From Kekulé's Tetravalent Methane to Five-, Six-, and Seven-Coordinate Protonated Methanes[1]

GEORGE A. OLAH* AND GOLAM RASUL

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, CA 90089-1661

Introduction

One of the foundations of organic chemistry is Kekulé's[2] ground-breaking concept (suggested also independently by Couper[3]) of the tetravalency of carbon. The concept that carbon can form not more than four bonds and that carbon−carbon bonding results in chains or cyclic compounds (such as benzene) became the backbone of organic chemistry. It continues to serve well for the description of the overwhelming majority of organic molecules. The structure of higher bonded (coordinate) carbocations of which CH_5^+ is the parent, as well as an increasing number of other higher coordinate carbon compounds, however cannot be explained by Kekulé's four-bond classical theory. Olah's extensive studies pointed out the necessary involvement of two-electron three-center (2e-3c) bonding in these carbocations[4] which helped to establish the general concept that carbon is not limited in its ability to bind simultaneously to not more than four atoms or groups.[5]

Whereas CH_5^+ was originally observed in mass spectrometry, a variety of higher coordinate (nonclassical) carbocations were readily formed and studied under superacidic conditions in solutions or even as isolated salts.[5,6] The real significance of these ions is that they led to the realization of electrophilic substitution and related transformations of saturated hydrocarbons (alkanes) and in general of electrophilic activation of C−H and C−C single bonds. Varied electrophilic reactions became possible with saturated hydrocarbons, and a new area of chemistry began to emerge.

A significant number and great variety of compounds containing higher coordinate carbon is by now recognized.[5] Hypercarbon chemistry, as it is called, includes besides carbocations also carboranes, carbon-bridged organometallics, carbonyl clusters, etc. The rapidly developing field has been comprehensively reviewed.[5]

CH_5^+ is considered the parent of nonclassical carbocations containing a five-coordinate carbon atom. Extensive *ab initio* calculations including recent high-level studies (Car−Parrinello *ab initio* simulation and Kutzelnigg's CCSD(T)-R12 calculations)[7] reconfirmed the preferred C_s symmetrical structure[8] **1** for the CH_5^+ cation with a 2e-3c bond as originally suggested by Olah et al. in 1969.[9] The structure can be viewed as a proton inserted into one of the σ C−H bonds of methane to form a 2e-3c bond between carbon and two hydrogen atoms. At the same time ready bond to bond (isotopal) proton migration makes it a rather fluxional molecule, since the process involves low barriers.[9]

The calculated parent six-coordinate carbocation, diprotonated methane (CH_6^{2+}), has two 2e-3c bonding interactions in its minimum-energy structure **2** (C_{2v}).[10] On the basis of *ab initio* calculations,[11] we recently reported that even the parent seven-coordinate carbocation, triprotonated methane (CH_7^{3+}), is an energy minimum and has three 2e-3c bonding interactions in its minimum-energy structure **3** (C_{3v}). These results indicate the general importance of 2e-3c interactions in protonated alkanes.

1 CH_5^+ C_s **2** CH_6^{2+} C_{2v} **3** CH_7^{3+} C_{3v}
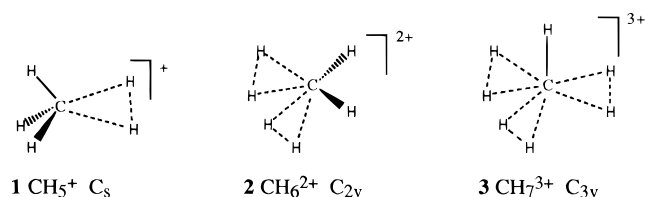
Protonated methanes and their homologs and derivatives are experimentally indicated in superacidic chem-

George A. Olah was born and educated in Hungary. After moving to America in 1957, he worked in industry (Dow Chemical Co.) until 1965, when he became Professor of Chemistry and head of the Chemistry Department at Western Reserve University, which subsequently became Case Western Reserve University in Cleveland, OH. In 1977 he moved to the University of Southern California in Los Angeles, where he is Distinguished Professor of Chemistry and director of the Loker Hydrocarbon Research Institute. His research interests are in synthetic, mechanistic, and structural chemistry, including reaction intermediates (most notably carbocations), superacids, and hydrocarbon chemistry. He is a member of the National Academy of Sciences and a member of foreign academies and societies. He has published 1100 scientific papers and 15 books and has been issued close to 100 patents. Olah's work has been acknowledged by awards, such as the ACS awards in synthetic organic chemistry and hydrocarbon or petroleum chemistry and the Roger Adams medal. In 1994 he was awarded the Nobel Prize in Chemistry for contributions in carbocation chemistry.

Golam Rasul was born in Bangladesh in 1960. He received his B.Sc. and M.Sc. from the University of Dhaka and M.S. (in computational chemistry) from the University of Massachusetts at Dartmouth. He obtained his Ph.D. in 1992 from the University of Southern California. He is currently a Research Assistant Professor at the Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California. His research interests involve the combined application of theory and experiment in structural−mechanistic studies.

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istry. Some higher coordinate methane derivatives can even be isolated as stable compounds.[12] Schmidbaur and co-workers have prepared the gold complex analogs of CH_5^+ and CH_6^{2+} and determined their X-ray structures. The monopositively charged trigonal bipyramidal[13] $\{[(C_6H_5)_3PAu]_5C\}^+$ and the dipositively charged octahedral[14] gold complex $\{[(C_6H_5)_3PAu]_6C\}^{2+}$ contain five- and six-coordinate carbon. Considering the isolobal relationship (i.e., similarity in bonding) between LAu^+ and H^+, the gold complexes represent the isolobal analogs of CH_5^+ and CH_6^{2+}, respectively.

In context of the study of protonated alkanes and their chemistry, it is timely to review the parent five-, six-, and seven-coordinate carbocations CH_5^+, CH_6^{2+}, and CH_7^{3+}, respectively. Some organometallic analogs, particularly Schmidbaur's gold complexes, are also discussed. Because of their structural similarity,[5] we also compare these ions with their corresponding isoelectronic boron analogs.

Protonated Methane CH_5^+ (Methonium Ion)

Protonated methane, CH_5^+, was first observed as a stable species by Russian investigators[15] in mass spectroscopy of methane at relatively high source pressures.[16] Evidence for CH_5^+ in the gas phase also came from the studies of the reactions of CH_3^+ and its deuterated analogs with H_2, HD, and D_2 by mass spectrometric studies using a variable temperature selected ion-flow method, which indicated the scrambling of hydrogen and deuterium atoms in the isotopic CH_5^+ ions.[17] Lee et al.[18-20] carried out IR spectroscopic studies using a laser excitation method and observed CH_5^+ weakly coordinated to H_2 (*vide infra*).

Evidence for CH_5^+ in the condensed phase came from the hydrogen–deuterium exchange of methane in the deuteriated superacids.[9] Direct spectroscopic observation of the ion is difficult due to its expected low concentration and fast exchange in superacids. However, ESCA studies[21] of matrices of superacids (FSO_3H-SbF_5 or $HF-SbF_5$) saturated with methane at $-180\,°C$ and in a high vacuum of 10^{-9} Torr showed that the observed 1s ESCA shift differed by less than 1 eV (the limit of resolution) from that of methane. This is considered to be that due to CH_5^+. Neutral methane is at best sparsely soluble in superacids, if at all. In the high vacuum used therefore neutral methane would be pumped off from the system. The relatively unchanged 1s carbon binding energy in CH_5^+ compared to that of CH_4 is consistent with **1** in which most of the positive charge is spread out over the hydrogen atoms, leaving the carbon atom with relatively little positive charge.

Of the possible C_s symmetrical **1**, C_{2v} symmetrical **4**, C_{4v} symmetrical **5**, and D_{3h} symmetrical **6** structures of

protonated methane, on the basis of semiempirical SCF calculations, Olah and Klopman originally expressed[9] preference for the front-side-protonated C_s form **1**, resembling a complex between CH_3^+ and a hydrogen molecule, resulting in the formation of a 2e-3c bond. This

4 C_{2v} **5** C_{4v} **6** D_{3h}
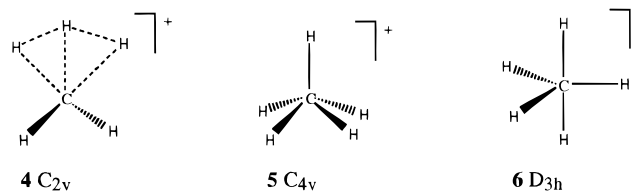
preference was also based on the observation that CH_5^+ readily cleaves into CH_3^+ and H_2. A quarter century of ever increasing levels of quantum mechanical calculations[8a,22-28] still seem to bear out the validity of this conclusion. At the MP2(FU)/6-31G** level the C_s symmetrical form **1** is the energy minimum structure.[28] Frequency calculations at the same level show that the other forms of CH_5^+ are not minima on the potential energy surface.[29] Structure **4** was located as a transition structure for intramolecular hydrogen transfer in ion **1**. At the MP2(FU)/6-311++G(2df,2pd) level the calculated[28] C–H and H–H distances in the 2e-3c interactions are 1.180 and 0.980 Å, respectively. Single-point energies at the QCISD(T)/6-311++G(3df,3pd)//MP2(FU)/6-311++G-(2df,2pd) level showed, however, that structure **1** is only 0.86 kcal/mol more stable than **4**. The authors also showed that, after the zero point vibrational energies (ZPE) are corrected, **1** and **4** have essentially the same energy at absolute zero temperature. Hydrogen scrambling in **1** in accordance with experimental observations is therefore very facile.

Schleyer et al. used[8a] even higher level *ab initio* calculations on the structures of **1** and **4**. The CCSD(T)/TZ2P(f,d) + ZPE (CCSD/TZ2P + f) level of calculations[8a] showed that the energy difference between **1** and **4** is extremely small. They suggested that CH_5^+ is a highly fluxional molecule without a definite structure[8a] and suggested that the 2e-3c bonding representation of the ion is thus necessarily oversimplified. More recently, however, Marx and Parrinello reported[7a] the extensive *ab initio* electronic structure calculations, known as Car–Parrinello *ab initio* simulation,[30] on CH_5^+ which include the quantum effects of the nuclei. These calculations showed that CH_5^+ is best described by the C_s structure **1** with 2e-3c bonding. Kutzelnigg et al. also recently performed[7b] high-level CCSD(T)-R12 calculations with large basis sets on CH_5^+. Their studies again reconfirmed the preferred C_s symmetrical structure **1** for the CH_5^+ cation. It is thus concluded that whereas CH_5^+ undergoes

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very readily low-energy bond to bond rearrangements as postulated by Olah et al. as early as 1969,[9] it is still best represented by its C_s symmetry structure and can be considered the parent carbonium ion. In the context of our understanding of the meaning of chemical structure depiction of CH_5^+ as a five-coordinate, but vaguely pentavalent, carbocation seems by all tests well founded.

Several attempts were made[18−20,31−33] to observe and experimentally determine the structure of CH_5^+ in the gas phase as well as to observe and study it in the condensed state. The infrared spectrum of the CH_5^+ ion solvated by a hydrogen molecule, $CH_5^+(H_2)$, was reported by Boo and Lee.[19] The spectrum contains a broad C−H stretching band centered at 2966 cm^{-1}. The observed frequency matches with the *ab initio* calculated[34] frequency of the structure containing eclipsed-C_s $CH_5^+(H_2)$ (**7**) after appropriate scaling. Lee's group has also reported[19,20] the

7 C_s
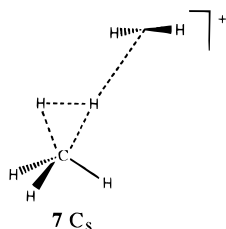
infrared spectra of $CH_5^+(H_2)_n$ ($n = 1−6$). The data show the scrambling of CH_5^+ through large-amplitude motions such as the CH₃ internal rotation and in-plane wagging motion. The scrambling slowed on attaching solvent H₂ molecules to the core ion. It was concluded that complete freezing of the scrambling motions is achieved when the first three H₂ molecules bind to the CH_5^+ core. Molecular dynamics methods were used to simulate the internal motion of these ionic complexes.

Gas phase studies of the existence and structure of cluster ions $CH_5^+(CH_4)_n$ were reported by Hiraoka and Kebarle[32] and by Hiraoka and Mori[33] by pulsed electron-beam mass spectrometry. The observed enthalpy and free energy changes are again compatible with the C_s symmetrical structure **1**.

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) study of the reactivity of protonated perdeuteriomethane and deuteriated methanes, generated under various pressure conditions in an external chemical ionization ion source, toward ammonia was studied by Heck.[35] Competition between proton and deuterium transfer from protonated perdeuteriomethane and deuteriated methanes to ammonia shows chemically distinguishable hydrogens. From the experimental results it was concluded that "the chemical behavior of protonated methane appears to be compatible with the theoretically predicted stable structure with C_s symmetry, involving a two-electron three-center bond associating two hydrogens and the carbon atom. Interconversion of this structure due to exchange between one of those hydrogens and one

of the three remaining hydrogens appears to be a fast process which is induced by interactions with the chemical ionization gas".

The radiolysis of solid methane in liquid argon at 77 K by γ-rays was shown by Libby et al.[36,37] to give polymers of an average molecular formula $C_{20}H_{40}$. It is probable that the CH_5^+ ion may be involved in a positive-ion polymerization of solid ion methane. The most abundant ion in the radiolysis of methane gas is $CH_4^{•+}$, which in the presence of neutral methane forms CH_5^+ and $CH_3^•$ ($CH_4^{•+} + CH_4 \rightleftharpoons CH_5^+ + CH_3$). Ionization of methane and subsequent ion−molecule reactions ($CH_4 + C_nH_{2n+1} \rightleftharpoons H_2 + C_{n+1}^+H_{2n+3}$) followed by neutralization may form the heavier hydrocarbons.[37]

Using the (triphenylphosphine)gold(I) ligand (LAu$^+$) as the isolobal substitute for H$^+$, Schmidbaur et al. have prepared[13] the monopositively charged gold complex $\{(Ph_3PAu)_5C\}^+$ (**8**), an analog of CH_5^+. The structure of

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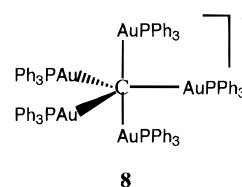
the compound was determined by analytical and spectroscopic studies as well as by its single-crystal X-ray crystallography. The X-ray data show a trigonal bipyramidal structure **8** (C_3 symmetry). The remarkable stability of this gold complex may be due to significant metal−metal bonding. However, the isolation and study of this substituted CL_5^+ complex greatly contributed to our knowledge of higher coordinate carbocations.

Schmidbaur et al. also prepared[38a] the five-coordinate triauriated and disilyl-substituted carbocation complex $\{(Ph_3PAu)_3C(Me_3Si)_2\}^+$. X-ray data show a distorted trigonal pyramidal structure in the crystal lattice. Hypercoordinate tetraauriate ethanium cation $\{MeC(Ph_3PAu)_4\}^+$ with a square pyramidal structure was also reported.[38b] This represents an isolobal analog of protonated ethane $CH_3CH_4^+$. *Ab initio* calculation for $CH_3CH_4^+$ at the MP2/6-31G* level predicts a C_s symmetrical structure with a 2e-3c bond.[25]

Boron and carbon are consecutive first-row elements. A trivalent carbocation is isoelectronic with the corresponding neutral trivalent boron compounds. Similarly, pentavalent monopositively charged carbonium ions are isoelectronic with the corresponding neutral pentavalent boron compounds. The BH_5 molecule, which is isoelectronic with CH_5^+, is also C_s symmetrical on the basis[39,40] of high-level *ab initio* calculations. Experimentally H−D exchange was observed when BH_4^- was treated with

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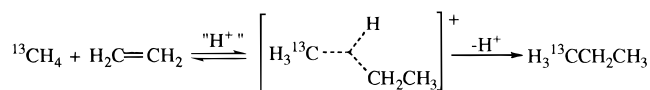(40) Watts, J. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 825.

deuteriated strong acids (and vice versa) by Olah et al.,[41] indicating the intermediacy of BH_5. The first direct experimental observation (by infrared spectroscopy) of BH_5 has, however, only recently been reported.[42] The X-ray structure of the five-coordinate gold complex $[(Cy_3P^+)B(AuPPh_3)_4]$ was also reported by Schmidbaur et al.[43] This square pyramidal compound represents the isolobal analog of BH_5. The study of a stable gold complex containing five-coordinate boron further strengthens the relationship of the bonding nature in higher coordinate boron and carbon compounds.

CH_5^+ and its substituted analogs are of particular significance to our understanding of the electrophilic reactivity of methane, the parent saturated hydrocarbon (alkane). Hydrogen–deuterium exchange of methane in deuteriated superacids is itself an example of electrophilic substitution.[9]

$$CH_4 \xrightarrow{\text{"}D^+\text{"}} \left[H_3C\cdots\overset{H}{\underset{D}{\diagdown}} \right]^+ \xrightarrow{-H^+} CH_3D$$
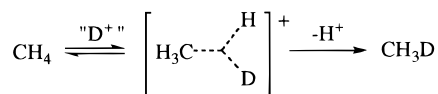
Ethylation of $^{13}CH_4$ with ethylene over superacid catalyst gave $^{13}CH_3CH_2CH_3$ in the equivalent of a Friedel–Crafts alkylation.[44]

$$^{13}CH_4 + H_2C{=}CH_2 \xrightarrow{\text{"}H^+\text{"}} \left[H_3{}^{13}C\cdots\overset{H}{\underset{CH_2CH_3}{\diagdown}} \right]^+ \xrightarrow{-H^+} H_3{}^{13}CCH_2CH_3$$

A variety of other related substitution reactions were also found to be feasible with strong electrophiles.[4,5]
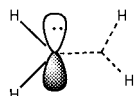
Schreiner, Schleyer, and Schaefer, on the basis of theoretical calculations, suggested[45] that electrophilic substitution of methane may proceed by, instead of insertion of the electrophile into a CH bond via 2e-3c bonding, substitution of the "nonbonded electron pair" of methane. This was concluded because calculations showed higher stability of

$$C\cdots\overset{H}{\underset{H}{\diagdown}} \quad \text{over} \quad C\cdots\overset{H}{\underset{E}{\diagdown}}$$
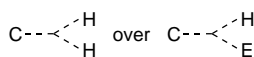
bonds in CH_5^+ analogs. Whereas this observation is significant, nonbonded electron-pair formation in methane can be considered only when methane would tend to flatten out from its tetrahedral form. This would, however, be prohibitively energetic[46] (>100 kcal/mol) and thus unlikely.
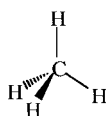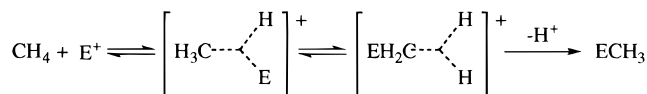

tetrahedral methane   flat methane with non-bonded electron pair

Electrophilic substitution of methane is to be considered as an insertion process into a CH bond, which, however, could be followed by very facile bond to bond proton migration to the more symmetrical, energetically

favored form of CH_4E^+ which subsequently gives the substituted methane by proton elimination.[47a]

$$CH_4 + E^+ \rightleftharpoons \left[H_3C\cdots\overset{H}{\underset{E}{\diagdown}} \right]^+ \rightleftharpoons \left[EH_2C\cdots\overset{H}{\underset{H}{\diagdown}} \right]^+ \xrightarrow{-H^+} ECH_3$$

Diprotonated Methane CH_6^{2+} (Protiomethonium Dication)

Carbon not only can be involved in a single 2e-3c center bond formation, but is also shown to be capable of simultaneously participating in two 2e-3c bonds in some carbodications. Diprotonated methane, CH_6^{2+} (**2**), is the parent of such carbodications. *Ab initio* calculations show that the C_{2v} symmetrical structure **2**, with two orthogonal 2e-3c interactions, is the only minimum on the potential energy surface.[10] At the HF/6-31G* level, the C–H bond length of each of the 2e-3c interactions is 1.208 Å, considerably longer than that of 2c-2e bonds (1.123 Å). The H–H bond length in each of the 2e-3c interactions is 0.972 Å. Thus, structure **2** can be visualized as a complex of H_2 with the p-orbital of the carbon atom of the planar C_{2v} symmetrical CH_4^{2+} dication. CH_6^{2+} is thermodynamically unstable toward deprotonation, loss of $H_2^{\bullet+}$, and loss of H_3^+ by 63.1, 18.6, and 126.8 kcal/mol, respectively. However, there is a high deprotonation barrier, calculated to be 35.4 kcal/mol. Structures **10** (D_{3h}), **11** (C_{5v}), **12** (D_{2d}), **13** (O_h), and **14** (C_{4v}) were calculated to be saddle points on the potential energy surface of CH_6^{2+} and were found to be 5.7, 12.0, 17.4, 41.5, and 35.2 kcal/mol, respectively, higher in energy than **2** at the HF/6-31G**//HF/6-31G* level.[10]

10 D_{3h} **11** C_{5v} **12** D_{2d}

13 O_h **14** C_{4v}
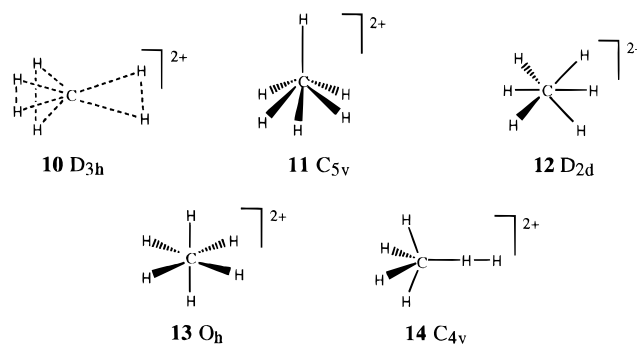
It should be pointed out that the second protonation of CH_5^+ to the *gitonic* dication CH_6^{2+} is the limiting case. Onium ions capable of further interaction (coordination) with protic superacids can undergo the equivalent of protolytic (electrophilic) solvation, which in the limiting case can lead to *de facto* diprotonation. This greatly enhances their reactivity (rendering them superelectrophiles).[47b]

Similar to the five-coordinated CH_5^+ analog gold complex, Schmidbaur et al. have also prepared and isolated[14]

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the dipositively charged CH_6^{2+} analog octahedral gold complex $\{[(C_6H_5)_3PAu]_6C\}^{2+}$ (**15**) containing six-coordinate


15 O_h
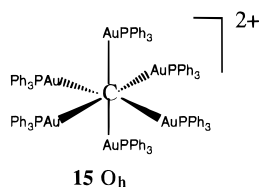
carbon atoms. They also succeeded in determining its X-ray structure. Complex **15** is an isolobal mimic of the experimentally yet unobserved diprotonated methane **2**. Molecular orbital calculations also indicated[48] that the dicationic carbon-centered gold complex is stable. Relativistic electronic structure calculations gave further insight into the bonding and electron distribution of the gold complex. Further six-coordinated carbon-containing carbocations reported so far are the experimentally obtained and studied pyramidal dication $\{C_6(CH_3)_6\}^{2+}$ of Hogeveen[49] and calculationally studied CLi_6^{2+} of Schleyer.[50]

Six-coordinate dipositively charged carbocations are isoelectronic with the corresponding positively charged hexavalent boron compounds. The structure and energetics of the parent six-coordinated boronium ion BH_6^+, isoelectronic with CH_6^{2+}, have recently been studied.[51a] The C_{2v} symmetric form **16** was found to be a stable

16 C_{2v}
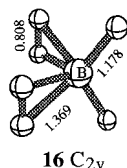
minimum for BH_6^+. Structure **16** is isostructural with CH_6^{2+}. Six-coordinated BH_6^+ (**16**) also contains two 2e-3c bonds and two 2c-2e bonds. The MP2/6-31G** calculated B–H bond distance of 2e-3c interactions is 1.369 Å. This is slightly shorter than that found in the 2e-3c B–H bond (1.427 and 1.444 Å) of the C_s structure of BH_5 at the same theoretical level. Recently DePuy et al. were able to generate BH_6^+ in the gas phase.[51b]

Protonation of BH_5 to form **16** is calculated to be remarkably exothermic by 154.4 kcal/mol. On the basis of the calculations, it is suggested[51a] that the ion–molecule reaction of BH_4^+ and H_2 might be a suitable way to generate BH_6^+ (**16**) in the gas phase. It is now also considered probable that, in the studied protonation of BH_4^- in superacids,[41] BH_5 is formed in equilibrium with BH_6^+, a fact not considered at the time. More stabilized analogs, including Schmidbaur type gold complexes, e.g., $\{[(C_6H_5)_3PAu]_{6-n}BH_n\}^+$, could probably be prepared and studied.

$$BH_4^- + H^+ \rightleftharpoons BH_5 \underset{}{\overset{H^+}{\rightleftharpoons}} BH_6^+$$

$$BH_3 + H_2$$
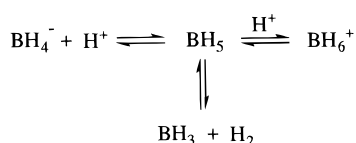
Triprotonated Methane, CH_7^{3+} (Diprotiomethonium Trication)

We have recently reported[11] the investigation of triprotonated methane, the parent seven-coordinate carbo-

cation, CH_7^{3+}, by *ab initio* calculations. At the MP2/6-31G** level the C_{3v} symmetric form **17** is found to be a stable minimum for triprotonated methane, CH_7^{3+}. Structure **17** is a propeller-shaped molecule resembling a complex between CH^{3+} and three hydrogen molecules, resulting in the formation of three 2e-3c bonds. In such a small first-row trication charge–charge repulsion is substantial. However, the bonding interactions of trication **17** are strong enough to counter this charge–charge repulsion. The C–H bond distances of 2e-3c interactions (1.282 and 1.277 Å) are slightly longer than that found in the 2e-3c C–H bond (1.181 Å) of the C_s structure of CH_5^+. The H–H distance in the 2e-3c interactions is 1.085 Å. This is 0.351 Å longer than that found in the free hydrogen molecule at the same level of theory, and it is also slightly longer than that in H_2^+ (1.031 Å). Intramolecular proton transfer through transition structure **18** in the trication
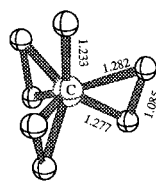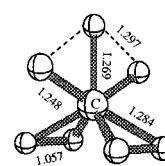

17 C_{3v} **18** C_{2v}

was shown to be very facile. Dissociation into CH_6^{2+} and H^+ was calculated to be expectedly highly exothermic by 241.1 kcal/mol while dissociation into CH_4^{2+} and H_3^+ is even more exothermic by 19.2 kcal/mol. While experimental verification of CH_7^{3+} will be extremely difficult, more stabilized analogs, including Schmidbaur type gold complexes, e.g., $\{[(C_6H_5)_3PAu]_{7-n}CH_n\}^{3+}$, again may be feasible.

Similar to five- and six-coordinate CH_5^+ and CH_6^{2+}, seven-coordinate tripositively charged CH_7^{3+} is isoelectronic with the corresponding dipositively charged heptavalent boronium dication BH_7^{2+} (**19**) (MP2/6-31G** level).[51a]
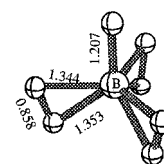
19 C_{3v}

The C_{3v} symmetric form **19** was found to be the only minimum for BH_7^{2+}. Structure **19** is also a propeller-shaped molecule resembling a complex between BH^{2+} and three dihydrogen molecules, resulting in the formation of three 2e-3c bonds. The boronium dication **19** is indeed isostructural with its carbon analog CH_7^{3+}.

We also searched[11] for minimum-energy structures of tetraprotonated methane, CH_8^{4+}. However, at MP2/6-

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31G** all efforts proved futile. CH_8^{4+} remains even computationally elusive as charge–charge repulsion appears to have reached its prohibitive limit. The isoelectronic boron analog BH_8^{3+} (**20**), however, was found[51a] to be an

20 T_d
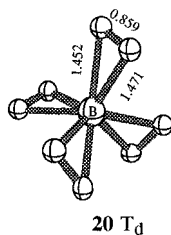
energy minimum. Structure **20** (MP2/6-31G** level) can be viewed as four dihydrogens (oriented tetrahedrally) complexed with a tripositively charged boron atom, B^{3+}.

Summary and Significance

Carbon can extend its bonding from Kekulé's tetravalent methane to five-, six-, or seven-bonded (coordinate) protonated methanes, CH_5^+, CH_6^{2+}, and CH_7^{3+}, and their analogs. Higher coordinate carbocations are now well recognized. They are readily formed under superacidic conditions and are the key to our understanding of the electrophilic reactivity of C–H or C–C single bonds and of hypercarbon chemistry in general. Some of their derivatives, such as Schmidbaur gold complexes, can even be isolated as stable crystalline compounds. The chemistry of higher coordinate carbon (i.e., hypercarbon chemistry) is rapidly expanding.[5]

It is rewarding to see that whereas it was the study of the basic chemistry of protonated methanes such as CH_5^+ and CH_6^{2+} which established the ability of carbon to bind simultaneously more than four atoms or groups, the application of this new principle to more general hypercarbon chemistry is gaining substantial practical significance. Not only do we now understand the essentials of such acid-catalyzed hydrocarbon conversions as the isomerization and alkylation of alkanes essential for the production of lead-free high octane gasoline, but this understanding is also opening the door to utilize methane (i.e., natural gas) to produce gasoline and other valuable hydrocarbon products. High acidity superacid systems capable of bringing about such conversions are not limited to liquid acid systems (such as $FSO_3H–SbF_5$ (Magic Acid), $HF–SbF_5$ (fluoroantimonic acid), triflic acid systems, etc.). Some solid superacids (such as Nafion-H resin, certain zeolites, and other supported systems) are already of substantial practical, even industrial, use. Recently Thauer discovered a metal-free hydrogenase enzyme, which seems to act in a way related to superelectrophilic carbocation chemistry, the scope of which thus seems to include even some of nature's own processes.[52,53]

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