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Chemical Applications of Topology and Group Theory. 34. Structure and Bonding in Titanocarbohedrene Cages[1]

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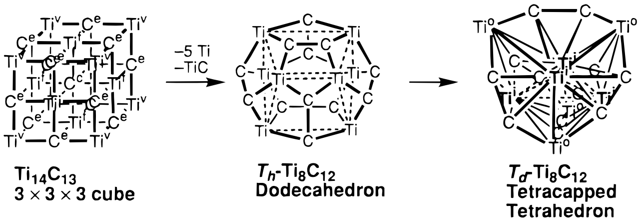
Chemical bonding models are developed for the titanocarbohedrenes $Ti_{14}C_{13}$ and Ti_8C_{12} by assuming that the Ti atoms use a six-orbital sd^5 manifold and there is no direct Ti···Ti bonding. In the 3 × 3 × 3 cubic structure of $Ti_{14}C_{13}$, the 8 Ti atoms at the vertices of the cube are divided into two tetrahedral sets, one Ti(III) set and one Ti(IV) set, and the 6 Ti atoms at the midpoints of the cube faces exhibit square planar TiC_4 coordination with two perpendicular three-center four-electron bonds. The energetically unfavorable T_h dodecahedral structure for Ti_8C_{12} has 8 equivalent Ti(III) atoms and C_2^{4-} units derived from the complete deprotonation of ethylene. In the more energetically favorable T_d tetracapped tetrahedral structure for Ti_8C_{12}, the C_2 units are formally dianions and the 8 Ti atoms are partitioned into inner tetrahedra (Ti^i) bonded to the C_2 units through three-center Ti−C_2 bonds and outer tetrahedra (Ti^o) bonded to the C_2 units through two-center Ti−C bonds. The Ti atoms in one of the Ti_4 tetrahedra are Ti(0) and those in the other Ti_4 tetrahedron are Ti(III). Among the two such possibilities, the lower energy form has the $(Ti^0)^o{}_4(Ti^{III})^i{}_4$ configuration, corresponding to dicarbene C_2 ligands with two unpaired electrons in the carbon−carbon π-bonding similar to the multiple bond in triplet O_2. This contrasts with the opposite $(Ti^{III})^o{}_4(Ti^0)^i{}_4$ configuration in the higher energy form of T_h-Ti_8C_{12}, corresponding to ethynediyl ligands with full C≡C triple bonds and unpaired electrons in the C sp hybrid orbitals for σ-bonding to Ti.

Introduction

An important development in metal cluster chemistry during the past decade was the discovery by Castleman and coworkers[2−4] of binary metal−carbon clusters of the stoichiometries M_8C_{12} (M = Ti, Zr, Hf, V, etc.), now known as metallocarbohedrenes or "metcars". Shortly after the original report of Ti_8C_{12}, Pilgrim and Duncan[5] discovered the larger cluster $Ti_{14}C_{13}$ and showed that the photofragmentation of $Ti_{14}C_{13}$ results in the successive extrusion of Ti atoms to give Ti_8C_{13}, presumably a carbon-centered Ti_8C_{12} cage. Subsequent work[6,7] suggests that Ti_8C_{12} can be isolated in the solid state although it appears to be highly air-sensitive and has been obtained only in a mixture with other Ti-containing materials.

The metallocarbohedrenes have been characterized mainly by their mass spectra, so that there is very limited direct experimental evidence for their structures. A natural structure for $Ti_{14}C_{13}$ (Figure 1) is a 3 × 3 × 3 cube with C atoms in the center (C^c) and at the midpoints of each of the 12 edges (C^e) and Ti atoms at the 8 vertices (Ti^v) and the 6 face midpoints (Ti^f). The originally proposed[2,8] structure for Ti_8C_{12} consists of a regular dodecahedron with 8 Ti and 12 C vertices in adjacent pairs (Figure 1), so that the ideal I_h symmetry of a regular dodecahedron is reduced to its subgroup T_h by elimination of the 5-fold symmetry. This structure for Ti_8C_{12} can be derived from the structure for $Ti_{14}C_{13}$ by the reductive elimination of the 6 Ti^f atoms. However, numerous computational studies,[9−14] indicate that a T_d structure for Ti_8C_{12} based on a Ti_8 tetracapped tetrahedron (Figure 1) is energetically much more favorable than the T_h structure. In the T_d structure of Ti_8C_{12}, the 8 Ti atoms are partitioned into 4 inner (Ti^i) and 4 outer (Ti^o) 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[15] from the original Ti_8 cube. In both the originally proposed T_h and the energetically more favorable T_d structures for Ti_8C_{12}, the 12 C atoms appear in 6 C_2 pairs rather than as 12 C atoms outside bonding distances from any other C atoms.



$Ti_{14}C_{13}$
3 × 3 × 3 cube

T_h-Ti_8C_{12}
Dodecahedron

T_d-Ti_8C_{12}
Tetracapped Tetrahedron

Figure 1. Conversion of the 3 × 3 × 3 cubic $Ti_{14}C_{13}$ to T_h-Ti_8C_{12} and subsequently to T_d-Ti_8C_{12}. Representative Ti atoms of the different types are labeled on the $Ti_{14}C_{13}$ and T_d-Ti_8C_{12} structures.

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These structure proposals for $Ti_{14}C_{13}$ and Ti_8C_{12} (Figure 1) are consistent with recent gas-phase vibrational spectroscopy data obtained from infrared resonance-enhanced multiphoton ionization spectra.[16] The vibrational spectrum of Ti_8C_{12} exhibits a band at 1395 cm^{-1} which is shifted to 1345 cm^{-1} in $Ti_8{}^{13}C_{12}$, suggesting assignment as a ν(C−C) frequency indicative of direct carbon−carbon bonding such as found in the C_2 units of the proposed structure. No comparable band is found in the vibrational spectrum of $Ti_{14}C_{13}$, in accord with the absence of direct C−C bonding in the 3 × 3 × 3 cubic structure (Figure 1).

This paper relates the structure and bonding in these titanocarbohedrenes to those in other organometallic and coordination compounds using the following assumptions: (1) Only s and d orbitals are used for chemical bonding, consistent with the models proposed by Landis and co-workers[17−19] for early transition metal hydrides and alkyls. (2) The Ti atoms are bonded only to C atoms, not to other Ti atoms, and the relatively long Ti···Ti distances prevent interaction between the unpaired electrons on different Ti(III) atoms.

The 3 × 3 × 3 Cube in $Ti_{14}C_{13}$

If the 13 C atoms in $Ti_{14}C_{13}$ are considered formally as C^{4-}, then 10 of the Ti atoms must be d^0 Ti^{4+} and the remaining 4 Ti atoms must be d^1 Ti^{3+} in order for $Ti_{14}C_{13}$ to be neutral. This cannot be achieved with the full O_h symmetry of the 3 × 3 × 3 cubic $Ti_{14}C_{13}$ structure, where there is no symmetry-equivalent set of only 4 Ti atoms. Symmetry reduction from O_h to T_d is necessary to separate the 8 Ti^v atoms of the $Ti_{14}C_{13}$ cube into two $Ti^v{}_4$ countertetrahedra, one of which consists of only Ti(III) and the other of only Ti(IV). This symmetry reduction is supported by the ab initio Hartree−Fock self-consistent field calculations of Rohmer, Bénard, Bo, and Poblet[13] but not by the gradient-corrected density functional calculations of Dance.[10] The separation of the four Ti(III) atoms in this $Ti_{14}C_{13}$ structure from each other prevents coupling of the unpaired electrons, leading to 4 unpaired electrons for a $Ti_{14}C_{13}$ unit.

The 3 × 3 × 3 cubic $Ti_{14}C_{13}$ structure can be constructed with 52 Ti−C bonds as follows: (1) The 4 $Ti(III)^v$ atoms are each bonded to 3 C atoms (all C^e), leading to 12 Ti−C bonds using trigonal pyramidal coordination. (2) The 4 $Ti(IV)^v$ atoms are each bonded to 4 C atoms ($C^c + 3C^e$), leading to 16 Ti−C bonds using "inverted" tetrahedral coordination[20] similar to the bridgehead C atoms in the stable tricyclo[2.1.0.0^{2,5}]pentane. (3) The 6 Ti^f atoms are each bonded to 4 carbon atoms (all C^e), leading to 24 Ti−C bonds. However, use of two three-center four-electron (3c-4e) bonds rather than four two-center two-electron (2c-2e) bonds is necessary, since a planar square, having an inversion center, cannot be formed by sd^3 hybrids, which use only gerade atomic orbitals.[1]

These 52 Ti−C bonds require 104 (=52 × 2) electrons, leaving 4 of the 108 valence electrons in $Ti_{14}C_{13}$ for the 4 tetrahedrally disposed $Ti(III)^v$ atoms.

Dodecahedral (T_h) versus Tetracapped Tetrahedral (T_d) Structures for Ti_8C_{12}

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 $Ti_{14}C_{13}$ cube with concurrent formation of one new 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.[21] However, eliminating the C "ligands" from the Ti^f atoms on the faces ultimately leaves nothing bonded to Ti^f, so that the Ti^f atoms, rather than the C "ligands" attached to them, are what is eliminated from the cluster structure. The effect of this Ti atom elimination on the structure around the face of a $Ti_{14}C_{13}$ cube is depicted in Figure 2.

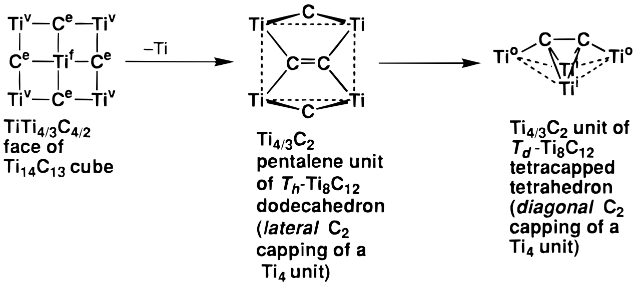

Figure 2. Effect of Ti atom elimination on the atoms in the face of the $Ti_{14}C_{13}$ cube to give T_h-Ti_8C_{12} and subsequently T_d-Ti_8C_{12}.

In the T_h-Ti_8C_{12} structure initially produced by this sextuple Ti reductive elimination from $Ti_{14}C_{13}$ (Figure 1), each C atom is bonded to 2 Ti atoms, leading to a total of 24 Ti−C σ bonds in T_h-Ti_8C_{12}. From the tetravalency of C, the C=C bonds in the C_2 units of T_h-Ti_8C_{12} 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. The formal Ti oxidation state in T_h-Ti_8C_{12} is thus +3, and all of the Ti atoms are equivalent with one unpaired electron, each leading to the anticipated 8 unpaired electrons[12,22] for T_h-Ti_8C_{12}.

A major drawback to this T_h-Ti_8C_{12} structure is the poor location of the C=C bonds in the $C_2{}^{4-}$ units for π-bonding to the Ti atoms to supplement the 24 Ti−C σ bonds. In the energetically more favorable tetracapped tetrahedral T_d-Ti_8C_{12} structure, each C atom is bonded to 3 rather than only 2 Ti atoms, so that the total structure has 36 rather than only 24 Ti−C bonding interactions.[9,10,13,14] These Ti−C bonding interactions can be partitioned into 12 2c-2e Ti−C bonds similar to the σ bonds found in metal alkyls and 12 3c-2e Ti−C_2 bonds similar to the π bonds in metal−olefin complexes. In T_d-Ti_8C_{12}, the 4 Ti atoms of the inner tetrahedron (Ti^i) each form three 3c-2e Ti−C_2 bonds whereas the 4 Ti atoms of the outer tetrahedron (Ti^o) each form three 2c-2e Ti−C bonds. The total of 24 titanium−carbon bonds (12 2c-2e Ti−C bonds and 12 3c-2e Ti−C_2 bonds) and the 6 C−C bonds in the 6 C_2 units require a total of 60 electrons. This leaves 20 electrons of the original 80 valence electrons of the T_d-Ti_8C_{12} unit to partition between the 8 Ti atoms, for an average $d^{2.5}$ configuration corresponding to an average formal Ti oxidation state of +1.5. This electron-counting scheme also corresponds to $C_2{}^{2-}$ for the C_2 ligands in T_d-Ti_8C_{12}.

The symmetry of the T_d-Ti_8C_{12} structure suggests a formal oxidation state assignment with the Ti atoms in one of the Ti_4 tetrahedra having a 0 oxidation state and the Ti atoms in the other Ti_4 tetrahedron having a +3 oxidation state, leading to the observed average Ti oxidation state of +1.5. Within this general scheme, there are two possible formal oxidation state

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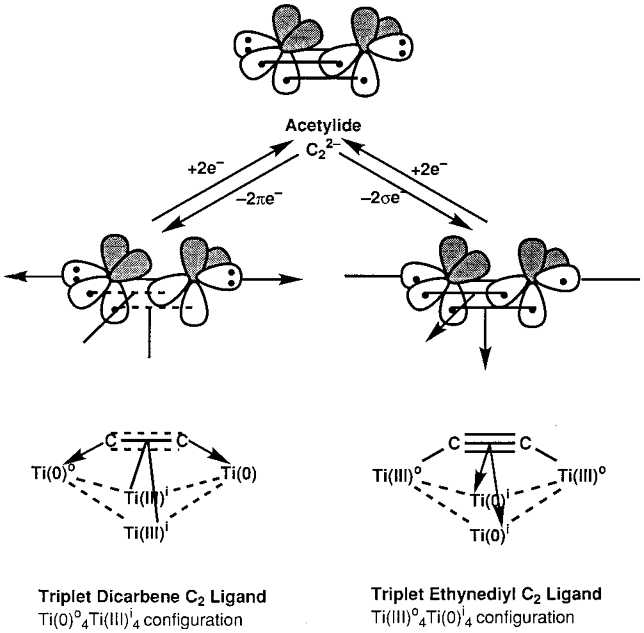

Triplet Dicarbene C_2 Ligand
Ti(0)$^o_4$Ti(III)$^i_4$ configuration

Triplet Ethynediyl C_2 Ligand
Ti(III)$^o_4$Ti(0)$^i_4$ configuration

Figure 3. Relationship between the dicarbene and ethynediyl C_2 ligands postulated for the $(Ti^0)^o_4(Ti^{III})^i_4$ and $(Ti^{III})^o_4(Ti^0)^i_4$ forms, respectively, of *T_d*-Ti_8C_{12}.

assignments, namely, $(Ti^0)^o_4(Ti^{III})^i_4$ and $(Ti^{III})^o_4(Ti^0)^i_4$, corresponding to different partitions of the electrons in the C_2 ligand (Figure 3) between the inner Ti^i_4 and outer Ti^o_4 tetrahedra. For both of these formal oxidation state assignments, the 20 nonbonding electrons available for the 8 Ti atoms are allocated so that each of the 4 Ti(0) atoms has two nonbonding electron pairs and each of the 4 Ti(III) atoms has a single electron, in accord with the d^4 and d^1 electronic configurations of Ti(0) and Ti(III), respectively. In the more energetically favorable[14] $(Ti^0)^o_4(Ti^{III})^i_4$ oxidation state assignment, the σ-bonding of Ti^o to the C_2 ligand, now considered as a neutral species for electron-counting purposes, corresponds to a dative bond with the a C_2 ligand furnishing both electrons of the 2c-2e $C \rightarrow Ti^o$ dative bond and the π-bonding of Ti^i to the C_2 ligand corresponds to 3c-2e covalent bonds with one electron for each bond coming from the C_2 ligand and the other electron coming from Ti^i. The neutral C_2 ligand can thus be considered to be a triplet "dicarbene" with a carbon−carbon bond order of "$1^1/_2$", similar to the oxygen−oxygen bond in normal triplet O_2, so that the two unpaired electrons reside in the π-bonding orbitals. However, in the less energetically favorable $(Ti^{III})^o_4(Ti^0)^i_4$ oxidation state assignment, the σ-bonding of Ti^o to the C_2 ligand corresponds to a covalent 2c-2e bond, with a Ti and C atom each furnishing one electron, and the π-bonding of Ti^i to the C_2 ligand consists of 3c-2e dative bonds, with both electrons for each bond coming from the C_2 ligand, similar to the usual picture of the olefin→metal dative bond in metal−olefin complexes.[21,23,24] In this case, the neutral C_2 ligand can be considered as an "ethynediyl" diradical with the two unpaired electrons in the two sp hybrid σ-orbitals used for the Ti^o-C 2c-2e bonding. Reduction of the neutral C_2 ligand to the acetylide C_2^{2-} eliminates this dicarbene−ethynediyl distinction (Figure 3) since, in the two-electron reduction of the dicarbene C_2, the two new electrons fill the two holes in the π-bonding orbitals whereas, in the two-electron reduction of the ethynediyl C_2, the two new electrons pair with the electrons in the σ-bonding orbitals, leading to the same C_2^{2-} "acetylide" species.

Any of the Ti_8C_{12} structures is obviously coordinately unsaturated, even relative to the 12-electron configuration of a filled sd^5 shell. In this connection, experimental work has found Ti_8C_{12} and related species to be reactive toward various small molecules (acetone, oxygen, water, halogens, ethylene, benzene, pyridine, alcohols, etc.),[4,25−30] leading to the following observations: (1) Reactions with π-bonding molecules such as ethylene and benzene stop at the adducts $Ti_8C_{12}L_4$. (2) Reactions with polar Lewis bases such as H_2O and alcohols go as far as $Ti_8C_{12}L_8$. (3) Chlorinating agents such as CH_3Cl convert Ti_8C_{12} to $Ti_8C_{12}Cl_4$.

These observations are consistent with reported ab initio computational studies[31] as well as the structural models discussed above in the following ways: (1) The π-bonding molecules only bind to the 4 Ti(0) sites where back-bonding involving the 4 d electrons and the Ti atom is feasible. The Ti(0) sites in an adduct such as $Ti_8C_{12}(C_2H_4)_4$ have the 12-electron configuration of a filled six-orbital sd^5 manifold. (2) Lewis bases not heavily involved in back-bonding can bind both to the 4 Ti(0) sites and to the 4 Ti(III), sites leading to the observed $Ti_8C_{12}L_8$ adducts. (3) A halogen adduct such as $Ti_8C_{12}Cl_4$ can be formulated as $[Ti_8C_{12}]^{4+}[Cl^-]_4$ in which all 4 of the Ti(III) atoms, namely, 4 of the Ti^i atoms in *T_d*-Ti_8C_{12}, have been oxidized to Ti(IV), leading to a species expected to be diamagnetic.

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