.0 | -200.2 | -165.2 |
| C ₁ -C ₇ | | | -200.2 | -165.3 |

Table 7 shows the bond energy of hexacoordinated carbon

compounds 111-113 and pentacoordinated hypervalent carbon compounds 86a, 87 estimated by the Bond-EDA method. The C-C bond energy of ethane (148.4 kcal/mol), propane (147.7 kcal/mol), ethylene (212.2 kcal/mol) and allene (244.5 kcal/mol) are calculated to compare with the corresponding molecules.

C₁-C₆, C₁-C₇ and C₁-C₈ are unique in their bond type because they are longer than the CC single bond distances (e.g. 1.53 Å for ethane) and shorter than the CC double bond distances (e.g. 1.33 Å for ethylene). That is, these bond lengths are in between. The bond angles are for C₇-C₁-C₈: 122.3° and for O₇-C₁-O₈: 117.2° are almost like the angles of the olefinic bonds: 120°. The bonds in the equatorial direction are created by the sp²-hybridized orbitals. The *p*-orbital forms the axial directions. That means the three-center-four-electron (3c-4e bond) bond is formed with the help of the axially directed *p*-orbital.

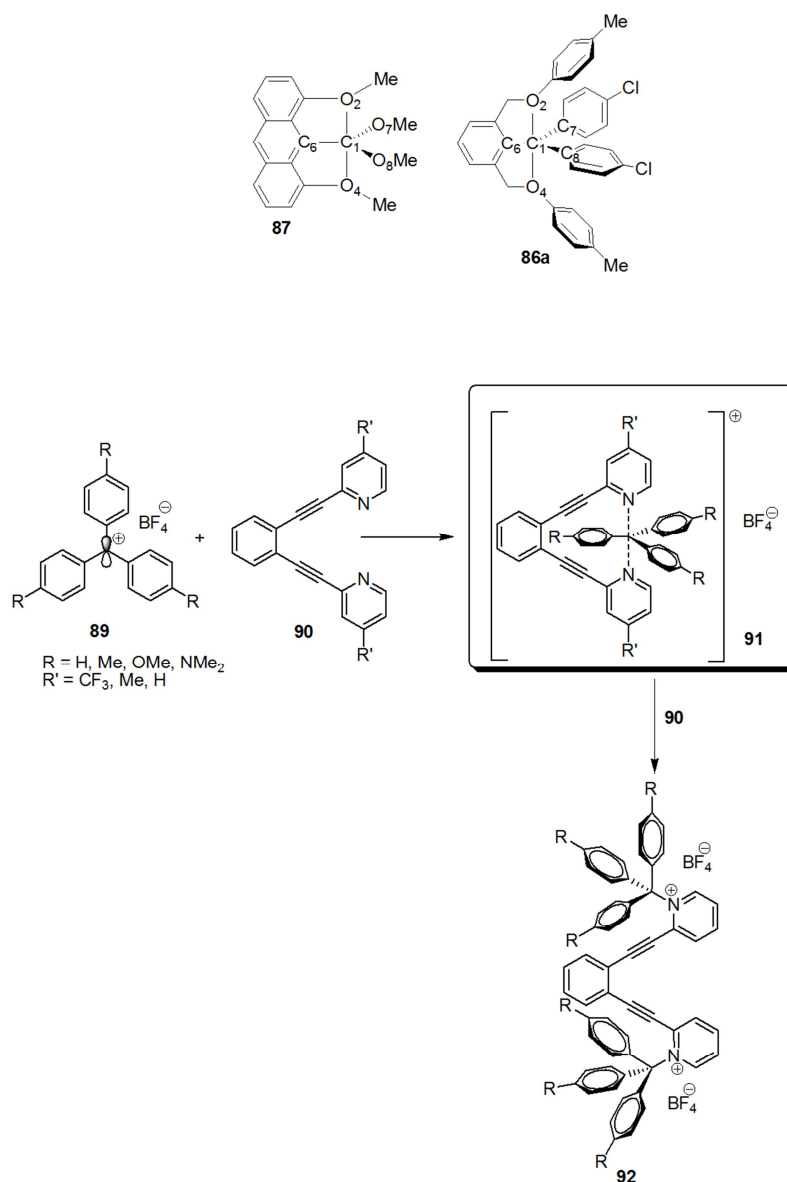


Figure 19. Titration of compound 89 using compound 90 to form hypervalent 10-C-5 carbon compound 91.

Complex 91 was synthesized for the first time by Karim et al., which $[N-C-N]^+$ bond has 3c-4e character and is *hypervalent* compound. The $[N-C-N]^+$ bond is a weak interaction and has similarities to hydrogen-halogen bond. Karim et al. has synthesized the pentacoordinated *hypervalent* compound 91 by the following strategy; they synthesized first the compound 89, which consist a carbenium ion, whose cation resonance stabilized by aromatic rings. By addition of compound 90 that has a bidentate lewis base character, the pentacoordinated *hypervalent* compound 91 was characterized by NMR-spectroscopy, titration-calorimetry, which could not be isolated and has a short half-life (figures 17-21). According to the authors, the studied interaction of axial bond by far the strongest *hypervalent* $[N-C-N]^+$ bond, which has been reported yet. [72, 73]. When the bidentate ligands were selected, a relatively stable complex 91 was detected. In the case of the monodentate lewis bases such as pyridine, a compound is detected that has a tetrahedron structure (figure 17). As expected, the theory developed by Forbus et al. also here observed regarding to experimentally: *to form a stable hypervalent compound it was needed to decrease reductions in the Lewis basicity of bidentate ligands or to decrease Lewis acidity of the carbennium ion, which here was observed.* [74]

Karim et. al. have been able to establish a compound that includes a linear (3c-4e) three center four-electron $[N-C-N]^+$ bond (tetrel bond). This bond is a bilateral overlap of the free p-orbital of the carbenium ion with *non-bonding* orbitals of two lewis bases. This bond is identical in terms of its geometry and energy to $[N-I-N]^+$ halogen bond [75] and amounts to ~ 50 kJ / mol change in free energy, which was

determined with isothermal titration calorimetry. [compound 89]/[compound 90] (mol/mol).

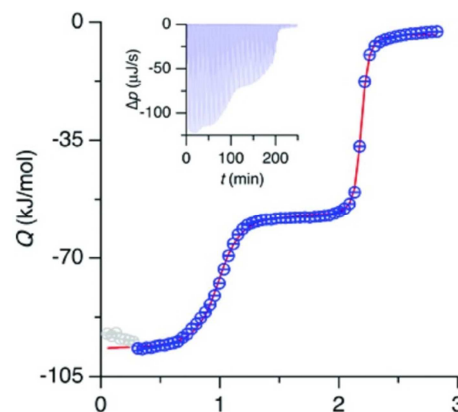


Figure 20. Titration of compound 89 using compound 90 to form *hypervalent* 10-C-5 carbon compound 91.

It is a symmetric three-center four electron bond, which was proven by a single set of NMR signals in low temperature. The electron density of this bond was modulated with different substitutions (figure 19). However, by computation on the DFT level, they could not obtain the symmetric $[N-C-N]^+$ geometry. The formation of *hypervalent* carbon compounds can be detected with 2D-NMR. For example, *hypervalent* carbon compound 91 (3c) with the characteristic two red spots, proving that the nitrogen atoms of the pyridine groups are already attached to both sides of the carbocation. If one of the nitrogen atoms (5c) is not bound, then there are three distinctive green spots to detect (figure 21).

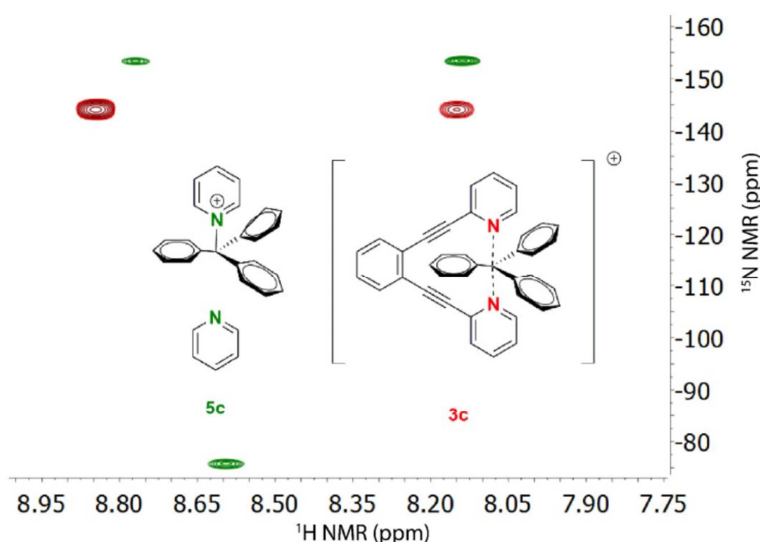


Figure 21. 2D-NMR spectra of *hypervalent* carbon.

Another interesting study of *hypervalent* carbon clusters was carried out by Veljkovic et al.. A number of *hypervalent* clusters were produced. They transported the carbon clusters $C_{28}H_4$ generated in the plasma by the Ar or H_2 gas stream

downstream through a vacuum chamber to the ion source of the mass spectrometer. Small binary carbon cluster $C_{28}H_4$ (hydrogenated fullerene) has been detected. The empty fullerene were determined as tetravalent and strongly binds

four hydrogen atoms, which significantly weakens two different sets of bonds and leads to an open-shell electronic structure.

The mass spectrometry studied in detail shows the presence of $C_{28}H_4^+$ (figure 22). By surface ionization the presence of $C_{28}H_4^+$ ion can also be detected.

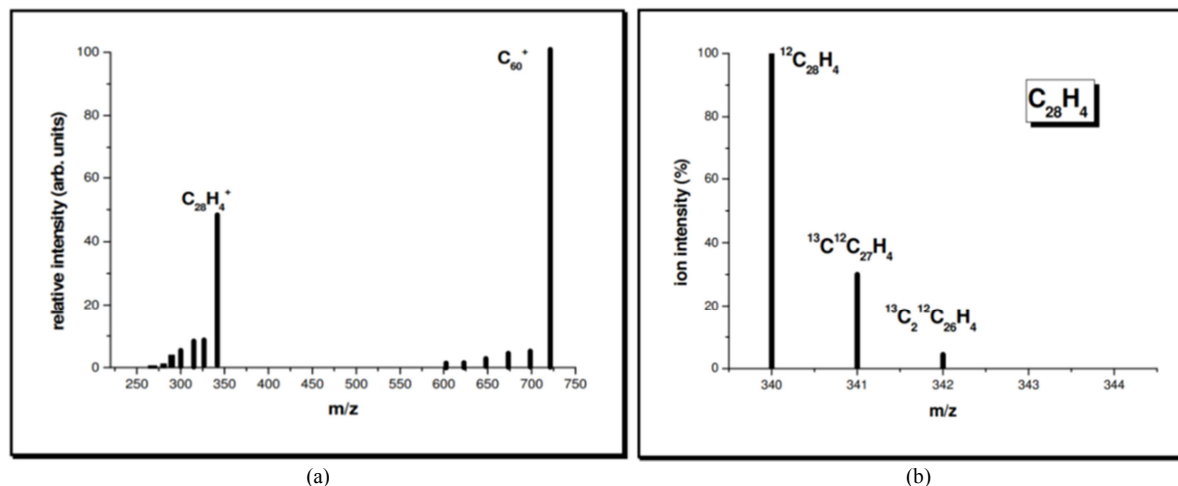


Figure 22. (a) Surface ionization spectrum of $C_{28}H_4$ (surface ionization). (b) A mass spectrum of carbon clusters (electron impact).

A very interesting DFT calculation was made by Pierrefixe et al. performed via the *hypervalent* noble gas-carbon compounds. Pierrefixe et al. found out, that carbon atom is in equilibrium with *hypervalent* and *non-hypervalent* states. In addition, they found, strangely enough, that the formation of the *hypervalent* carbon compound with noble gases does not bring any potential energy generation in comparison to the

non-hypervalent state (figure 23). The noble gas/methyl cation complexes $[Ng-CH_3-Ng]^+$ ($Ng = He, Ne$) has a perfect D_{3h} -symmetric structure with a stable *hypervalent* carbon atom with two equivalent C-Ng bonds. Finally, they proposed to classify the nature of five-coordinate carbon species in terms of a spectrum between the *non-hypervalent* carbon and the *hypervalent* carbon. [75]

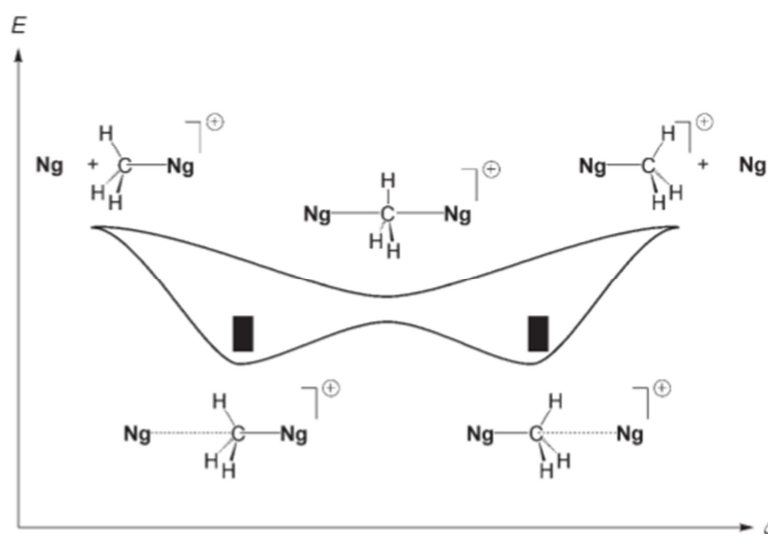


Figure 23. Single-well (top line: $Ng = He, Ne$) and double-well (bottom line: $Ng = Ar-Rn$) potential energy surface along the S_N2 reaction coordinate z of $Ng+CH_3Ng^+$.

Pierrefixe et. al. performed a number of DFT calculations using ZORA-OLYP / QZ4P. They calculated the complex $[X-CR_3-X]$, where is $R = H, CN$ and $X = F, Cl, Br, I, At$, whereby they calculated additionally the kinetic constant of the folding barriers from structure A to structure B ($k^{umbrella}$, figure 22). If the energy required to flip from structure A to structure B is zero, the compound have been designated as *hypervalent compound*. In this case, the structures: $[Br-C(CN)_3-Br]^+$, $[I-C(CN)_3-I]^+$, $[At-C(CN)_3-At]^+$ were

considered *hypervalent* carbon compounds, and all others referred to as *non-hypervalent* compounds.

In summary, the higher the electronegativity of the axial atoms, the higher the potential energy of the compound that is required to reach the *hypervalent* S_N2 barrier. In addition, as Forbus et al. have previously postulated, one needs equatorial ligands that stabilize electrons through the mesomerism effect and have a slightly electron-withdrawing effect (figure 24). [76]

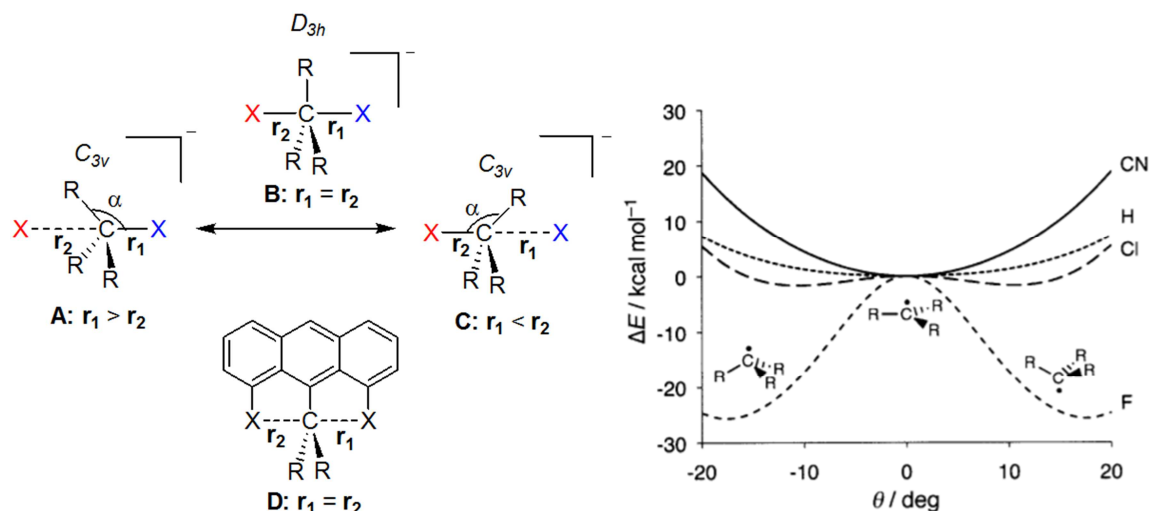


Figure 24. Graphic: Relative energy, ΔE , of CR_3 as a function of the distortion angle θ ($\theta = \alpha - 90^\circ$, see structure A and C for $R = F, Cl, H$, and CN , computed at ZORA-OLYP/TZ2P).

Table 8. [a] Computed at ZORA-OLYP/TZ2P. [b] Force constants of $k^{umbrella}$ mode and heterolytic $C-X^{ax}$ interaction energy, ΔE_{int} , between the corresponding molecular fragments frozen to the geometry they adopt in the overall D_{3h} -symmetric species. [c] Difference in axial bond distances in equilibrium structure. [d] Complexation energy of $X^- + CR_3X$. [e] Central S_N2 energy barrier. [f] Central S_N2 energy barrier with zero-point vibrational energy correction.

| $[X-CR_3-X]R$ | X | Rigidity of CR_3 ^[b] $k^{umbrella}$ [a.u.] | $C-X$ ^[a] [kcal mol ⁻¹] | I_1-r_2I [Å] ^[c] | Complex [kcal mol ⁻¹] ^[d] | Barrier [kcal mol ⁻¹] ^[e] | Barrier+ΔZPE [kcal mol ⁻¹] ^[f] | C Valency |
|---------------|----|------------------------------------------------------------|---------------------------------------------------|----------------------------------|-----------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------|-----------------|
| H | F | -0.0906 | -45 | 1.25 | -15.7 | 8.03 | 7.71 | non-hypervalent |
| H | Cl | -0.0717 | -31.8 | 1.55 | -9.0 | 8.77 | 8.23 | non-hypervalent |
| H | Br | -0.0571 | -28.7 | 1.55 | -8.0 | 6.30 | 5.78 | non-hypervalent |
| H | I | -0.0501 | -25.4 | 1.53 | -7.3 | 5.34 | 4.82 | non-hypervalent |
| H | At | -0.0437 | -23.7 | 1.44 | -6.6 | 3.90 | 3.40 | non-hypervalent |
| CN | F | -0.0537 | -83.5 | 0.69 | -53.8 | 4.26 | 3.83 | non-hypervalent |
| CN | Cl | -0.0197 | -53.3 | 0.75 | -25.5 | 1.00 | 0.76 | non-hypervalent |
| CN | Br | 0.0047 | -47.9 | 0.44 | -22.8 | 0.04 | 0.00 | hypervalent |
| CN | I | 0.0024 | -43.1 | 0.00 | -21.0 | 0.00 | 0.00 | hypervalent |
| CN | At | 0.0026 | -41.9 | 0.00 | -21.2 | 0.00 | 0.00 | hypervalent |

Another DFT (B3LYP, M06-2X and MP2) methods were applied for the molecules, to the design of a wide series of the potentially 10-C-5 neutral compounds based on 6-azabicyclotetradecanes: $XC^1-(YC_6H_4CH_2)_3N$ 93-95, $XC^1[Y-(t-BuC_6H_3)CH_2]_3N$ 96-98 and carbatranophanes ($X=Me, F, Cl$; $Y=O, NH, CH_2$; $Z=O, CH_2, (CH_2)_2, (CH_2)_3$) 99-110, shown in figure 23. Carbatranophanes 93-110 were characterized by a steric compression of their axial 3c-4e $XC^1 \leftarrow N$ fragment with respect to that in the parent molecules. The stabilization of *hypervalent* carbon depends on (figure 24):

The magnitude of the revealed influence the valence

surrounding of the central carbon atom C^1 ,

The size and the nature of the side chains (Z) that link the “ p -electron cap” with a tetradecane backbone.

This circumstance allowed obtaining 10-C-5 structures with the configuration of the bonds around the C^1 atom, which corresponds to practically an ideal trigonal bipyramid. In these compounds, the values of the covalence ratio $C^1 \leftarrow N$ of approximately 0.6 for the coordination $C^1 \leftarrow N$ contacts with a covalent contribution (atoms in molecules (AIM) and natural bond orbital (NBO)) are record in magnitude (figure 25).

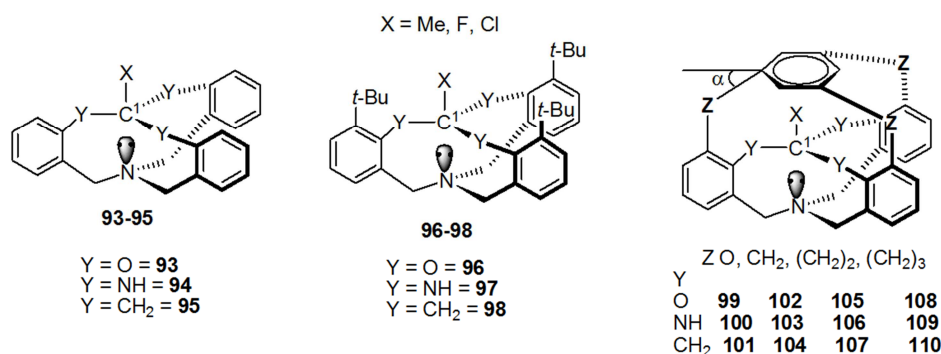


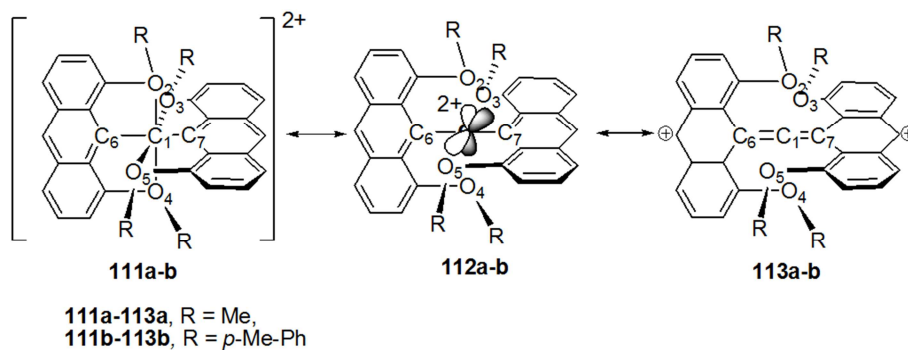
Figure 25. DFT calculation of Carbatranophanes 93-110.

Hexacoordinated *hypervalent* carbon

The first DFT calculations of compounds 111a-113a and 111b-113b were carried out by Kikuchi et. al. and showed that the hexacoordinated *hypervalent* carbon has a geometric

octahedron structure. 2,6-bis(methylphenyloxymethyl)phenyl groups as basic structure bearing a carbon atom have three-center four-electron bonds and Kohn-Sham orbital characters.

Table 9. DFT calculation of bond length of compounds 111a-113a and 111b-113b.



| Bond length (Å) | 111a-113a | 111b-113b |
|-------------------------------------------------------------|-----------|-----------|
| C ₁ -C ₆ | 1.345 | 1.369 |
| C ₁ -C ₇ | 1.345 | 1.369 |
| C ₁ -O ₃ | 2.579 | 2.484 |
| C ₁ -O ₄ | 2.575 | 2.484 |
| C ₁ -O ₅ | 2.575 | 2.484 |
| Angle (°) | | |
| O ₂ C ₁ O ₅ | 93.1 | 90.1 |
| C ₆ C ₁ C ₇ | 179.8 | 180.0 |
| O ₂ C ₁ O ₄ | 173.8 | 174.7 |
| O ₃ C ₁ O ₅ | 173.8 | 174.7 |
| Dihedral angle (°) | | |
| O ₂ C ₇ C ₆ O ₅ | 89.6 | 90.0 |
| O ₂ C ₆ C ₁ O ₄ | 177.5 | 180.0 |

Another theoretical study of Akiba et al. showed that *hexacoordinated* carbon should be also enough stable to synthesize (figure 26).

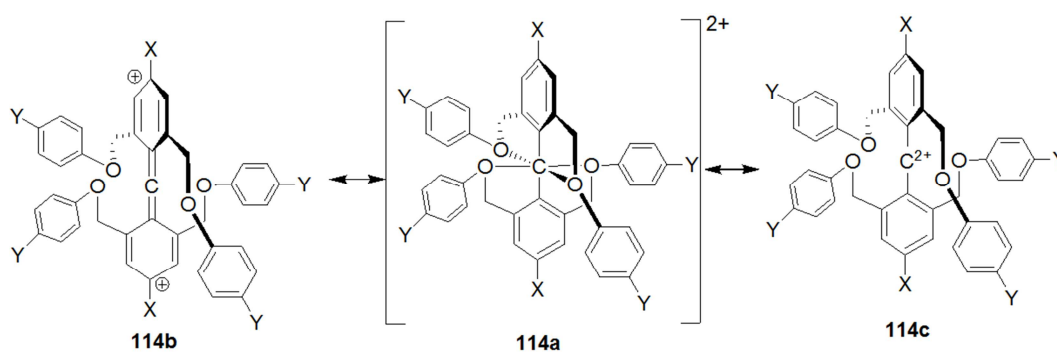


Figure 26. Resonance effect of hexacoordinated hypervalent carbon compound 114a-c.

Table 10. Calculation of C-O bond length using different groups.

| Entry | Substituent | σ (C-O) |
|------------|------------------|----------------|
| X (Y = Me) | | |
| X1 | NMe ₂ | -0.83 |
| X2 | NH ₂ | -0.63 |
| X3 | OH | -0.37 |
| X4 | OMe | -0.27 |
| X5 | Me | -0.17 |
| X6 | H | 0.00 |
| X7 | F | 0.06 |
| X8 | Cl | 0.23 |

| Entry | Substituent | σ (C-O) |
|-------|-----------------|----------------|
| X9 | COOH | 0.45 |
| X10 | COOMe | 0.45 |
| X11 | COMe | 0.50 |
| X12 | CF ₃ | 0.54 |
| X13 | CN | 0.66 |
| X14 | NO ₂ | 0.78 |

A hexacoordinated *hypervalent* carbon compound with an ideal octahedral structure was proposed theoretically in a previous study. [77] However, there is no report telling of

success in synthesizing the compound and/or its derivatives. In order to perform a theoretical design for stronger *hypervalent* bonds, the present study systematically investigated the substituent effects at the *para* position of phenyl groups of axial C-C and equatorial C-O bonds by the substitution of 14 functional groups involving both electron-donating, -withdrawing groups. The results showed that the substituent effect at the axial position is more influential than that at the equatorial position. In the axial case, a good correlation between the C-C and C-O distances was found and the *hypervalent* C-O bonds were strengthened as the substituent becomes more electron-withdrawing. In the latter case, both electron-donating and -withdrawing groups slightly weaken the *hypervalent* C-O bonds (Table 10).

After Akiba et al. have theoretically calculated the hexacoordinated *hypervalent* carbon; the synthesis of hexacoordinated *hypervalent* compound was successful for the first time. Allenic character of compound 118 was described by Akiba et. al. detected by ^{13}C -NMR (94.2 and 216.1 ppm, 118a-b) and by IR (1909 cm^{-1}). The central carbon atom of the allenic groups of 118a shifts at 216.1 ppm and the hexacoordinated *hypervalent* carbon of 118b shifts at 94.2 ppm (figure 25). According to the X-ray structure analysis, C-C-C angle is 168° and therefore bent. They were able to obtain a X-ray structure analysis and could show that

two types of non-equivalent oxygen exists, whereby those two non-equivalent oxygens can also be observed in ^1H -NMR at -85°C with two *singlets*. These two singlets become one singlet (12H) at room temperature. They have proven for the first time by X-ray analysis that central carbon atom is bound sixfold as octahedral structure (118b). Their synthesis strategy is as followed [79]: They synthesized first the compound 116 starting from commercially available compound 115 using Lithium aluminum hydride (LiAlH_4) as reducing agent to the corresponding alcohol of 115 that is forming *in situ*. After the addition of a strong acid “hydroperchloric acid” to the reaction environment, water is eliminated, whereby a salt 116 is formed. Compound 116 serves as an electrophile resource for the nucleophilic attack of the *in situ* formed Lithium Compound-117 in the presence of DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone), whereby the compound 118a-b is formed. The compounds 118a and 118b are two different compounds, which can be only compound 118a in room temperature isolated. Hypervalent carbon compound 118b is not enough stable at room temperature and could be isolated. Compound 118b could be formed at low temperature from compound 118a. The interaction of the equatorial ligand to the central carbon atom of *hypervalent* carbon compound 118b could be showed using NMR at -85°C (figure 27).

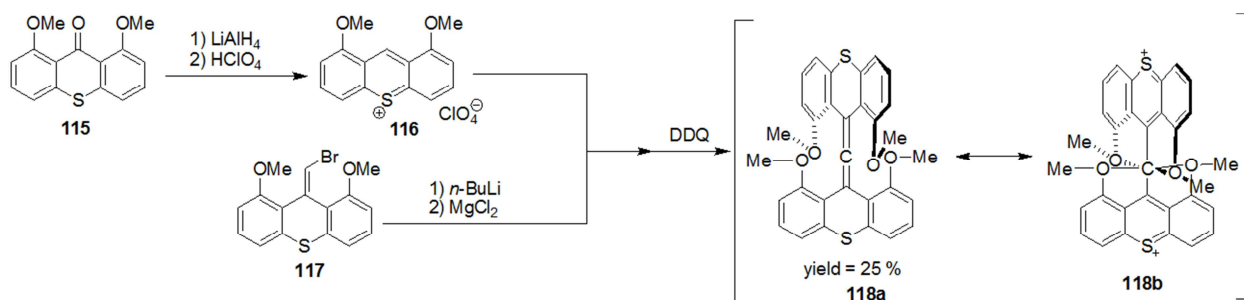


Figure 27. Synthesis strategy of allene carbon for synthesis of hypervalent carbon starting from thioxanthone 115 and vinyl bromide 117.

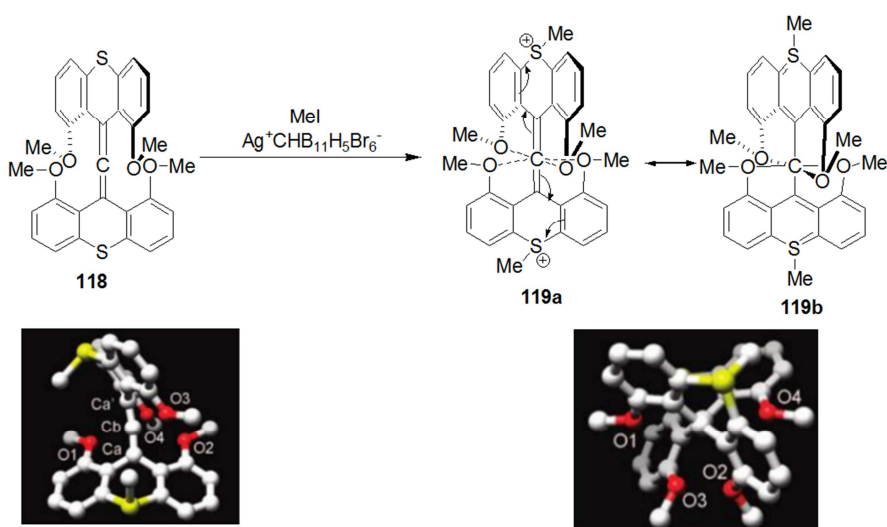


Figure 28. Synthesis of hexacoordinated hypervalent carbon by Akiba et al.

After that, they synthesized the hexacoordinated *hypervalent* carbon compound 119a-b using compound 118a-

b, iodomethane and $\text{Ag}^+\text{CHB}_{11}\text{H}_5\text{Br}_6^-$, and the single crystals of the salt 119a-b were obtained in CD_2Cl_2 . According to

Yamaguchi et al., 119a-b is similar to 118a-b, having a comparably bent allene and four O atoms approaching the central carbon atom with similar O-C-O angles. The C-O distances of 2.641-2.750 Å in 119a-b are generally shorter than those of 118 (2.663-2.815 Å), consistent with the double positive charge on 119a-b. The significant difference between the two structures 118a-b and 119a-b is, in compound 118a-b, the C-O distances separate into two shorter and two longer C-O lengths, whereas all four are nearly equivalent in 119a-b. In both structures, all four C-O distances are considerably longer than that of a typical covalent C-O bond (1.43 Å) but significantly shorter than the sum of the van der Waals radius (3.25 Å) (figure 28). [78]

4. Conclusion of hypervalent Carbon Chemistry and Its Future

Although the *hypervalent* compounds of main group elements have been known since 1886, the first *hypervalent* carbon compounds were published in 1979 by Forbus et al. After that, Akiba et al. synthesized a number of new *hypervalent* carbon compounds. *Hypervalent* compounds produced have very interesting chemical and physical properties that are worthy of further study. Although these compounds are mostly sensitive to moisture, they have great potential to be industrially produced and used in the unusual reactions. Possible applications include among other things: in oxidation reactions as strong oxidizing agent, in rearrangement reaction, in activation of inactive small molecules (such as P₄, N₂, CO, CO₂ ...etc.), in catalysis, in umpolung reactions, in molecular machines (for example: as molecular switch)... etc. This handful of established compounds, which have been known since 1979, will therefore remain in the focus of science in order to be further developed. In any case, new synthesis strategies with new ligands are needed in order to better understand the chemical and physical properties of *hypervalent* carbon compounds.

In summary, it can be said that every multi-binding (more than four) carbon compound should be analyzed and defined differently. According to the examples above, there are indeed *hypercoordinated* carbon compounds and *hypervalent* compounds in the literature. However, it is sometimes difficult to distinguish which compound has which character. This means that the multi-binding carbon compounds produced or calculated up to now can be either *hypervalent* or *hypercoordinated*. There are minimum four important criteria that must be met in order to classify the carbon compounds as *hypervalent* or *hypercoordinated*:

- 1) The bond length
- 2) The existence of three center 4 electron bond(s) in carbon compounds and its binding energy
- 3) The geometric structure of the central carbon atom.
- 4) The stabilizing ligands (mostly multidentate ligands) that bind to the central carbon.
- 5) The DFT calculation, the X-ray structure analysis and / or the spectroscopic methods that are used in order to

classify the compounds.

- 6) The reaction tendency of the carbon compound with possible reactants.

If these conditions or 'part of these conditions' are met, then a statement can be made as to whether the compound is a *hypervalent* carbon compound or not. For the first criterion, the *hypervalent* or *hypercoordinated* carbon bond must have a bond length longer than a simple covalent σ -bond and shorter than a van der Waals bond. For the second criterion, the bond must have a 3 center and 4 electrons and the energy of the bond must be lower than a simple covalent σ -bond energy (see the bond energies of the above examples). That is, 2 electrons occupy the bonding σ -orbitals and the other 2 electrons occupy the non-bonding '*n*'-orbitals (figure 1). The geometric structure should correspond also with the fourth criterion to classify the compound as *hypervalent*. This means that a stabilized ligand (mostly multidentate ligands) must provide at least two non-binding orbitals (four electrons) in order to bind, for example, with the axially directed p-orbital of the carbocation (e.g. see figures 16 and 27). The heteroatoms that directly bond to carbon are mostly: N, O, S (e.g. see figures 16, 18, 25 and 27). The geometric structures of the *hypervalent* carbon compounds in the literature were mostly in trigonal bipyramidal and octahedron form (see figures 16 and 27), the ligands of which are mostly with non-binding orbitals (free electrons of the heteroatom). These *hypervalent* carbon compounds can be confirmed by NMR spectroscopy and IR spectroscopy. The penta- and hexacoordinated planar carbon compounds, on the other hand, were mostly referred to as *hypercoordinated* in the literature.

One of the most important properties of describing a compound as *hypervalent* is to study its tendency to react with other reactances. Although there are numerous examples in the literature about the reaction possibilities of the other *hypervalent* main group compounds, unfortunately there are no examples in the literature about the reaction possibilities of the synthesized *hypervalent* carbon compounds. For example, *hypervalent* iodine compounds are often used as oxidizing agents both in industry and in preparative organic synthesis. As long as no test reactions (e.g. oxidation of an easily oxidizable compound as a test reaction) of the synthesized multiple binding carbon compound to classify as *hypervalent* or *hypercoordinated*, most scientists avoid, as shown in this review, the statements as to whether the compounds are *hypervalent* or *hypercoordinated compounds*.

References

- [1] Jensen, W. B. *J. Chem. Educ.* 2006, 83 (12), 1751. <https://doi.org/10.1021/ed083p1751>
- [2] Musher, J. I. *Angew. Chemie Int. Ed. English* 1969, 8 (1), 54. <https://doi.org/10.1002/anie.196900541>
- [3] IUPAC Compendium of Chemical Terminology. In: Gold Book. Version: 2 <https://doi.org/10.1351/goldbook.HT07054>

- [4] Curnow, O. J. *J. Chem. Educ.* 1998, 75 (7), 910. <https://doi.org/10.1021/ed075p910>
- [5] Sugden, S. *Nature* 1930, 125, 778-779. <https://doi.org/10.1038/125778a0>
- [6] Sugden, S. In “*The Parachor and Valency*”, Chapter 6; Knopf: New York, 1930.
- [7] Rundle, R. E. *J. Am. Chem. Soc.* 1947, 69 (6), 1327. <https://doi.org/10.1021/ja01198a028>
- [8] Pimentel, G. C. *J. Chem. Phys.* 1951, 19 (4), 446. <https://doi.org/10.1063/1.1748245>
- [9] Mitchell, K. A. R. *Chem. Rev.* 1969, 69 (2), 157. <https://doi.org/10.1021/cr60258a001>
- [10] Pettit, L. D. *Q. Rev. Chem. Soc.* 1971, 25 (1), 1. <https://doi.org/10.1039/QR9712500001>
- [11] Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* 1980, 102 (26), 7753. <https://doi.org/10.1021/ja00546a019>
- [12] Martin, J. C. *Science* 1983, 221 (4610), 509. <https://doi.org/10.1126/science.221.4610.509>
- [13] Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* 2002, 102 (7), 2523. <https://doi.org/10.1021/cr010003+>
- [14] Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* 1996, 96 (3), 1123. <https://doi.org/10.1021/cr940424+>
- [15] Zhdankin, V. V. *Adv. Het. Chem.* 2016, 119, 57. <https://doi.org/10.1016/bs.aihch.2015.11.001>
- [16] Varvoglis, A. *Synthesis* 1984, 709. <https://doi.org/10.1055/s-1984-30945>
- [17] Wirth, T. *Angew. Chemie Int. Ed.* 2005, 44 (24), 3656. <https://doi.org/10.1002/anie.200500115>
- [18] Wirth, T.; Kita, Y.; Wirth, T. *Hypervalent iodine chemistry*; Springer, 2016; Vol. 373.
- [19] Havare, N. *Int. J. Chem. Stud.* 2018, 2 (4), 10. <http://www.chemistryjournal.in/archives/2018/vol2/issue4/2-5-12>
- [20] Havare, N. *Enantioselective Epoxidierung mit Metall (salen)-Komplexen — Oxidative Spaltung und Umlagerung organischer Verbindungen*, Freiburg, 2012.
- [21] Havare, N.; Plattner, D. A. *Org. Lett.* 2012, 14, 19. <https://doi.org/10.1021/ol301675v>
- [22] Havare, N.; Plattner, D. A. *Helv. Chim. Acta* 2012, 95 (10), 2036. <https://doi.org/10.1002/hlca.201200444>
- [23] Dess, D. B.; Martin, J. C. *J. Org. Chem.* 1983, 48 (22), 4155. <https://doi.org/10.1021/jo00170a070>
- [24] Grelier, G.; Darses, B.; Dauban, P. *Beilstein J. Org. Chem.* 2018, 14 (1), 1508. <https://doi.org/10.3762/bjoc.14.128>
- [25] Viktor V. Zhdankin In “*Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds*”; John Wiley & Sons, 2013.
- [26] Miyake, H.; Kano, N.; Kawashima, T. *Inorg. Chem.* 2011, 50 (18), 9083. <https://doi.org/10.1021/ic2012765>
- [27] Kano, N.; O'Brien, N. J.; Uematsu, R.; Ramozzi, R.; Morokuma, K. *Angew. Chemie* 2017, 129 (21), 5976. <https://doi.org/10.1002/ange.201701718>
- [28] Kano, N.; Yamamura, M.; Kawashima, T. *Dalt. Trans.* 2015, 44 (37), 16256. <https://doi.org/10.1039/C5DT02038G>
- [29] Kano, N.; Sasaki, K.; Miyake, H.; Kawashima, T. *Organometallics* 2014, 33 (9), 2358. <https://doi.org/10.1021/om500291k>
- [30] Kano, N.; Yoshinari, N.; Shibata, Y.; Miyachi, M.; Kawashima, T.; Enomoto, M.; Okazawa, A.; Kojima, N.; Guo, J.-D.; Nagase, S. *Organometallics* 2012, 31 (23), 8059. <https://doi.org/10.1021/om300915y>
- [31] Kano, N.; Yanaizumi, K.; Meng, X.; Kawashima, T. *Heteroat. Chem.* 2012, 23 (5), 429. <https://doi.org/10.1002/hc.21033>
- [32] Akiba, K. *Heteroat. Chem.* 2011, 22 (3–4), 207. <https://doi.org/10.1002/hc.20726>
- [33] Baumgartner, T.; Jäkle, F. In “*Main Group Strategies towards Functional Hybrid Materials*”, Wiley-VCH Verlag, 2018.
- [34] Olah, G. A.; Prakash, Surya G. K.; Wade, K.; Molnár, Á.; Williams, R. E. In “*Hypercarbon Chemistry*”, Wiley, 2011.
- [35] Akiba, K. In “*Chemistry of Hypervalent Compounds*”, Ed., Wiley-VCH, New York, 1999, Chapter 1.
- [36] Akiba, K. In “*Organo Main Group Chemistry: Chapter 12: Hypervalent Carbon Compounds: Can Hexavalent Carbon Exist?*” pp. 251-263.
- [37] Forbus T. R., Martin J. C. *J. Am. Chem. Soc.* 1979, 101 (17), 5057. <https://doi.org/10.1021/ja00511a042>
- [38] Gillespie, R. J.; Silvi, B. *Coord. Chem. Rev.* 2002, 233-234, 53. [https://doi.org/10.1016/S0010-8545\(02\)00102-9](https://doi.org/10.1016/S0010-8545(02)00102-9)
- [39] Von Ragué Schleyer, P. In “*New Horizons of Quantum Chemistry*”, Springer, 1983; pp 95–109.
- [40] Jernrnis, E. D.; Chandrasekhar, J.; Wurthwein, E.-U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1982, 104, 4275. <https://doi.org/10.1021/ja00379a051>
- [41] Schleyer, P. v. R.; Wurthwein, E.-U.; Kaufmann, E.; Clark, T.; Pople, J. A. *J. Am. Chem. Soc.* 1983, 105, 5930. <https://doi.org/10.1021/ja00356a045>
- [42] Schleyer, P. v. R.; Kapp, J. *Chem. Phys. Lett.* 1996, 255, 363. [https://doi.org/10.1016/0009-2614\(96\)00391-0](https://doi.org/10.1016/0009-2614(96)00391-0)
- [43] Zhizhong, W.; Xiang, Z.; Auchin, T. *J. Mol. Struct. THEOCHEM.* 1998, 453 (1–3), 225. [https://doi.org/10.1016/S0166-1280\(98\)00209-7](https://doi.org/10.1016/S0166-1280(98)00209-7)
- [44] Hehre, W. J.; Random L.; Schleyer, P.v.R.; Pople, J. A. In “*Ab Initio Molecular Orbital Theory*”, Wiley VCH Verlag GmbH: New York, 1986.
- [45] Grimley, R. T. “*The characterization of high temperature vapors*” by JL Magrave, Wiley, New York 1967, 195.
- [46] Kudo, H. *Nature* 1992, 355 (6359), 432. <https://doi.org/10.1038/355432a0>
- [47] Lievens, P.; Thoen, P.; Bouckaert, S.; Bouwen, W.; Vanhoutte, F.; Weidele, H.; Silverans, R. E.; Navarro-Vazquez, A.; Schleyer, P. v. R. *Eur. Phys. J. D-Atomic, Mol. Opt. Plasma Phys.* 1999, 9 (1), 289. <https://doi.org/10.1007/s100530050442>

- [48] Gutsev, G. L. *Chem. Phys.* 1992, 166 (1–2), 57. [https://doi.org/10.1016/0301-0104\(92\)87005-T](https://doi.org/10.1016/0301-0104(92)87005-T)
- [49] Wang, Z.-X.; Schleyer, P. von R. *Science* 2001, 295, 2465. <https://doi.org/10.1126/science.1060000>
- [50] Exner, K.; Schleyer, P. von R. *Science* 2000, 290 (5498), 1937. <https://doi.org/10.1126/science.290.5498.1937>
- [51] Hogeveen, H.; P. Kwant, W. *Acc. Chem. Res.* 1975, 8, 413. <https://doi.org/10.1021/ar50096a004>
- [52] Sirigu, A.; Bianchi, M.; Benedetti, E. *J. Chem. Soc. Chem. Commun.* 1969, 596, 1969. <https://doi.org/10.1039/C2969000596A>
- [53] Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *J. Chem. Soc. A.* 1968, 2865. <https://doi.org/10.1039/J19680002865>
- [54] Toom, L.; Kütt, A.; Leito, I. *Dalton Trans.* 2019, 48, 7499. <https://doi.org/10.1039/C9DT01062A>
- [55] Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K.-C.; Reed, C. A. *Angew. Chem. Int. Ed.* 2004, 43, 5352. <https://doi.org/10.1002/ange.200460005>
- [56] Albano, V. C.; Sansoni, M.; Chini, P.; Matinego, S. *J. Chem. Soc. Dalton Trans.* 1973, 651. <https://doi.org/10.1039/DT9730000651>
- [57] Scherbaum, F.; Crohmann, A.; Muller, C.; Schmid baur, H. *Angew. Chem. Int. Ed. Engl.* 1989, 28, 463. <https://doi.org/10.1002/anie.198904631>
- [58] Gabbai, F. P.; Schier, A.; Riede, J.; Schmidbaur, H. *Chem. Ber.* 1997, 130, 111. <https://doi.org/10.1002/cber.19971300118>
- [59] Asvany, O.; Kumar P, P.; Redlich, Britta; Hegemann, I.; Schlemmer, S.; Marx, D. *Science* 2005, 309, 1219. <https://doi.org/10.1126/science.1113729>
- [60] Vassilev-Galindo, V.; Pan, S.; J. Donald, K.; Merino, G., *Nature Reviews Chemistry* 2018, 2, Article Nr. 0114 <https://doi.org/10.1038/s41570-018-0114>
- [61] Grande-Aztatzti, R.; Cabellos, J. L.; Islas, R.; Infante, I.; Mercero, J. M.; Restrepo, A.; Merino, G., *Physical. Chem. Chemical Phys.* 2015, 17, 4620. <https://doi.org/10.1039/C4CP05659K>
- [62] Guo, J.-G.; Feng, L.-Y.; Dong, C.; Zhai, H.-J., *J. Phys. Chem. A.* 2018, 122, 42, 8370. <https://doi.org/10.1021/acs.jpca.8b08573>
- [63] Mckee, W. C.; Agarwal, J.; Schaefer, H. F.; Von Schleyer, P. *Angew. Chem.* 2014, 126, 8009. <https://doi.org/10.1002/ange.201403314>
- [64] Willgerodt, C. *J. Pract. Chem.* 1886, 33, 154. <https://doi.org/10.1002/prac.18860330117>
- [65] Lucas, H. J.; Kennedy, E. R. *Org. Synth.* 1942, 22, 69. <https://doi.org/10.15227/orgsyn.022.0070>
- [66] Forbus Jr, T. R.; Martin, J. C. *Heteroat. Chem.* 1993, 4 (2–3), 113. <https://doi.org/10.1002/hc.520040206>
- [67] Monnier, F.; Taillefer, M. *Angew. Chem.* 2009, 121 (38), 7088. <https://doi.org/10.1002/ange.200804497>
- [68] Yamashita, M.; Mita, Y.; Yamamoto, Y.; Akiba, K. *Chem. Eur. J.* 2003, 9 (15), 3655. <https://doi.org/10.1002/chem.200204354>
- [69] Akiba, K.; Moriyama, Y.; Mizozoe, M.; Inohara, H.; Nishii, T.; Yamamoto, Y.; Minoura, M.; Hashizume, D.; Iwasaki, F.; Takagi, N.; others. *J. Am. Chem. Soc.* 2005, 127 (16), 5893. <https://doi.org/10.1021/ja043802t>
- [70] Frisch, Mj. Gaussian 03 Rev. E. 01. <http://www.gaussian.com/>. Published online 2004. <http://www.gaussian.com/2004>
- [71] Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; others. *J. Comput. Chem.* 1993, 14 (11), 1347. <https://doi.org/10.1002/jcc.540141112>
- [72] Dong, W.; Li, Q.; Scheiner, S. *Molecules* 2018, 23 (7), 1681. <https://doi.org/10.3390/molecules23071681>
- [73] Scheiner, S. *J. Phys. Chem. A* 2017, 121 (29), 5561. <https://doi.org/10.1021/acs.jpca.7b05300>
- [74] Karim, A.; Schulz, N.; Andersson, H.; Nekouishahraki, B.; Carlsson, A.-C. C.; Sarabi, D.; Valkonen, A.; Rissanen, K.; Gräfenstein, J.; Keller, S.; Erdelyi, M. *J. Am. Chem. Soc.* 2018, 140 (50), 17571. <https://doi.org/10.1021/jacs.8b09367>
- [75] Hakkert, S. B.; Erdélyi, M. *J. Phys. Org. Chem.* 2015, 28 (3), 226. <https://doi.org/10.1002/poc.3325>
- [76] Pierrefixe, S. C. A. H.; Poater, J.; Im, C.; Bickelhaupt, F. M. *Chem. Eur. J.* 2008, 14 (23), 6901. <https://doi.org/10.1002/chem.200800013>
- [77] Pierrefixe, S. C. A. H.; van Stralen, S. J. M.; van Stralen, J. N. P.; Fonseca Guerra, C.; Bickelhaupt, F. M. *Angew. Chem.* 2009, 121 (35), 6591. <https://doi.org/10.1002/ange.200902125>
- [78] Kikuchi, Y.; Ishii, M.; Akiba, K.; Nakai, H. *Chem. Phys. Lett.* 2008, 460 (1–3), 37. <https://doi.org/10.1016/j.cplett.2008.05.079>
- [79] Yamaguchi, T.; Yamamoto, Y.; Kinoshita, D.; Akiba, K.; Zhang, Y.; Reed, C. A.; Hashizume, D.; Iwasaki, F. *J. Am. Chem. Soc.* 2008, 130 (22), 6894. <https://doi.org/10.1021/ja710423d>

Biography



Nizam Havare was born in Samandağ, Turkey. He studied B.Sc. in Department of Chemistry at University of Mersin and obtained his B.Sc. degree in 2003 with very good. He studied his master and obtained his “Dipl.-Chem.” degree with good from University of Paderborn in 2006. He completed his Ph.D. degree at the University of Freiburg. His second (should be first) postdoc was about hypervalent chemistry of main group elements at the university of Tokyo. He did his second postdoc at Stanford University under the supervision of Prof. Barry M. Trost in 2016. He worked additionally as a chemistry and physics teacher in various types of schools in Germany and still keeps oscillating between teaching at schools and research at universities.