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Hexanuclear Cobalt Carbonyl Carbide Clusters: The Interplay between Octahedral and Trigonal Prismatic Structures

Jijun Zhao,[†] Jingcheng Xu,[†] and R. Bruce King*,[‡]

State Key Laboratory of Materials Modification by Laser, Electron, and Ion Beams, School of Physics and Optoelectronic Technology & College of Advanced Science and Technology, Dalian University of Technology, Dalian 116024, China, and Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

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The six-vertex cobalt carbonyl clusters $[Co_6C(CO)_n]^{2-}$ (n = 12, 13, 14, 15, 16) with an interstitial carbon atom have been studied by density functional theory (DFT). These DFT studies indicate that the experimentally known structure of $[Co_6C(CO)_{15}]^{2-}$ consisting of a Co_6 trigonal prism with each of its edges bridged by carbonyl groups is a particularly stable structure lying more than 20 kcal/mol below any other $[Co_6C(CO)_{15}]^{2-}$ structure. Addition of a CO group to this $[Co_6C(CO)_{15}]^{2-}$ structure gives the lowest energy $[Co_6C(CO)_{16}]^{2-}$ structure, also a Co_6 trigonal prism with one of the vertical edges bridged by two CO groups and the remaining eight edges each bridged by a single CO group. However, this $[Co_6C(CO)_{16}]^{2-}$ structure is thermodynamically unstable with respect to CO loss reverting to the stable trigonal prismatic $[Co_6C(CO)_{15}]^{2-}$. This suggests that 15 carbonyl groups is the maximum that can be attached to a Co_6C skeleton in a stable compound. The lowest energy structure of $[Co_6C(CO)_{14}]^{2-}$ has a highly distorted octahedral Co_6 skeleton and is thermodynamically unstable with respect to disproportionation to $[Co_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{13}]^{2-}$. The lowest energy $[Co_6C(CO)_{13}]^{2-}$ structure is very similar to a known stable structure with an octahedral Co_6 skeleton. The lowest energy $[Co_6C(CO)_{12}]^{2-}$ structure is a relatively symmetrical D_{3d} structure containing a carbon-centered Co_6 puckered hexagon in the chair form.

1. Introduction

The chemistry of metal carbonyl carbide clusters dates back to the discovery in 1962 of the iron carbonyl carbide $Fe_5C(CO)_{15}$ cluster as an unexpected stable side product isolated in trace quantities (<0.5%) after careful chromatographic separation from certain reactions of iron carbonyls with alkynes.[1] The structure of $Fe_5C(CO)_{15}$ was shown by X-ray diffraction to consist of an Fe_5 square pyramid with an interstitial carbon atom bonded to all five iron atoms. At the time of its discovery and structural elucidation $Fe_5C(CO)_{15}$ was considered to be an almost unprecedented example of five-coordinate carbon.

The very low yield (<1%) in the original synthesis of $Fe_5C(CO)_{15}$ discouraged the development of the chemistry of related metal carbonyl carbide clusters for some time. Eventually, however, other types of metal carbonyl carbide clusters were discovered including carbon-centered octahedral derivatives such as $Ru_6C(CO)_{17}$ (ref 2). In addition a variety of ionic metal carbonyl carbide clusters were discovered such as octahedral $[Co_6C(CO)_{13}]^{2-}$ (ref 3), trigonal prismatic $[Co_6C(CO)_{15}]^{2-}$ (ref 4), and square antiprismatic $[Co_8C(CO)_{18}]^{2-}$ (ref 4). The two clusters $[Co_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{13}]^{2-}$ are particularly interesting since their stoichiometries differ only by two carbonyl groups but their Co_6 skeletons are based on totally different polyhedra, namely, a trigonal prism for $[Co_6C(CO)_{15}]^{2-}$ and an octahedron for $[Co_6C(CO)_{13}]^{2-}$. In fact, two carbonyl groups can be thermally eliminated from the trigonal prismatic $[Co_6C(CO)_{15}]^{2-}$ to give the octahedral $[Co_6C(CO)_{13}]^{2-}$ simply by heating in tetrahydrofuran solution. This

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* To whom correspondence should be addressed. E-mail: rbking@chem.uga.edu.

[†] Dalian University of Technology.

[‡] University of Georgia.

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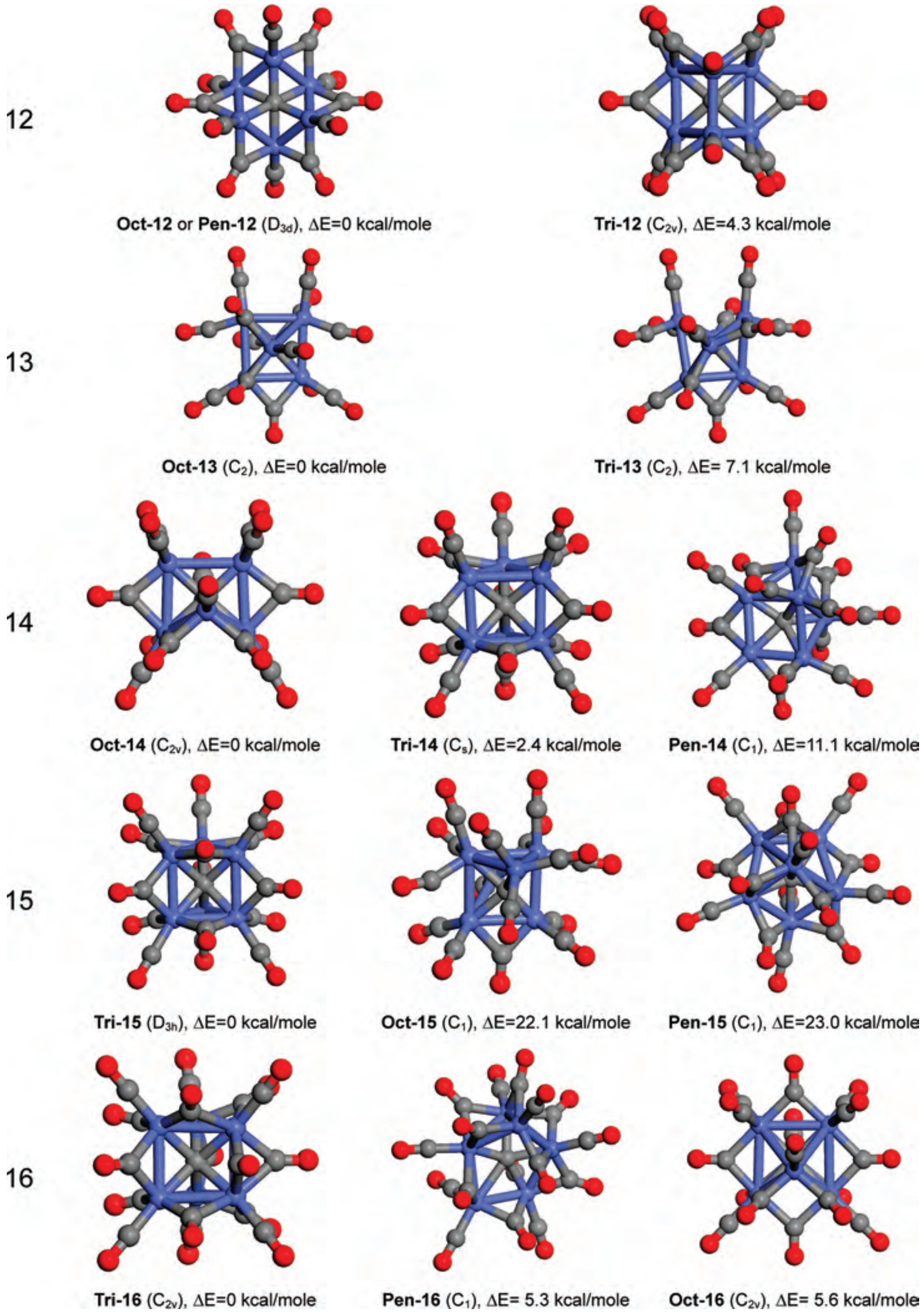

Oct-12 or **Pen-12** (D_{3d}), ΔE=0 kcal/mole

Tri-12 (C_{2v}), ΔE=4.3 kcal/mole

Oct-13 (C_2), ΔE=0 kcal/mole

Tri-13 (C_2), ΔE= 7.1 kcal/mole

Oct-14 (C_{2v}), ΔE=0 kcal/mole

Tri-14 (C_s), ΔE=2.4 kcal/mole

Pen-14 (C_1), ΔE=11.1 kcal/mole

Tri-15 (D_{3h}), ΔE=0 kcal/mole

Oct-15 (C_1), ΔE=22.1 kcal/mole

Pen-15 (C_1), ΔE=23.0 kcal/mole

Tri-16 (C_{2v}), ΔE=0 kcal/mole

Pen-16 (C_1), ΔE= 5.3 kcal/mole

Oct-16 (C_{2v}), ΔE= 5.6 kcal/mole

Figure 1. The 13 optimized structures of $[Co_6C(CO)_n]^{2-}$ (n = 12, 13, 14, 15, and 16).

reaction is remarkable in that loss of two carbonyl groups from $[Co_6C(CO)_{15}]^{2-}$ causes rearrangement of the Co_6 skeleton from a trigonal prism to an octahedron.

Historically the Wade–Mingos rules[5−8] were developed to understand the structures of stable borane derivatives. However, in many cases, they can be adapted to metal carbonyl clusters by using isolobal relationships. Thus in the octahedral $[Co_6C(CO)_{13}]^{2-}$ cluster there are 14 electrons available for skeletal bonding in the Co_6 unit with six of these electrons arising from six $Co(CO)_2$ groups, two more electrons from the thirteenth carbonyl group, four electrons from the interstitial carbon atom, and the final two electrons from the −2 charge. These 14 skeletal electrons correspond to the $2n + 2$ number of skeletal electrons for a deltahedron having six vertices, which is the Co_6 octahedron observed experimentally. Such deltahedra satisfying the Wade–Mingos rules[5−8] with $2n + 2$ skeletal electrons can be regarded as three-dimensional aromatic systems.[9,10] For boron hydride derivatives having $2n + 2$ skeletal electrons, for example, the dianions $B_nH_n^{2-}$ or the isoelectronic carboranes $C_2B_{n-2}H_n$, this aromatic stability is reflected in unusually high thermal

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and oxidative stability or low chemical reactivity or both. This three-dimensional aromatic stabilization is most apparent in 12-vertex icosahedral derivatives, such as $B_{12}H_{12}^{2-}$, and ten-vertex bicapped square antiprismatic derivatives, such as $B_{10}H_{10}^{2-}$.

The other known Co_6C cluster, namely, the trigonal prismatic $[Co_6C(CO)_{15}]^{2-}$, is seen to have 18 skeletal electrons using an electron-counting procedure similar to that used above for $[Co_6C(CO)_{13}]^{2-}$. These 18 skeletal electrons correspond to $2n + 6$ skeletal electrons for a six-vertex cluster corresponding to an *arachno* system expected by the Wade−Mingos rules to have a polyhedral structure with two openings, that is, nontriangular faces, or one large opening in a triangulated network. However, the actual structure of $[Co_6C(CO)_{15}]^{2-}$ is a trigonal prism with three rectangular faces, as well as two triangular faces,[4] and thus does not correspond to a six-vertex polyhedron expected by the Wade−Mingos rules for an *arachno* compound. An alternative skeletal bonding model for $[Co_6C(CO)_{15}]^{2-}$ uses the 18 skeletal electrons to form two-center two-electron Co−Co bonds along each of the nine edges of the trigonal prism. Using this model, $[Co_6C(CO)_{15}]^{2-}$ has a formally edge-localized skeleton analogous to cyclohexane whereas $[Co_6C(CO)_{13}]^{2-}$ is a globally delocalized three-dimensional aromatic system. Thus the double decarbonylation of $[Co_6C(CO)_{15}]^{2-}$ to give $[Co_6C(CO)_{13}]^{2-}$ may be viewed as a three-dimensional analogue of the dehydrogenation of cyclohexane to benzene.[11]

The double decarbonylation of $[Co_6C(CO)_{15}]^{2-}$ to give $[Co_6C(CO)_{13}]^{2-}$ is not likely to be a concerted process but instead involve a $[Co_6C(CO)_{14}]^{2-}$ intermediate. By the Wade−Mingos rules,[5−8] this intermediate would be a *nido* system with $2n + 4 = 16$ skeletal electrons for $n = 6$. Such a *nido* system by the Wade−Mingos rules should be a polyhedron with a single nontriangular face, namely, the pentagonal pyramid for a six-vertex system. Such a pentagonal pyramid is found in the known[12] hexaborane B_6H_{10}.

In this paper, we describe the use of density functional theory (DFT) to evaluate the chemistry of $[Co_6C(CO)_n]^{2-}$ ($n = 12$, 13, 14, 15, and 16) derivatives, both as models in general for metal clusters with interstitial carbon atoms and, more specifically, to understand the chemistry of the known $[Co_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{13}]^{2-}$, including the interplay between octahedral and trigonal prismatic structures. The systems with $n = 13$ and 15 represent the experimentally known structures and thus provide a test of our theoretical methods by comparison with experimental data. The system with $n = 14$ represents a potential reaction intermediate in the known double decarbonylation of $[Co_6C(CO)_{15}]^{2-}$ to give $[Co_6C(CO)_{13}]^{2-}$. The remaining two systems with $n = 12$ and 16 were studied in order to establish what might happen upon further decarbonylation of $[Co_6C(CO)_{13}]^{2-}$, possibly by photochemical methods, or addition of carbon monoxide to $[Co_6C(CO)_{15}]^{2-}$.

In order to facilitate investigation of the large number of possible structures for these $[Co_6C(CO)_n]^{2-}$ ($n = 12$, 13, 14, 15, and 16) clusters, the starting structures for these DFT optimizations were chosen to represent the geometries of greatest chemical interest. These include the octahedron and trigonal prism observed experimentally for $[Co_6C(CO)_{13}]^{2-}$ and $[Co_6C(CO)_{15}]^{2-}$, respectively, and the pentagonal pyramid, which is an unknown structure in M_6 metal carbonyl clusters but one predicted by the Wade−Mingos rules[5−8] for $[Co_6C(CO)_{14}]^{2-}$. By varying the arrangements of carbonyl groups on these three basic types of Co_6 skeletons, a total of more than a thousand initial structures were optimized. Those found to have the lowest energies for a given starting structure and number of carbonyl groups are considered to be the optimal structures and thus are discussed in this paper.

2. Theoretical Methods

DFT calculations were performed to optimize the large number of structural isomers of the $Co_6C(CO)_n$ clusters. We employed a DMol package[13] and adopted the generalized gradient approximation (GGA) with the PW91 functional[14] for exchange−correlation interaction. A DFT-based relativistic semi-core pseudopotential (DSPP) fitted to all-electron relativistic results[15] and a double numerical basis set including d-polarization functions (DND)[13] were used in the calculations. The convergence criterion was set to be 10^{-6} a.u. for the total energy in the self-consistent field iterations. Normal mode analyses were performed on the lowest-energy configurations for each cluster stoichiometry to confirm that they are all true minima on the potential energy surface.

Because of the large number of possible structures, we focused on three Co_6 skeletons for our starting configurations, namely, the octahedron (Oct) found experimentally in $[Co_6C(CO)_{13}]^{2-}$ (ref 3), the trigonal prism (Tri) found experimentally in $[Co_6C(CO)_{15}]^{2-}$ (ref 4), and the pentagonal pyramid (Pen) found in other structures such as B_6H_{10} (ref 12). For each Co_6 skeleton of different stoichiometry, we considered all possible arrangements of carbonyl groups leading to a total of 1165 different starting structures (see Table S1, Supporting Information, for a detailed list). We also investigated 330 starting structures in which the Co_6 geometry is a square pyramid capped on one of the triangular faces. However, no new structures competitive in energy were obtained from this starting point.

Among the 15 possible combinations of the five stoichiometries and the three Co_6 starting polyhedra, two of the starting polyhedra for both $[Co_6C(CO)_{12}]^{2-}$ and $[Co_6C(CO)_{13}]^{2-}$ gave the same final optimized structures. The 13 final optimized structures of lowest energies for $[Co_6C(CO)_n]^{2-}$ ($n = 12$, 13, 14, 15, and 16) after considering all of these starting structures are depicted in Figure 1. Figure 2 depicts the underlying Co_6 polyhedra in the structures depicted in Figure 1 showing all of the Co−Co edges in the starting structures, even those >3.0 Å. The Co−Co distances of the underlying polyhedra depicted in Figure 2 are listed in Table 1 with the clearly nonbonding distances in square brackets. The distances between the interstitial carbon atoms and the cobalt vertices all fell within the range 1.81 to 2.09 Å except for those in the three highly distorted higher energy structures **Pen14**, **Oct15**,

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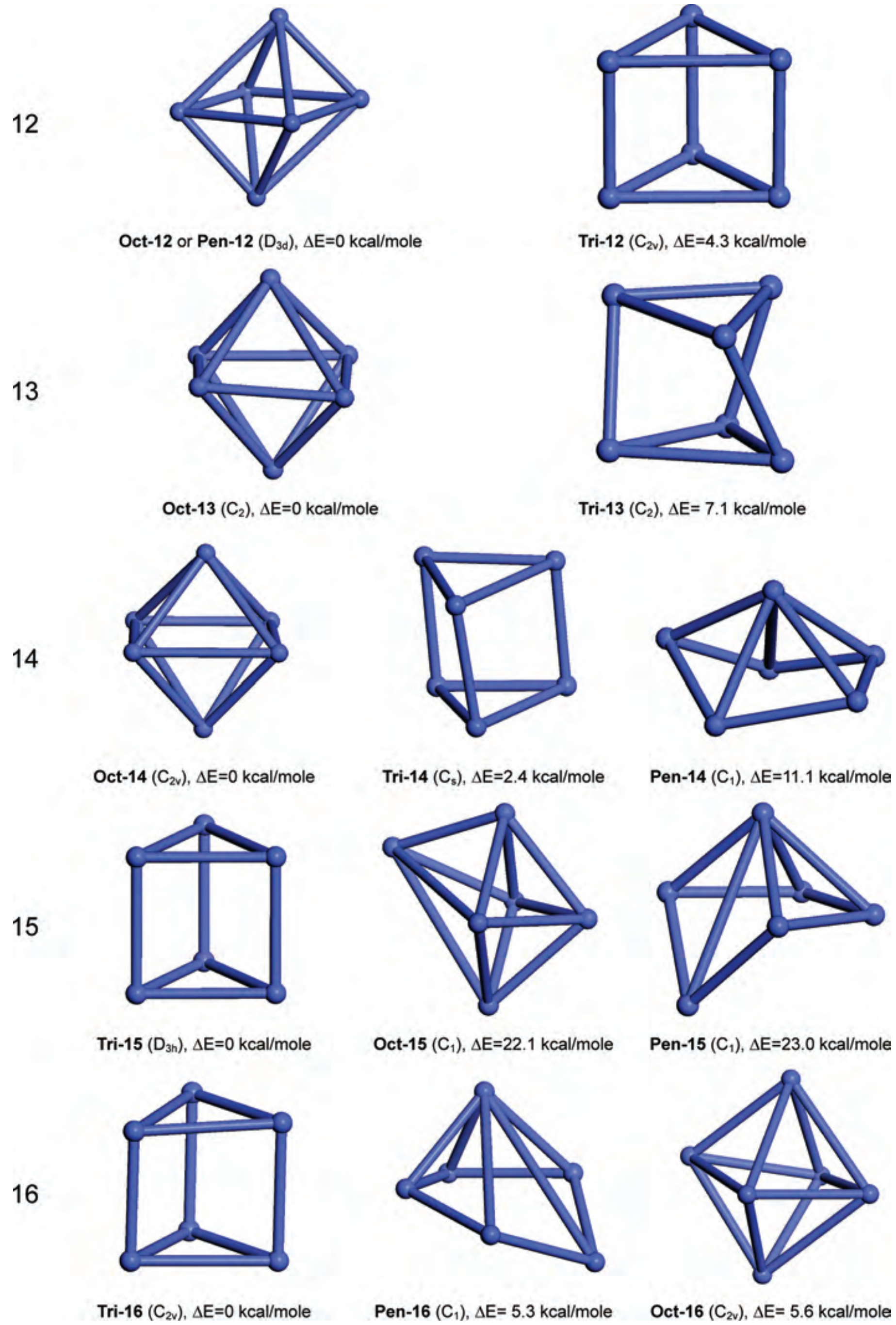

Figure 2. The underlying Co_6 polyhedra of the structures depicted in Figure 1 including all of the edges of the original polyhedron, even those longer than 3.0 Å.

and **Pen16**. These exceptionally long Co−C distances are discussed in the text.

3. Results and Discussion

3.1. Structures and Energies. 3.1.1. $[Co_6C(CO)_{12}]^{2-}$. In the lowest energy and relatively symmetrical D_{3d} structure for $[Co_6C(CO)_{12}]^{2-}$ (**Oct12** in Figure 1), the six cobalt atoms form a puckered hexagon in the chair conformation with a Co−Co bond length of 2.43 Å (Table 1). Each cobalt atom bears a terminal carbonyl group, and there are single carbonyl groups bridging each Co−Co edge. A second higher energy **Tri12** structure (Figure 1) is also found for $[Co_6C(CO)_{12}]^{2-}$ at 4.3 kcal/mol above **Oct12**. The Co_6 unit in **Tri12** forms a pair of rectangles sharing an edge in a structural unit related to the carbon skeleton of bicyclo[2.2.0]butane. The outer carbonyl bridged edges of **Tri12** are 2.45 Å (Table 1), which is very close to the likewise carbonyl bridged edges in **Oct12**. The unbridged Co−Co edge of **Tri12** common to both rectangles is only slightly longer at 2.48 Å. All six outer edges of the Co_6 unit have bridging carbonyl groups and each cobalt atom has a terminal carbonyl group.

3.1.2. $[Co_6C(CO)_{13}]^{2-}$. The lowest energy structure for $[Co_6C(CO)_{13}]^{2-}$ is the distorted octahedral structure **Oct13** (Figure 1), which is the structure found experimentally.[3] Among the 12 Co−Co edges of the Co_6 octahedron in **Oct13**,

Table 1. The Co−Co Distances in the $[Co_6C(CO)_n]^{2-}$ (n = 12, 13, 14, 15, and 16) Structures with Those Considered Nonbonding in Square Brackets

structure	no. Co−Co bonds	Co−Co distance (Å)*
		$Co_6C(CO)_{12}$
Oct12 (D_{3d})	6	2.43(6), [2.91, 2.94, 2.95, 2.97, 2.98, 3.01]
Tri12 (C_{2v})	7	2.44(2), 2.45(3), 2.46, 2.48, [2.81, 2.85]
		$Co_6C(CO)_{13}$
Oct13 (C_2)	12	2.50, 2.51(3), 2.52, 2.67, 2.68, 2.74, 2.75, 2.77, 2.86, 2.87
Oct13 (expt)	12	2.47(2), 2.48, 2.50, 2.51, 2.65, 2.66, 2.67, 2.71, 2.75, 2.88, 2.93
Tri13 (C_2)	9	2.46, 2.48, 2.50(2), 2.51, 2.63, 2.66, 2.79(2)
		$Co_6C(CO)_{14}$
Oct14 (C_{2v})	12	2.56(4), 2.58, 2.59, 2.76, 2.81(4), 2.96
Tri14 (C_s)	9	2.49, 2.50, 2.53(2), 2.54, 2.57, 2.59, 2.65, 2.78
Pen14 (C_1)	9	2.43(2), 2.50, 2.52(2), 2.56, 2.58, 2.64, 2.68, [3.50]
		$Co_6C(CO)_{15}$
Tri15 (D_{3h})	9	2.55(6), 2.61(3)
Tri15 (expt)	9	2.54 (6), 2.58 (3)
Oct15 (C_1)	10	2.53(3), 2.54, 2.55(2), 2.60, 2.61, 2.63, 2.64, [3.56, 3.61]
Pen15 (C_1)	9	2.39, 2.50, 2.51, 2.55, 2.59(2), 2.60, 2.68, 2.70, [3.67]
		$Co_6C(CO)_{16}$
Tri16 (C_{2v})	9	2.44, 2.56(2), 2.60(2), 2.73(2), 2.74(2)
Pen16 (C_1)	8	2.50(2), 2.51, 2.53, 2.55, 2.56, 2.58, 2.63, [3.62, 4.07]
Oct16 (C_{2v})	12	2.62, 2.63, 2.64(2), 2.81, 2.83, 2.84, 2.85,2.86, 2.87, 2.88, 2.98

* Number of equivalent Co−Co bond distances given in parentheses.

five of them with lengths in the narrow range of 2.51 ± 0.01 Å are each bridged by a single carbonyl group (Table 1). This compares with the experimentally found values of 2.46 to 2.51 Å.[3] The seven remaining unbridged Co−Co edges are all significantly longer with lengths ranging from 2.67 to 2.87 Å (Table 1). This compares with the experimentally found range of 2.65 to 2.93 Å. Two cobalt atoms sharing an unbridged edge each have two terminal carbonyl groups. The remaining four cobalt atoms each have a single terminal carbonyl group.

A second structure **Tri13** for $[Co_6C(CO)_{13}]^{2-}$ was found at 7.1 kcal/mol above **Oct13**. The Co_6 framework in **Tri13** is derived from severe distortion of the trigonal prism starting structure but retaining the original nine Co−Co edges. Five of these edges have single bridging carbonyl groups and lengths in the range 2.46 to 2.51 Å (Table 1). The remaining four edges are unbridged with a wider 2.63 to 2.79 Å range of lengths. As in **Oct13**, two cobalt atoms each have two terminal carbonyl groups and the remaining cobalt atom has a single terminal carbonyl group.

3.1.3. $[Co_6C(CO)_{14}]^{2-}$.

The lowest energy structure for $[Co_6C(CO)_{14}]^{2-}$ is **Oct14** with a highly distorted octahedral Co_6 skeleton. Six of the twelve edges of **Oct14** are bridged by carbonyl groups and have lengths in the narrow range of 2.56 to 2.59 Å (Table 1). The remaining six unbridged edges are longer with lengths in the wider 2.76 to 2.96 Å range. Two of the cobalt atoms in **Oct14** each have terminal carbonyl groups. The remaining four cobalt atoms each have a single terminal carbonyl group.

The next higher energy structure for $[Co_6C(CO)_{14}]^{2-}$ is **Tri14** at 2.5 kcal/mol above Oct14. The Co_6 skeleton in **Tri14** is a distorted trigonal prism with eight of the nine edges bridged by carbonyl groups. Each cobalt atom has a single terminal carbonyl group. The unique unbridged Co−Co edge is an edge of a triangular face of length 2.78 Å (Table 1). The eight bridged Co−Co edges are all shorter with a wide range of lengths from 2.49 to 2.65 Å.

The final structure for $[Co_6C(CO)_{14}]^{2-}$ is **Pen14** at 11.1 kcal/mol above **Oct14**. The starting pentagonal pyramid in **Pen14** is clearly recognizable in the final structure since only one of its 10 Co−Co edges, namely an apical-basal edge, is lengthened to 3.50 Å, which is clearly a nonbonding distance. Of the nine remaining Co−Co edges, five are bridged by carbonyl groups with lengths in the range of 2.43 to 2.58 Å (Table 1). This range overlaps the 2.50 to 2.68 Å lengths of the unbridged Co−Co edges. The original pyramid apex and two basal cobalt atoms have two terminal carbonyl groups. The remaining three cobalt atoms each have a single terminal carbonyl group. The Co−C distance from the interstitial carbon atom to the cobalt atom bridging the basal edge of the Co_5 square pyramid in **Pen14** is an exceptionally long 2.51 Å.

3.1.4. $[Co_6C(CO)_{15}]^{2-}$.

The lowest energy structure for $[Co_6C(CO)_{15}]^{2-}$ is **Tri15** with a trigonal prismatic Co_6 skeleton. This predicted structure is very close to the experimental structure determined by X-ray crystallography.[4] Each of the nine edges of the prism is bridged by a single carbonyl group, and each cobalt atom bears a single terminal carbonyl group. The horizontal or basal edges of the trigonal prism are predicted to be 2.55 Å as compared with the experimental value[4] of 2.54 Å (Table 1). Similarly the vertical or interbasal edges are predicted to be 2.61 Å as compared with the experimental value of 2.58 Å. The predicted six Co−C distances of 1.97 Å in **Tri15** are close to the 1.95 Å distances found experimentally. The carbonyl carbon atoms in **Tri15** form a D_{3h} 15-vertex Frank−Kasper deltahedron[16] with 12 degree-5 vertices and three degree-6 vertices forming an equilateral triangle capping the faces of the underlying trigonal prism.[17]

This experimentally known[4] trigonal prismatic structure **Tri15** appears to be a particularly favorable structure since the next higher energy structure found for $[Co_6C(CO)_{15}]^{2-}$

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is **Oct15** at 22.1 kcal/mol above **Tri15**. The Co_6 polyhedron in **Oct15** is derived from an octahedron by stretching two edges from the same vertex to clearly nonbonding lengths of 3.56 and 3.61 Å. This gives a Co_5 square pyramid with one of the basal edges bridged by the sixth and remaining cobalt atom. The cobalt apex of the square pyramid has only a single terminal carbonyl group. The cobalt atom bridging a basal edge of the square pyramid has three terminal carbonyl groups consistent with its more exposed position in the structure. The distance from this cobalt atom to the interstitial carbon atom is elongated to 2.43 Å. The remaining cobalt atoms have two terminal carbonyl groups. The lengths of the three bridged Co−Co edges fall in the narrow range of 2.53−2.54 Å (Table 1). The lengths of the seven unbridged Co−Co edges fall in the somewhat wider range of 2.53−2.64 Å.

The final structure found for $[Co_6C(CO)_{15}]^{2-}$ is **Pen15** at 23.0 kcal/mol above **Tri15**. The Co_6 polyhedron in **Pen15** is derived from a pentagonal pyramid by lengthening one of the apical−basal edges to the obviously nonbonding distance of 3.67 Å. In **Pen15**, there is a unique carbonyl group bridging the three cobalt atoms in a face of the polyhedron. In addition, there are seven edge-bridging carbonyl groups and seven terminal carbonyl groups. The basal cobalt atom at the site of the broken edge is the one bearing two terminal carbonyl groups. The bonding Co−Co distances range from an unusually short 2.39 Å at one of the edges of the carbonyl-bridged face to 2.70 Å (Table 1).

3.1.5. $[Co_6C(CO)_{16}]^{2-}$. The lowest energy structure of $[Co_6C(CO)_{16}]^{2-}$ is **Tri16** (Figure 1), which is closely related to **Tri15** by adding a second carbonyl bridge to one of the vertical edges of the Co_6 prism. The length of this doubly bridged Co−Co vertical edge is 2.44 Å as compared with the 2.60 Å lengths of the two singly bridged Co−Co vertical edges (Table 1). The four horizontal or basal edges connected to the cobalt atoms of the unique doubly bridged vertical edge are 2.73 or 2.74 Å. The remaining two horizontal edges are shorter at 2.56 Å.

The next higher energy $[Co_6C(CO)_{16}]^{2-}$ structure is **Pen16** at 5.3 kcal/mol above **Tri16**. The Co_6 skeleton can be described as two pentagon "Siamese twins" sharing four of their five vertices and with a total of eight edges. Each of the eight edges is bridged by a single carbonyl group. Two of the six cobalt atoms each have two terminal carbonyl groups. The remaining four cobalt atoms each have a single bridging carbonyl group. The lengths of the edges in **Pen16** range from 2.50 to 2.63 Å (Table 1). Only four of the cobalt atoms are within the usual 1.81 to 2.09 Å of the interstitial carbon atom. The remaining two cobalt atoms have distances of 2.32 and 2.70 Å to the interstitial carbon atom.

The final structure found for $[Co_6C(CO)_{16}]^{2-}$ is **Oct16** at 5.6 kcal/mol above **Tri16**. In **Oct16**, one of the 12 edges of the underlying octahedron is lengthened to 2.98 Å. Four of the remaining edges form a quadrilateral with edges in the narrow range 2.62−2.64 Å (Table 1). The remaining edges include seven edges with lengths in the range 2.81−2.88 Å plus the original edge lengthened to 2.98 Å, considered just barely outside the bonding range. Eight of the edges, including the lengthened 2.98 Å edge, are each bridged by a single carbonyl group leaving four unbridged edges. Two cobalt atoms joined by an edge of length 2.85 Å each have two terminal carbonyl groups.

Table 2. Carbonyl Dissociation and Disproportionation Energies in kcal/mol

reaction	energy
$[Co_6C(CO)_{16}]^{2-} \rightarrow [Co_6C(CO)_{15}]^{2-} + CO$	−20.4
$[Co_6C(CO)_{15}]^{2-} \rightarrow [Co_6C(CO)_{14}]^{2-} + CO$	38.5
$[Co_6C(CO)_{14}]^{2-} \rightarrow [Co_6C(CO)_{13}]^{2-} + CO$	19.1
$[Co_6C(CO)_{13}]^{2-} \rightarrow [Co_6C(CO)_{12}]^{2-} + CO$	42.1
$2[Co_6C(CO)_{15}]^{2-} \rightarrow [Co_6C(CO)_{16}]^{2-} + [Co_6C(CO)_{14}]^{2-}$	59.0
$2[Co_6C(CO)_{14}]^{2-} \rightarrow [Co_6C(CO)_{15}]^{2-} + [Co_6C(CO)_{13}]^{2-}$	−19.3
$2[Co_6C(CO)_{13}]^{2-} \rightarrow [Co_6C(CO)_{14}]^{2-} + [Co_6C(CO)_{12}]^{2-}$	23.0

3.2. Thermodynamics: CO Dissociation Energies. Table 2 shows the energies for the successive loss of carbonyl groups from $[Co_6C(CO)_n]^{2-}$ based on the lowest energy structures. The most carbonyl-rich species studied in this work, namely, $[Co_6C(CO)_{16}]^{2-}$, loses exothermically one of its CO groups to give the apparently very stable $[Co_6C(CO)_{15}]^{2-}$. This suggests that 15 is the maximum number of CO groups that can be introduced into a stable $[Co_6C(CO)_n]^{2-}$ structure. The CO group readily lost from $[Co_6C(CO)_{16}]^{2-}$ to give $[Co_6C(CO)_{15}]^{2-}$ is most likely one of the two CO groups doubly bridging the unique edge in **Tri16** (Figure 1). Carbonyl dissociation from the lowest energy structures of the other stoichiometries $[Co_6C(CO)_n]^{2-}$ (n = 15, 14, or 13) is endothermic with the dissociation energy of CO from $[Co_6C(CO)_{14}]^{2-}$ at 19.1 kcal/mol, being less than half of the dissociation energy of CO from $[Co_6C(CO)_{15}]^{2-}$ or $[Co_6C(CO)_{13}]^{2-}$ at 38.5 or 42.1 kcal/mol, respectively. The latter dissociation energies are comparable with the bond dissociation energies[18] of 27, 41, and 37 kcal/mol for the simple metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively.

Table 2 also lists the energies for the disproportionation reactions $2[Co_6C(CO)_n]^{2-} \rightarrow [Co_6C(CO)_{n+1}]^{2-} + [Co_6C(CO)_{n-1}]^{2-}$, again based on the lowest energy structures. The known $[Co_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{13}]^{2-}$ are the most stable toward such disproportionation at 59.0 and 23.0 kcal/mol, respectively. However, the unknown $[Co_6C(CO)_{14}]^{2-}$ is thermodynamically unstable with respect to such disproportionation at −19.4 kcal/mol. These disproportionation energies are consistent with the fact that $[Co_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{13}]^{2-}$ are stable enough to be isolated, whereas the intermediate $[Co_6C(CO)_{14}]^{2-}$ has never been isolated or detected by spectroscopic methods.

3.3. Vibrational Frequencies. The infrared ν(CO) frequencies (Table S2 in the Supporting Information) are diagnostic as to whether the carbonyl groups are terminal, edge-bridging, or the exceptional example of a face-bridging carbonyl group in **Pen15**. Thus the terminal carbonyl groups are seen to exhibit ν(CO) frequencies in the range 2040−1900 cm^{-1} whereas the usual types of edge-bridging carbonyl groups exhibit significantly lower ν(CO) frequencies in the range 1860−1770 cm^{-1}. The exceptional face-bridging

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(18) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 12060.

carbonyl group in **Pen15** is predicted to exhibit a ν(CO) frequency at 1748 cm^{-1} (Table S2, Supporting Information) These trends are very typical in metal carbonyl chemistry.

The predicted ν(CO) infrared spectra for any of the derivatives discussed in this paper are so complicated that it is unlikely that all of the individual predicted ν(CO) frequencies will be resolved in actual experimental data. This is especially true since all of the species discussed in this paper are ionic requiring infrared spectra to be obtained in polar solvents such as tetrahydrofuran or acetonitrile or in the solid state where significant line broadening is expected. For example, the infrared spectrum of $[Et_4N]_2[Co_6C(CO)_{13}]$ in tetrahydrofuran is reported[3] to exhibit infrared ν(CO) bands at 2020vw, 1963vs, 1938m(sh), and 1804 cm^{-1} corresponding to the predicted ν(CO) frequencies (Table S2, Supporting Information) at 2025 cm^{-1}, {1982, 1976 cm^{-1} unresolved}, {1954, 1943, 1942, 1932, 1909 cm^{-1} unresolved}, and {1841, 1834, 1823, 1815, 1804 cm^{-1} unresolved}, respectively. Similarly, salts of $[Co_6C(CO)_{15}]^{2-}$ in acetonitrile are reported[4] to exhibit ν(CO) bands at 1987vs, 1824s, and 1780mw cm^{-1} corresponding to the predicted (CO) frequencies (Table S2, Supporting Information) at {1989, 1982, 1973, 1971, 1963 cm^{-1} unresolved}, {1872, 1851, 1847, 1842 cm^{-1} unresolved}, and {1821, 1818, 1813, 1808, 1806 cm^{-1} unresolved}, respectively. Thus the agreement between experimental and predicted ν(CO) frequencies for the known $[Co_6C(CO)_{13}]^{2-}$ and $[Co_6C(CO)_{15}]^{2-}$ is rather good (within ±25 cm^{-1}) when the poor resolution of ν(CO) spectra in polar solvents is considered.

4. Conclusions

These DFT studies indicate that the experimentally known structure of $[Co_6C(CO)_{15}]^{2-}$ consisting of a carbon-centered Co_6 trigonal prism with each of its edges bridged by carbonyl groups is a particularly stable structure lying more than 20 kcal/mol below any other $[Co_6C(CO)_{15}]^{2-}$ structure. Addition of a CO group to this $[Co_6C(CO)_{15}]^{2-}$ structure gives the lowest energy $[Co_6C(CO)_{16}]^{2-}$ structure, also a Co_6 trigonal prism with one of the vertical edges bridged by two CO groups and the remaining eight edges each bridged by a single CO group. However, this $[Co_6C(CO)_{16}]^{2-}$ structure is thermodynamically unstable with respect to CO loss reverting to the stable trigonal prismatic $[Co_6C(CO)_{15}]^{2-}$ structure. This suggests that 15 carbonyl groups is the maximum that can be attached to a Co_6C unit in a stable compound.

The lowest energy structure of $[Co_6C(CO)_{14}]^{2-}$ has a highly distorted octahedral Co_6 skeleton but is thermodynamically unstable with respect to disproportionation to $[Co_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{13}]^{2-}$. Octahedral $[Co_6C(CO)_{13}]^{2-}$ is the lowest energy structure found for this stoichiometry. It is stable toward CO dissociation and disproportionation, consistent with the fact that it is a known stable structure that has been synthesized and characterized by X-ray diffraction.[3] The lowest energy $[Co_6C(CO)_{12}]^{2-}$ structure is a relatively symmetrical D_{3d} structure with a carbon-centered Co_6 puckered hexagon in the chair form.

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Supporting Information Available: Number of configurations with different number of CO groups and different Co_6 skeletons (the total number of initial configurations of all combinations is 1165), infrared ν(CO) frequencies of the $[Co_6C(CO)_n]^{2-}$ derivatives ($n = 12$, 13, 14, 15, and 16), and Cartesian coordinates in Å for the optimized structures of 13 isomers shown in Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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