Russian Chemical Bulletin, Vol. 47, No. 5, May, 1998 833

Physical Chemistry

Topological aspects of metals in carbon cages: analogies with organometallic chemistry

R. B. King

Department of Chemistry, University of Georgia,
Athens, Georgia 30602, USA.
Fax: +1 (706) 542 9454

Metals can interact with carbon cages in the following ways: (1) stable carbon cages (*i.e.*, fullerenes) function as electronegative olefins in their exohedral η^2 bonding to transition metals; (2) endohedral metallofullerenes with a highly electropositive lanthanide (Ln) inside the carbon cage can be considered to be ionic with lanthanide cations, Ln^{3+}, and fullerene anions; (3) fullerenes too small for independent existence can be stabilized by internal covalent bonding to an endohedral metal atom using the central carbon atoms of pentagon triplets, *i.e.* triquinacene units, in complexes such as $M@C_{28}$ (M = Ti, Zr, Hf, and U), derived from the tetrahedral fullerene C_{28}; (4) metal atoms can occur as vertices of binary mixed metal-carbon cages in both early transition metal complexes of the types $M_{14}C_{13}$, M_8C_{12}, and $M_{13}C_{22}$ (*e.g.*, M = Ti) and copper-carbon cages of the types $Cu_{2n+1}C_{2n}^+$ ($n \le 10$), $Cu_7C_8^+$, $Cu_9C_{10}^+$, and $Cu_{12}C_{12}^+$. The presence of metal atoms as vertices of carbon cages changes radically their stoichiometries and thus their structures. Thus, early transition metals form cages such as $Ti_{14}C_{13}$ assumed to have titanium atoms at the vertices and face midpoints of a 3×3×3 cube and carbon atoms at the edge midpoints and center of the cube and $Ti_{13}C_{22}$ assumed to have titanium atoms at the edge midpoints and center of a 3×3×3 cube as well as C_2 units and carbon atoms at the vertices and face midpoints, respectively, of the cube. Elimination of the face metal atoms from the $Ti_{14}C_{13}$ structure as well as the center carbon atom, which has been achieved experimentally by photofragmentation, leads to the Ti_8C_{12} cluster. The structure of this cluster is based on a tetracapped tetrahedron with T_d symmetry with two distinct quartets of titanium atoms, six distinct C_2 pairs, and 36 direct Ti—C interactions. The copper-carbon cages of various stoichiometries are suggested to have prismatic, antiprismatic, or cuboctahedral structures in which the electronic configurations of the copper atoms approach the favored 18-electron rare gas configuration.

Key words: quantum-chemical calculations; fullerenes, endohedral complexes, metal-carbon cages, topology of bonding.

One of the most exciting developments during the past decade has been the discovery of new allotropes of carbon exhibiting finite molecular cage structures rather than the infinite polymeric structures found in diamond and graphite. The first such molecular carbon cage was C_{60}, which was shown to have a truncated icosahedral structure.[1] Subsequent studies led to the discovery of other molecular C_n cages (*e.g.*, n = 68, 70, 76, 80, 82,

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 862—869, May, 1998.

84, 86, 88, 90, and 96) exhibiting other polyhedral structures, albeit with much lower symmetry.[2] These molecular carbon cages are now called *fullerenes* in recognition of their resemblance to the architectural creations of R. Buckminster Fuller.

The initial isolation of C_{60} was followed shortly by investigation of its metal complexes.[3] This led to the discovery that C_{60} behaves towards transition metal complexes, particularly those of the late transition metals, not as a benzene derivative but as electronegatively substituted olefin, forming dihapto (η^2) derivatives analogous to olefin complexes, particularly those of tetracyanoethylene. The first example of such a complex to be structurally characterized was $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$, whose structure was already reported in 1991.[4] Since then numerous other related $\eta^2\text{-}C_{60}$ complexes have been reported with late transition metals as well as similar complexes of larger fullerenes such as C_{70}.[5,6] Complexes of this type may be called exohedral complexes since the metal is located outside the carbon cage.

Since the discovery of $\eta^2\text{-}C_{60}$ complexes several other types of interactions of metals with carbon cages have been found. Thus the so-called endohedral metallofullerenes have been discovered in which the carbon cage encapsulates a metal atom.[7] The first such metallofullerene was the lanthanofullerene La@C_{82}, which was first isolated in milligram quantities in 1991.[8] Since then a variety of other endohedral rare earth derivatives of fullerenes have been identified including Ln@C_{2n} (Ln = Sc, Y, La, Ce, Gd; n = 37—45), Ln_2@C_{80} (Ln = Sc, La), Sc_2@C_{2n} (n = 37, 41, 42), and Sc_3@C_{82}.[7]

These compounds, which all contain the relatively electropositive rare earths, can be interpreted as ionic derivatives where the fullerene carbon cage is reduced to a polyanion and the encapsulated rare earth is oxidized to Ln^{3+}. Similar fullerene anions can be obtained with the monopositive alkali metals as countercations, but these all have solid state structures with the alkali metal counterion outside the fullerene cage. Some alkali-metal fullerides of this type exhibit superconductivity with T_c values up to 33 K.[9] The ionic endohedral metallofullerenes appear to require a countercation with at least 3+ charge and a fullerene larger than C_{60}, apparently so that enough counterions necessary to balance the negative charge of the fullerene anions will all fit inside the carbon cage.

All of these interactions of metals with carbon cages discussed involve carbon cages, such as C_{60}, which are also stable in the absence of metal complexation. Carbon cage structures, which are not stable in the absence of metal complexation, can be stabilized by incorporation of metals. The simplest example is tetrahedral C_{28} structure, which is not stable in the free state but which can be stabilized by an endohedral tetravalent metal atom in M@C_{28} (M = Ti, Zr, Hf, U), which have been detected by mass spectrometry.[10] This is analogous to the stabilization of unstable organic molecules, such as cyclobutadiene[11] or trimethylenemethane,[12] by complexation with a metal carbonyl fragment such as $Fe(CO)_3$. In addition, binary metal-carbon cage structures, called *metallo-carbohedrenes* or "met-cars" for short, are known based on polyhedra having both metal and carbon vertices.[13] The first met-car to be discovered was Ti_8C_{12}, which was reported in 1992 by Guo, Kerns, and Castleman[14] as being formed in a plasma reactor apparatus and detected by mass spectrometry. Subsequent experimental work on met-cars has involved studies of early transition metal met-cars not only of the type M_8C_{12} (M = Ti, V, Zr, Hf) but also of the type $M_{14}C_{13}$ [15] using mass spectrometry for their identification. In addition to met-cars containing early transition metals, met-cars containing copper also appear to exist as indicated by the detection of ions of the type $Cu_{2n+1}C_{2n}{}^+$ ($n \leq 10$), $Cu_7C_8{}^+$, $Cu_9C_{10}{}^+$, and $Cu_{12}C_{12}{}^+$ by Yamada and Castleman[19] from the gas phase reaction of copper clusters with heated acetylene.

This paper surveys some aspects of the topology of metal-carbon cages in which the metal is essential to the stabilization of the cage with a particular focus on the relationship of such structures to those of simple organometallic compounds. As such this paper is a sequel to recent papers by the author on the topology of metal-free carbon allotrope structures.[20,21] In this connection the following specific points are discussed in this paper: (1) stabilization of small fullerene by covalent bonding to endohedral metal atoms; and (2) the topology of binary metal-carbon cage structures.

Stabilization of small fullerenes by covalent bonding to endohedral metal atoms

The topology of fullerene polyhedra. Schmalz, Klein, and their collaborators[22,23] have considered possible criteria for polyhedra forming stable carbon cages having no external groups and hence corresponding to allotropes of elemental carbon. The cages are considered to be constructed by bending planar carbon networks upon themselves in two directions.[22,23] The resulting carbon cage polyhedra thus have the following features:

(1) a three-valent σ-bonded surface corresponding to sp^2 carbon atoms with an extra p orbital to participate in delocalization leading to resonance stabilization;

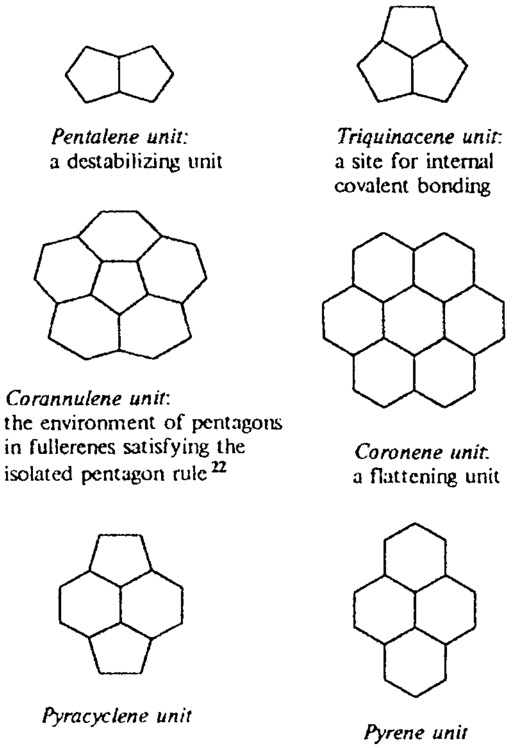
(2) a carbon cage topologically homeomorphic[24] to a sphere, *i.e.*, no "doughnut holes" as in a torus;

(3) all carbon rings (*i.e.*, polyhedral faces) are pentagons and hexagons to minimize ring strain and nonaromatic rings.

Some structural motifs in such fullerene polyhedra are depicted in Scheme 1. These structural motifs are given names corresponding to the trivial name of the simplest polycyclic hydrocarbon containing the structural motif in question.

Let us now consider some topological aspects of possible fullerene structures. The restriction to three σ bonds from each carbon vertex in the polyhedral surface

Scheme 1



Pentalene unit: a destabilizing unit

Triquinacene unit: a site for internal covalent bonding

Corannulene unit: the environment of pentagons in fullerenes satisfying the isolated pentagon rule[22]

Coronene unit: a flattening unit

Pyracyclene unit

Pyrene unit

relates the number of vertices (v) to the number of edges (e) by the following equation:

$$2e = 3v. \tag{1}$$

Furthermore, the number of vertices (v), edges (e), and faces (f) in a polyhedron homeomorphic to a sphere must satisfy Euler's relationship:

$$v - e + f = 2. \tag{2}$$

Combining Eqs. (1) and (2) gives the following two equations:

$$\sum_n nf_n = 2e, \tag{3}$$

$$v + \sum_n f_n = e + 2, \tag{4}$$

where f_n is the number of n-sided faces (or rings).

Eliminating e and v from Eqs. (1)—(4) gives the required balance between smaller and larger rings in a carbon cage described by the following equation ($n \geq 6$):

$$3f_3 + 2f_4 + f_5 - \sum_{n \geq 6}(n - 6)f_n = 12. \tag{5}$$

Equation (5) expresses the fact that 12 "units of curvature" are needed to close a graphite sheet into a cage homeomorphic to a sphere and shows that these units of curvature can be made up with minimum deviation from the hexagonal rings of graphite by using exactly 12 pentagons in accord with criterion (3).

Note that f_6 vanishes from Eq. (5) since $n - 6 = 0$ for $n = 6$. Fullerene polyhedra with only pentagonal and hexagonal faces, all vertices of degree 3, and 12 pentagonal faces thus satisfy Eq. (5) with any number of hexagonal faces. Motzkin and Grünbaum[25] have proven the following theorem relating to possible fullerenes satisfying these topological criteria.

Motzkin—Grünbaum theorem: For every even vertex count with $v \geq 24$ there exist at least one fullerene containing only pentagonal and hexagonal faces (and all vertices of degree 3) and the smallest fullerene has a regular dodecahedron structure with $v = 20$.

Fullerene structures with pentalene units: the isolated pentagon rule. These elementary topological concepts used alone predict a large number of possible fullerenes including fullerenes as small as C_{20}. Additional concepts must be introduced to select a limited number of preferred fullerene structures from this large number of possible fullerene structures and to rationalize the observation of C_{60} rather than C_{20} as the smallest isolable fullerene. In this connection an important additional concept for determining fullerene structures is the so-called *isolated pentagon rule* (IPR)[22] which avoids the destabilizing eight-membered pentalene-type cycle around any two pentagonal faces sharing an edge (see Scheme 1). Such pentalene units are destabilizing for the following reasons.

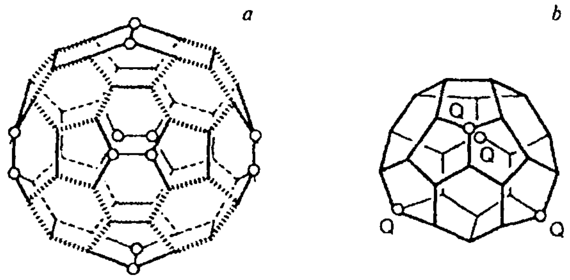
1. The Hückel criterion for aromaticity favors cycles containing ($4n + 2$) rather than $4n$ π-electrons, where n is an integer. Pentalene units have 8 π-electrons which is an unstable "$4n$-type" number.

2. Topological and geometrical considerations suggest that hexagonal faces favor flat surfaces (*e.g.*, graphite) whereas pentagonal faces favor curved surfaces (*e.g.*, the regular dodecahedron). Thus pentagonal faces lead to positive curvature whereas hexagonal faces favor zero curvature. Fusion of two pentagonal faces by sharing an edge concentrates much of the curvature of the polyhedral surface into a limited region leading to unnecessary strain in the corresponding fullerene. Klein[26,27] has proven the following theorem concerning the IPR.

IPR fullerene theorem: for every even vertex count $v \geq 70$ there exist at least one fullerene satisfying the IPR, and the smallest fullerene satisfying the IPR is the truncated icosahedron with $v = 60$.

Experimental observations are in excellent agreement with this theorem since the smallest isolable fullerene has been found to be C_{60} (Fig. 1, *a*), and the next higher isolable fullerene is C_{70}.

Small fullerenes with triquinacene units: covalent bonding to endohedral atoms. The stabilization of small fullerene structures by covalent bonding to an endohedral atom is related to the presence of triquinacene units (also called pentagonal trihedra[28]) in the carbon cage structure. Fullerene structures containing such triquinacene units (*e.g.*, C_{28}, Fig. 1, *b*) necessarily also contain



C_{60} (I_h) C_{28} (T_d)

Fig. 1. The structure of C_{60} (*a*) and C_{28} with the four central triquinacene carbon atoms indicated by Q (*b*).

Table 1. The smallest fullerene structures

Fullerene	f_5	f_6	q	Symmetry	Hexagon configuration	Triquinacene carbon configuration
C_{20}	12	0	20	I_h	No hexagons	Regular dodecahedron
C_{24}	12	2	12	D_{6d}	Linear	Hexagonal antiprism
C_{26}	12	3	8	D_{3h}	Trigonal planar	Bicapped trigonal prism
C_{28}	12	4	4	T_d	Tetrahedral	Tetrahedron

pentalene units (*i.e.*, two-thirds of a triquinacene unit) and thus violate the IPR. For this reason carbon cages containing triquinacene units are not stable in the absence of endohedral metal atoms. However, the central carbon atom of a triquinacene unit may be considered to have a "free valence" for bonding either to an external atom such as hydrogen or to form a covalent bond with an endohedral metal atom.[28] The configuration of triquinacene units in structures of fullerenes with small numbers of carbon atoms can therefore dictate the coordination polyhedron of an endohedral metal atom. The resulting endohedral metallofullerene structure thus has covalent metal-carbon bonds to the central carbon atoms of the triquinacene units and resembles the homoleptic σ-bonded alkyls and aryls of the same metal.

Consider a fullerene structure with a sufficiently small number of carbon atoms so that the 12 pentagonal faces required by Eq. (5) are sufficient to "isolate" the relatively small number of hexagonal faces. Such a small fullerene structure satisfies an *isolated hexagon rule* (IHR) analogous to the IPR discussed above. In this connection note that the number of hexagons in any fullerene, f_6, must satisfy the equation

$$f_6 = 0.5(v - 20), \qquad (6)$$

but the Motzkin—Grünbaum theorem[25] (see above) forbids a fullerene structure with 22 vertices and a single hexagonal face. Also note that a direct consequence of the IHR is the ability to draw a benzenoid structure with three alternating double bonds in each of the hexagonal face of the small fullerene without affecting the ability to have similar benzenoid structures in the limited number of other hexagonal faces. Thus the central carbon atom in the triquinacene units in an IHR fullerene structure can go from sp^2 to sp^3 hybridization by forming an external or endohedral covalent bond while still allowing all of the hexagonal rings to have favorable benzenoid structures.

Table 1 summarizes the smallest fullerene structures with q central triquinacene carbon atoms. These fullerene structures are described in some detail by Laidboeur, Cabrol-Bass, and Ivancuic[29] and all satisfy the IHR. Note that a fullerene as small as C_{30} with D_{5h} symmetry already violates the IHR since its structure contains a pentagonal ring of edge-sharing hexagons.

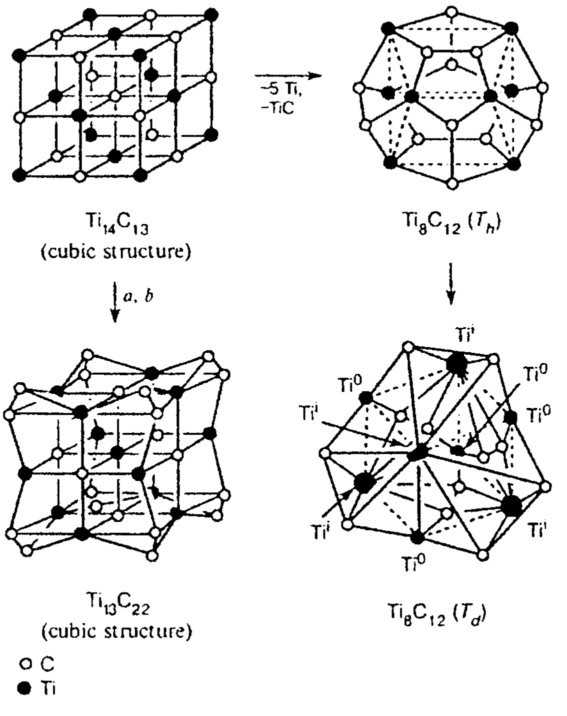
Among the IHR small fullerenes listed in Table 1 the tetrahedral C_{28} structure (see Fig. 1, *b*) is the only fullerene structure in which the triquinacene carbon configuration corresponds to a common coordination polyhedron, namely the tetrahedron, so that this C_{28} structure is uniquely suitable for covalent bonding to an endohedral atom. In fact, the shape of C_{28} may be simply regarded as that of a regular tetrahedron with four carbon atoms (the central triquinacene carbon atoms) at the vertices and a hexagon of carbon atoms, analogous to benzene, located on each of the four faces.[30] Each hexagon has a closed-shell electronic structure analogous to benzene corresponding to six electrons for each hexagon. This uses 24 of the total of 28 π-electrons in C_{28} thereby leaving an unpaired electron on each of the four central triquinacene carbon atoms (indicated by Q in Fig. 1, *b*), which therefore are well situated for tetrahedral coordination to an endohedral metal atom. In this connection, the species $M@C_{28}$ (M = Ti, Zr, Hf, U) have been experimentally detected by mass spectrometry.[10] The MC_4 tetrahedral central metal coordination presumed to be present in these $M@C_{28}$ species is thus similar to that in the corresponding tetrahedral metal alkyls, MR_4 (*e.g.*, M = Ti, Zr, Hf; R = Me, $PhCH_2$, Me_3CCH_2, Me_3SiCH_2, *etc.*)[31] thereby providing a connection between endohedral metal-carbon cage structures and organometallic structures.

The C_{28} fullerene forming the basis of the $M@C_{28}$ structures is the smallest member of a series of fullerenes in which the topologically required 12 pentagonal faces appear as four separate triquinacene units. Details of a geometrical construction for all such fullerenes have been recently described by Fowler and Cremona.[32]

The topology of binary metal-carbon cage structures

Early transition metal-carbon cage structures. The original binary metal-carbon cage structures were the early transition metal cages M_8C_{12} (M = Ti, Zr, Hf, V) reported by Castleman and co-workers.[13–16] Pilgrim and Duncan[17] subsequently discovered the large cluster $Ti_{14}C_{13}$ and showed that the photofragmentation of $Ti_{14}C_{13}$ leads to Ti_8C_{13}, presumably a carbon-centered M_8C_{12} cage, through a successive Ti atom extrusion. More recently Wang and Cheng[18] have shown that the stoichiometry $Ti_{13}C_{22}$ is favored in the negative ion mass spectra of titanium-carbon systems. The stoichiometries of all of these clusters were established only by mass spectrometry so that there is no direct experimental evidence for their structures. The relationship between probable structures of these clusters is depicted in Scheme 2. A natural structure for $Ti_{14}C_{13}$ is a 3×3×3 cube with carbon atoms in the center and at the midpoints of each of the 12 edges and titanium atoms at the vertices and face midpoints. The face midpoint titanium atoms in the $Ti_{14}C_{13}$ structure (see Scheme 2) form four direct Ti—C bonds in square planar coordination with the edge carbon atoms but there are no direct C—C bonds. The hypervalent carbon atom in the center of the cube is assumed to be within bonding distances of the six face titanium atoms similar to the interstitial carbon atoms in a variety of carbon-centered metal carbonyl octahedral clusters such as $Ru_6C_9(CO)_{17}$ [33] and $Co_6C(CO)_{13}$.[34] The $Ti_{14}C_{13}$ cluster can be regarded as a mixed oxidation state titanium derivative with an average titanium oxidation state of $3^5/_7$, not far from the group oxidation state of +4 for titanium assuming a −4 oxidation state for each of the 13 isolated carbon atoms.

Scheme 2

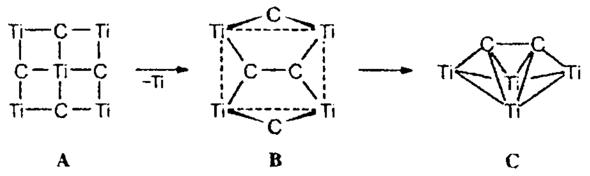


Note: *a* — Ti—C atoms interchange; *b* — replacement of carbon atoms at the vertices by C_2 units; Ti^i and Ti^0 are the inner and outer quartet of titanium atoms in the tetracapped tetrahedral structure, respectively.

The cluster $Ti_{13}C_{22}$ ($Ti_{13}C_6(C_2)_8$) found in the negative ion mass spectra of titanium-carbon systems[18] can also be assigned a cubic structure similar to $Ti_{14}C_{13}$ but with interchanged roles of the titanium and carbon atoms. Thus a relatively low-energy structure[18] for $Ti_{13}C_{22}$ is found to be the same 3×3×3 cube as $Ti_{14}C_{13}$ but with C_2 pairs at the vertices, carbon atoms at the face midpoints, and titanium atoms at the center and edge midpoints (see Scheme 2).

The conversion of $Ti_{14}C_{13}$ to Ti_8C_{12} can occur through a series of six reductive elimination processes involving in turn the six faces of the 3×3×3 titanium cube with concurrent formation of one C—C bond during each reductive elimination process. Such processes are at least formally similar to reductive elimination processes in transition metal chemistry such as those involved as the key steps of a number of homogeneous catalysis mechanisms.[35] However, eliminating the carbon "ligands" from the face titanium atoms ultimately leaves nothing bonded to the face titanium atoms so these titanium atoms, rather than the carbon "ligands" attached to them, is what is eliminated from the cluster structure. The effect of this titanium atom elimination on the structure around the face of a titanium cube is depicted in Scheme 3.

Scheme 3



Note: **A** — the $TiTi_{4/3}C_{4/2}$ face of $Ti_{14}C_{13}$ cub; **B** — the $Ti_{4/3}C_2$ pentalene unit of Ti_8C_{12} dodecahedron with T_h symmetry (lateral capping of a Ti_4 unit by a C_2 unit); **C** — the $Ti_{4/3}C_2$ unit of Ti_8C_{12} tetracapped tetrahedron with T_d symmetry (diagonal capping of a Ti_4 unit by a C_2 unit).

The Ti_8C_{12} structure produced by this sextuple titanium reductive elimination from $Ti_{14}C_{13}$ is the one originally proposed by Castleman and co-workers,[14] namely that of a regular dodecahedron with 8 titanium vertices and 12 carbon vertices in adjacent pairs so that the ideal I_h symmetry of a regular dodecahedron is reduced to its subgroup T_h by elimination of the fivefold symmetry. This Ti_8C_{12} structure can also be constructed from the Ti_8 cube of $Ti_{14}C_{13}$ (see Scheme 2) by capping each (square) face by a C_2 unit so that the carbon-carbon bond of the C_2 unit is parallel with two edges of the face; such capping can conveniently be designated as *lateral* capping (see Scheme 3). In such a laterally capped Ti_4 square face each carbon atom is bonded to two titanium atoms leading to a total of 24 Ti—C bonds in Ti_8C_{12}; the titanium atoms in the T_h structure of Ti_8C_{12} remain approximately at the vertices of a cube. From the tetravalency expected for carbon, the carbon-carbon bonds in these C_2 units can be inferred to be double bonds so that these C_2 units are formally C_2^{4-} derived from the complete deprotonation of ethylene. Similar C_2^{4-} units derived from ethylene are postulated[36,37] to occur in a variety of solid state metal carbides with experimental evidence in these cases coming from C=C bond distances in the range 1.32 to 1.47 Å consistent with double bonding. The formal titanium oxidation state in this Ti_8C_{12} ($Ti_8(C_2)_6$) structure, formulated with C_2^{4-} units, is +3. All of the titanium atoms are equivalent in the T_h structure of Ti_8C_{12}.

This T_h structure for Ti_8C_{12} derived directly from a regular Ti_8C_{12} dodecahedron or from a Ti_8 cube with all six faces laterally capped by C_2 units, although esthetically satisfying, is clearly unrealistic since the carbon-carbon double bonds in the C_2^{4-} units are not well located for π-bonding to the titanium atoms despite the fact that the titanium atoms are highly electron deficient (*i.e.*, far short of the favored 18-electron rare gas configuration). This is consistent with numerous computational studies,[38—42] which indicate that a T_d tetracapped tetrahedral structure (see Scheme 2) for Ti_8C_{12} is energetically much more favorable than the T_h structure noted above. In the T_d structure the eight titanium atoms are partitioned into four inner and four outer titanium atoms corresponding to vertices of degrees 6 and 3, respectively, in the underlying tetracapped tetrahedron, which can be obtained by a sextuple square-diamond process[43,44] from the original Ti_8 cube. The six Ti_4 quartets from the faces of the original cube are still recognizable in the tetracapped tetrahedron. Topologically, the T_d tetracapped tetrahedral structure for Ti_8C_{12} is derived from a Ti_8 cube by capping each of the six (square) faces with C_2 units so that the carbon-carbon bond of the C_2 unit is parallel to a diagonal of the square; such capping can conveniently be designated as *diagonal* capping (see Scheme 3). In the diagonally capped T_d structure of Ti_8C_{12} each carbon atom is bonded to three rather than only two titanium atoms so that the total structure has 36 rather than only 24 Ti—C bonds. The T_d structure with diagonal capping of each face by a C_2 unit thus uses the electrons of the C_2 units more effectively than the T_h structure with lateral capping of each face by a C_2 unit for relieving the extreme electron deficiency of the titanium atoms.

There remains the interesting question of the formal titanium oxidation state in the T_d tetracapped tetrahedral Ti_8C_{12} structure, particularly since this is the energetically most favored structure. If the six diagonally capping C_2 units are each considered as forming six Ti—C σ bonds, then they correspond to completely deprotonated ethane units, namely C_2^{6-}, and the titanium average formal oxidation state works out to be +4.5, which is unreasonable since it is larger than the group oxidation state of +4 for titanium. The C_2 units in the T_d structure of Ti_8C_{12} are more reasonably considered to be acetylide units, C_2^{2-}, forming two orthogonal π bonds with inner titanium atoms and two σ bonds with outer titanium atoms (see Scheme 3). The average formal titanium oxidation state in T_d tetracapped tetrahedral Ti_8C_{12} is +1.5. This can arise, for example, from the mean of the outer titanium atoms, *i.e.*, the caps, having the +3 oxidation state corresponding to their three Ti—C σ bonds apiece and the inner titanium atoms having the zero oxidation state corresponding to six Ti—C interactions arising from π bonds from three different carbon-carbon multiple bonds to each inner titanium atom.

Copper-carbon cage structures. Yamada and Castleman[19] have detected by mass spectrometry a variety of copper-carbon clusters obtained from the gas phase reaction of copper clusters with acetylene. The most common stoichiometries are $Cu_{2n+1}C_{2n}^+$ (n < 10), $Cu_7C_8^+$, $Cu_9C_{10}^+$, and $Cu_{12}C_{12}^+$. Dance[45] has discussed possible structures for these clusters based on prismatic, antiprismatic, and cuboctahedral configurations of copper atoms and discrete C_2 units capping quadrilateral faces of the copper polyhedra either laterally or diagonally (see above). Neutral copper atoms are sufficiently electron rich (*i.e.*, 11 valence electrons before considering electrons arising from carbon ligands) that copper-carbon clusters can be constructed according to Dance,[45] where the copper atoms have the favored 18-electron configuration of the next noble gas similar to that of most stable metal carbonyl derivatives and related organometallic compounds.

Consider for example the cuboctahedral structure proposed by Dance[45] for $Cu_{12}C_{12}$ ($Cu_{12}(C_2)_6$) in which each of the six square faces of the cuboctahedron are diagonally capped by C_2 units (Fig. 2). Each copper vertex of the cuboctahedron is bonded to four adjacent copper atoms and three carbon atoms of C_2 units nearest to the carbon vertex in question. If all of these bonds are assumed to be ordinary two-center two-electron σ bonds,

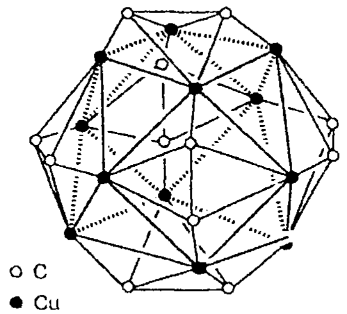


Fig. 2. The proposed structure for the $Cu_{12}C_{12}$ cluster containing a Cu_{12} cuboctahedron with the six square faces diagonally capped by C_2 units.

then each copper atom acquires a total of seven electrons from its 7 σ bonds (four Cu—Cu and three Cu—C) to attain the favored 18-electron rare gas electronic configuration.

* * *

Metals can interact with carbon cages in a variety of ways. Thus stable carbon cages (*i.e.*, fullerenes) function as electronegative olefins in their exohedral bonding to transition metals forming η^2 complexes involving one carbon-carbon double bond on the surface of the cage. Endohedral metallofullerenes are known in which a highly electropositive lanthanide (Ln) is located inside the carbon cage; these species can be given ionic formulations with lanthanide cations, Ln^{3+}, and fullerene anions. There is also mass spectroscopic evidence that fullerenes too small for independent existence can be stabilized by internal covalent bonding to an endohedral metal atom involving the central carbon atoms of triquinacene units, *i.e.*, pentagonal trihedra. The best example of such a small fullerene is tetrahedral C_{28}, which has four tetrahedrally oriented triquinacene units and accordingly appears to be stabilized by an endohedral tetrahedral tetravalent metal atom in $M@C_{28}$ (M = Ti, Zr, Hf, and U), identified by mass spectrometry.

Metal atoms can also occur as vertices of carbon cages. The presence of metal atoms as vertices of carbon cages changes radically their stoichiometries and therefore their structures. Early transition metals form cages such as $Ti_{14}C_{13}$ assumed to have titanium atoms at the vertices and face midpoints of a 3×3×3 cube and carbon atoms at the edge midpoints and center of the cube as well as $Ti_{13}C_{22}$, which is assumed to have a similar structure to $Ti_{14}C_{13}$ but with reversed roles of the titanium atoms and carbon atoms and with C_2 units rather than single carbon atoms at the vertices of the 3×3×3 cube. Elimination of the face metal atoms from the $Ti_{14}C_{13}$ structure as well as the center carbon atom, which has been achieved experimentally by photofragmentation, leads to the Ti_8C_{12} cluster, which was actually discovered before $Ti_{14}C_{13}$. The original proposed structure of Ti_8C_{12} based on a distorted pentagonal dodecahedron with the vertices decorated with titanium and carbon atoms to retain T_h symmetry, six distinct C_2 pairs, and 24 direct Ti—C interactions is less favorable energetically than an alternative structure based on a tetracapped tetrahedron with T_d symmetry, again six distinct C_2 pairs, and 36 direct Ti—C interactions. Copper also appears to be a vertex atom in metal-carbon cages, for which prismatic, antiprismatic, and cuboctahedral structures can be proposed in which the electronic configurations of the copper atoms approaches the favored 18-electron rare gas configuration.

The author expresses his gratitude to Prof. M. A. Duncan for helpful comments and suggestions during the preparation of this manuscript.

References

1. H. W. Kroto, A. W. Allaf, and S. P. Balm, *Chem. Rev.*, 1991, **91**, 1212.
2. F. Diederich and R. L. Whetten, *Acc. Chem. Res.*, 1992, **25**, 119.
3. P. J. Fagan, J. C. Calabrese, and B. Malone, *Acc. Chem. Res.*, 1992, **25**, 132.
4. P. J. Fagan, J. C. Calabrese, and B. Malone, *Science*, 1991, **252**, 1160.
5. A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead, and S. R. Parkin, *J. Am. Chem. Soc.*, 1991, **113**, 8953.
6. A. L. Balch, L. Hao, and M. M. Olmstead, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 188.
7. F. T. Edelmann, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 981.
8. Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, and R. E. Smalley, *J. Phys. Chem.*, 1991, **95**, 7564.
9. R. C. Haddon, *Acc. Chem. Res.*, 1992, **25**, 127.
10. T. Guo, M. D. Diener, Y. Chai, M. J. Alford, R. E. Haufler, S. M. McClure, T. Ohno, J. H. Weaver, G. E. Scuseria, and R. E. Smalley, *Science*, 1992, **257**, 1661.
11. R. E. Davis and P. E. Riley, *Inorg. Chem.*, 1980, **19**, 674.
12. A. Almenningen, A. Haaland, and K. Wahl, *Acta Chem. Scand.*, 1969, **23**, 1145.
13. A. W. Castleman, Jr., *Z. Phys. D*, 1993, **26**, 159.
14. B. C. Guo, K. P. Kerns, and A. W. Castleman, Jr., *Science*, 1992, **255**, 1411.
15. S. F. Cartier, B. D. May, and A. W. Castleman, Jr., *J. Am. Chem. Soc.*, 1994, **116**, 5295.
16. H. T. Deng, K. P. Kerns, and A. W. Castleman, Jr., *J. Am. Chem. Soc.*, 1996, **118**, 446.
17. J. S. Pilgrim and M. A. Duncan, *J. Am. Chem. Soc.*, 1993, **115**, 9724.
18. L. S. Wang and H. Cheng, *Phys. Rev. Lett.*, 1997, **78**, 2983.
19. Y. Yamada and A. W. Castleman, Jr., *Chem. Phys. Lett.*, 1993, **204**, 133.
20. R. B. King, *J. Phys. Chem.*, 1996, **100**, 15096.
21. R. B. King, in *Concepts in Chemistry*, Eds. D. H. Rouvray and E. Kirby, Research Studies Press, Ltd., Taunton (England), 1996, 114.
22. T. G. Schmalz, W. A. Seitz, D. J. Klein, and G. E. Hite, *J. Am. Chem. Soc.*, 1988, **110**, 1113.
23. X. Liu, T. G. Schmalz, and D. J. Klein, *Chem. Phys. Lett.*, 1992, **188**, 550.
24. N. J. Mansfield, in *Introduction to Topology*, Van Nostrand, Princeton (New Jersey), 1963, 40.
25. B. Grünbaum and T. S. Motzkin, *Can. J. Math.*, 1963, **15**, 744.
26. D. J. Klein and X. Liu, *J. Math. Chem.*, 1992, **11**, 199.
27. D. J. Klein and X. Liu, *Int. J. Quantum Chem. Symposium*, 1994, **28**, 501.
28. C. Milani, C. Giambelli, H. E. Roman, F. Alasia, G. Benedek, R. A. Broglia, S. Sanguinetti, and K. Yabana, *Chem. Phys. Lett.*, 1996, **258**, 554.
29. T. Laidboeur, D. Cabrol-Bass, and O. Ivanciuc, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 811.
30. K. Zhao and R. M. Pitzer, *J. Phys. Chem.*, 1996, **100**, 4798.
31. M. Bottrill, P. D. Gavens, J. W. Kelland, and J. McMeeking, in *Comprehensive Organometallic Chemisrty*, Eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, 3, 459.

32. P. W. Fowler and J. E. Cremona, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2255.
33. A. Sirigu, M. Bianchi, and E. Benedetti, *Chem. Comm.*, 1969, 596.
34. V. G. Albano, D. Braga, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1986, 981.
35. R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 2nd Ed., Wiley-Interscience, New York, 1994.
36. R. B. King, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1533 [*Russ. Chem. Bull.*, 1994, **43**, 1445 (Engl. Transl.)].
37. R. B. King, *J. Organomet. Chem.*, 1997, **536—537**, 7.
38. I. Dance, *Chem. Comm.*, 1992, 1779.
39. I. Dance, *J. Am. Chem. Soc.*, 1996, **118**, 2699.
40. Z. Lin and M. B. Hall, *J. Am. Chem. Soc.*, 1993, **115**, 11165.
41. M.-M. Rohmer, M. Bénard, C. Henriet, C. Bo, and J.-M. Poblet, *Chem. Comm.*, 1993, 1182.
42. M.-M. Rohmer, M. Bénard, C. Bo, and J.-M. Poblet, *J. Am. Chem. Soc.*, 1995, **117**, 508.
43. W. N. Lipscomb, *Science*, 1966, **153**, 373.
44. R. B. King, *Inorg. Chim. Acta*, 1981, **49**, 237.
45. I. Dance, *Chem. Comm.*, 1993, 1306.

Received September 1, 1997