

# Hypothetical C<sub>60</sub> Metal-Cluster Fullerides and General Aspects of Tetrahedral Cluster Bonding

Norman Goldberg and Roald Hoffmann\*

Department of Chemistry and Materials Science Center, Cornell University,  
Ithaca, New York 14853-1301

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It is geometrically feasible to insert metal–metal-bonded M<sub>4</sub> tetrahedra and M<sub>6</sub> octahedra into the tetrahedral and octahedral holes, respectively, of the fcc C<sub>60</sub> lattice. The electronic structure of the hypothetical tetrahedral variants C<sub>60</sub>(M<sub>4</sub>)<sub>2</sub>, M = Rh, Co, is analyzed with approximate molecular orbital methods and band structure calculations. These compounds feature M–M and M–C<sub>60</sub> bonding and a variable degree of electron transfer to or from C<sub>60</sub>. The C<sub>60</sub>(M<sub>4</sub>)<sub>2</sub> phases should be metallic, but we have no way of predicting if they will be superconducting. A number of discrete molecular tetrahedral cluster compounds which serve as models for the solid state materials are analyzed. There is a clear indication that tetranuclear and even mononuclear Rh, Ir, and Co arene complexes should be relatively unstable.

## Introduction

The rich family of carbon clusters displays a range of unusual features which have sparked enormous interdisciplinary research since the discovery of the fullerenes<sup>1</sup> and their bulk synthesis<sup>2</sup> 5 years later. Certainly one of the most exciting results has been the finding of superconductivity in a number of metal-doped compounds of icosahedral C<sub>60</sub>.<sup>3,4</sup>

Solid C<sub>60</sub>, the host lattice for these metal-intercalation compounds, is a well-characterized material.<sup>5</sup> At room temperature it forms a face-centered-cubic (fcc) lattice with a lattice constant of 14.11 Å.<sup>6</sup> The radius (center to carbon distance) of C<sub>60</sub> is 3.53 Å, which leads to a shortest C–C contact between molecules of approximately 3.1 Å. This is a slightly smaller value than the 3.35 Å graphite layer contact.

The close-packed C<sub>60</sub> structure is capable of incorporating alkali metals—a reaction that is also well-known for graphite.<sup>7</sup> As demonstrated by crystallographic studies,<sup>8</sup> the metal atoms

are accommodated in the large tetrahedral and octahedral interstices formed by the fcc carbon sublattice. For each C<sub>60</sub> molecule in this lattice, there are one octahedral and two tetrahedral sites. Thus, were all the holes occupied by one M atom, the stoichiometry of the compound would be M<sub>3</sub>C<sub>60</sub>.

The incorporation of up to three alkali atoms per C<sub>60</sub> only marginally alters the structure of the C<sub>60</sub> sublattice. Larger amounts of metal force the carbon lattice to reconstruct and adopt orthorhombic (M<sub>4</sub>C<sub>60</sub>)<sup>9</sup> and body-centered-cubic (M<sub>6</sub>C<sub>60</sub>)<sup>10</sup> phases. In M<sub>3</sub>C<sub>60</sub> though, the fcc packing is preserved; the lattice constant is found to increase only slightly in K<sub>3</sub>C<sub>60</sub> (14.24 Å, compared to the 14.11 Å of the undoped crystal).

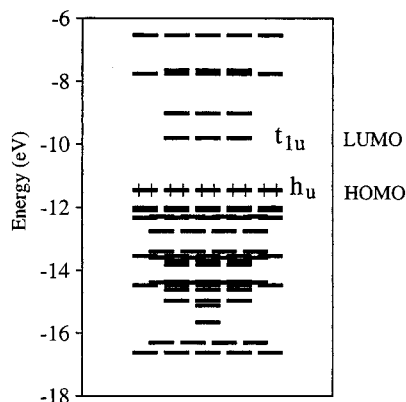
Among the above mentioned alkali-metal intercalation compounds, only the M<sub>3</sub>C<sub>60</sub> phases display superconductivity. In an explanation of this behavior, the C<sub>60</sub> energy levels certainly play an important role. The highest occupied molecular orbital (HOMO) of C<sub>60</sub> is a filled 5-fold degenerate h<sub>u</sub>. The lowest-lying unoccupied molecular orbital (LUMO), t<sub>1u</sub>, is 3-fold degenerate. C<sub>60</sub> possesses a substantial electron affinity and is able to accommodate up to five additional electrons in solution in this LUMO.<sup>11</sup> In the solid, the incorporated alkali-metal atoms donate their valence electrons to the C<sub>60</sub> molecules, leading to a half-filled highest-occupied crystal orbital (HOCO) in M<sub>3</sub>C<sub>60</sub>. This results in a half-filled (and relatively narrow) band at the Fermi level (E<sub>F</sub>). A large density of states (DOS) at the Fermi level, one prerequisite for effective electron–phonon coupling, follows.

There have been a number of further attempts to generate new C<sub>60</sub> intercalation compounds with possible interesting properties. Alkali-earth metals, as well as several main-group

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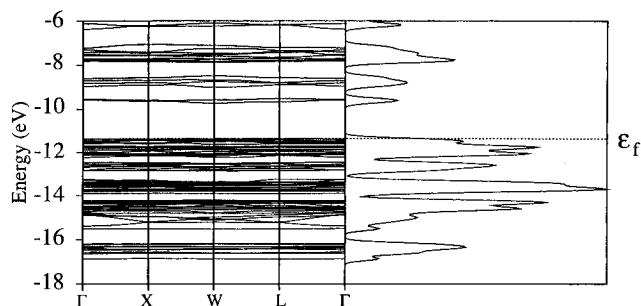
**Figure 1.** Molecular orbitals of  $C_{60}$ . Only the region around the HOMO is shown.

elements, have been successfully incorporated. There are several reports of amorphous  $C_{60}$ -metal compounds.<sup>12</sup> This  $C_{60}$ - $Fe_x$  phase shows a number of interesting catalytic properties. The exact structure of this intercalation compound has, however, not yet been determined.

In this work, we address the stability and bonding in some hypothetical  $C_{60}$  transition-metal phases containing metal clusters with metal-metal bonding.<sup>13</sup> There have been some previous calculations on discrete metal complexes with  $M = Cr$ ;<sup>14a</sup>  $M = Fe, Ru, Os$ ;<sup>14b</sup> and  $M = Pt$ .<sup>14c</sup> The analysis is carried out in the framework of the extended Hückel method and tight-binding theory.<sup>15,16</sup> We start by briefly looking at molecular  $C_{60}$  and three-dimensional fullerene phases and then extend our analysis to the bonding in a hypothetical  $C_{60}(M_4)_2$ , where  $M = Co$  and  $Rh$ . Our analysis of this interesting organic-inorganic cluster system<sup>17</sup> leads us naturally to look at the bonding in a number of structurally related discrete molecular metal clusters. The bonding in tetrahedral clusters with carbonyl and benzene ligands is examined, and general effects responsible for the lability of second-row transition-metal arene complexes are analyzed.

#### Tetrahedral Clusters in Tetrahedral Interstices: The $(M_4)_2C_{60}$ Phases ( $M = Co, Rh, Fe$ )

To understand the bonding in the hypothetical metal-fullerene phases, we need to obtain first a picture of the geometrical and electronic features of solid  $C_{60}$ . The by now familiar MO levels of an isolated icosahedral  $C_{60}$  molecule are shown in Figure 1. The HOMO-LUMO splitting is calculated



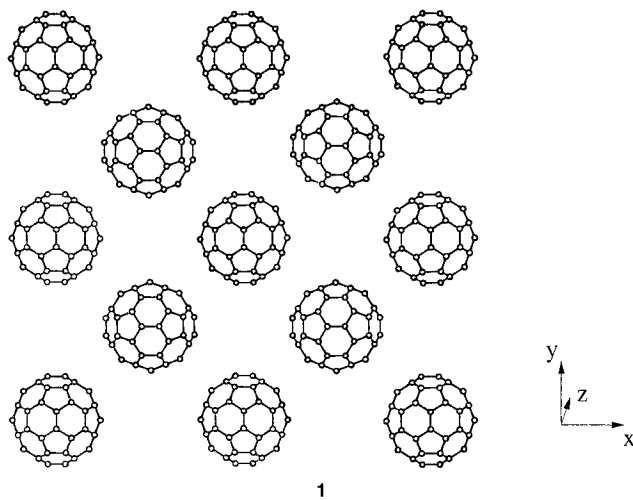
**Figure 2.** Band structure (left) and total density of states (DOS) of face-centered-cubic  $C_{60}$ . The Fermi level is at the top of the band; it seems to lie in a band only as a result of the computational artifact of band broadening.

by us to be 1.76 eV.

In the crystal, interaction between the molecules is small: the nearest neighbor  $C\cdots C$  contact in the solid is 3.13 Å, and this contact exists only between 12 of the 60 carbon atoms per molecule. Thus the bands in the face-centered-cubic crystal are hardly broadened,<sup>16a</sup> as can be seen in the computed band structure and DOS of the three-dimensional solid (Figure 2).

The bands are flat (Figure 2, left), and the DOS is very similar to the molecular orbital diagram shown above in Figure 1. The Fermi level is found to lie at  $-11.37$  eV. The large band gap above the Fermi level indicates that the solid—as confirmed experimentally—is an insulator.

Investigations of the structure of solid  $C_{60}$  alkali-metal intercalation compounds have revealed that the fullerenes prefer two distinct orientations in these crystals.<sup>5</sup> The 2-fold axes running through a fulvalene-type unit in each  $C_{60}$  are aligned with the principal axes of the unit cell. The  $C=C$  bond in these fulvalenoid subunits (also called the “6,6-juncture”) is parallel to either the  $x$  or the  $y$  axis (space group  $Fm\bar{3}m$ , No. 225), as depicted in **1**, a cut through the crystal in the  $xy$  plane.

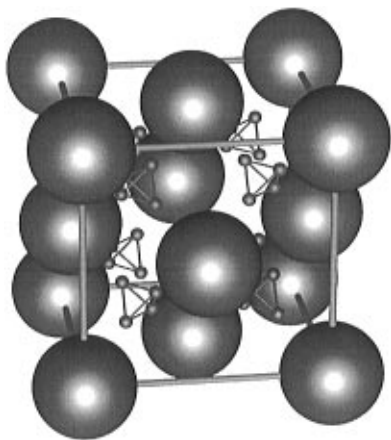


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In the  $M_3C_{60}$  phases, those two orientations (6,6-juncture parallel to  $x$  or  $y$ ) are randomly distributed over the crystal at low temperatures. To achieve a small translational unit cell, we orient the fullerenes in our calculations in a very specific way (space group  $Fm\bar{3}$ , No. 202). In this arrangement, the orientation of the  $C_{60}$  molecules is such that 8 of the 20 six-membered rings in the  $C_{60}$  molecules point exactly toward the centers of the tetrahedral holes.

How large is the tetrahedral hole in this  $C_{60}$  lattice? The distance from the center of a six-membered carbon ring to the center of the tetrahedral hole is 2.85 Å. There is room in there not only for one atom but for several. We became intrigued

by the idea of filling the hole with a tetrahedral transition-metal cluster; a schematic diagram of the proposed system is shown in 2.



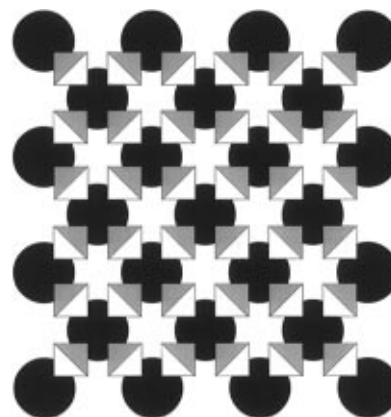
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Many tetrahedral M<sub>4</sub>L<sub>n</sub> clusters exist.<sup>18</sup> Archetypal among them is the transition-metal analogue of tetrahedrane Co<sub>4</sub>(CO)<sub>12</sub> or its congeners with M = Rh or Ir. These compounds differ in their carbonyl arrangement but share the structural feature of a near-perfect metal tetrahedron, with M–M bond lengths of 2.54, 2.72, and 2.69 Å for M = Co, Rh, and Ir. The center of the tetrahedron to metal atom distance is thus 1.55, 1.67, and 1.65 Å for these molecules; if naked M<sub>4</sub> clusters of the same size were placed in the tetrahedral holes of C<sub>60</sub>, an M to center of 6-ring distance of 1.30, 1.18, and 1.20 Å would result, or metal–carbon distances of 1.91, 1.85, and 1.86 Å, which are not all that unreasonable.

In terms of electron counting, group 9 metal tetrahedra seem the best choice to bind in the cavities. If one considers perfect η<sup>6</sup>-binding of the C<sub>6</sub> rings facing the tetrahedra, we would attain an 18-electron configuration at each M. This type of tetrahedral metal bonding, where 6 electrons per metal are supplied by the ligands, has long been known in the aforementioned metal clusters such as Co<sub>4</sub>(CO)<sub>12</sub> and Rh<sub>4</sub>(CO)<sub>12</sub> as well as in many substituted compounds. It should be noted that these molecules actually possess a C<sub>3v</sub> structure in solution with three carbonyl ligands bridging three basal metal atoms. In agreement with the experimental findings, our calculations indicate that these structures are energetically slightly favored as compared with the T<sub>d</sub> clusters we discuss here. For a better comparison, however, we focus on the bonding in the T<sub>d</sub> species only.

If all the tetrahedral holes in the fcc C<sub>60</sub> lattice (lattice constant 14.24 Å, taken from the experimental value of the alkali-metal fullerides<sup>8</sup>) were filled by Co<sub>4</sub> clusters, we would have a C<sub>60</sub>(Co<sub>4</sub>)<sub>2</sub> phase. An interesting alternative view of this structure (derived from 2) is shown in 3 (the sizes of the tetrahedra are exaggerated). Note the sheetlike structure of layers of C<sub>60</sub> and M<sub>4</sub>.

We first calculate the electronic structure of this C<sub>60</sub>(Co<sub>4</sub>)<sub>2</sub>, with a Co–Co distance of 2.54 Å taken from the Co<sub>4</sub>(CO)<sub>12</sub> cluster. The Fermi level is found to lie at –10.88 eV, in a region of high DOS. This material should therefore be metallic. A value of 0.045 for the average overlap population (OP) of a Co–C (bond distance 1.92 Å) indicates a relatively weak, yet bonding, interaction between the metal and carbon clusters. For a comparison, the OP at an equal Co–C distance in tetrahedral



3

Co<sub>4</sub>(benzene)<sub>4</sub> (we will discuss this model compound in the following section) has a value of 0.070. The crystal orbital overlap population (COOP) curve,<sup>16a</sup> not shown here, reveals that the levels around the Fermi energy are both Co–C as well as Co–Co antibonding.

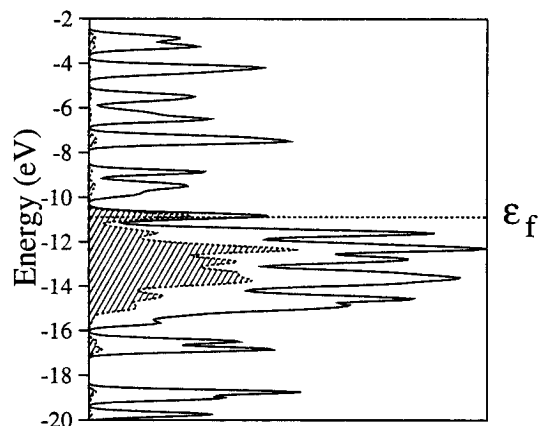
The Fermi level of the rhodium analogue, a C<sub>60</sub>(Rh<sub>4</sub>)<sub>2</sub> phase (lattice constant of 14.24 Å), is computed to be at –8.45 eV, thus considerably higher in energy than in the pure C<sub>60</sub> (calculated by us at –11.37 eV) and the hypothetical cobalt fullerene (–10.88 eV). Possible reasons for this unexpected finding will be discussed in some detail below; there is something special about arene–Rh bonding.

Might the C<sub>60</sub> lattice actually expand upon inclusion of the metal clusters? Calculations (which we do not trust, because the extended Hückel method does not do well at geometry optimization) indicate that the C<sub>60</sub>(Co<sub>4</sub>)<sub>2</sub> compound indeed energetically favors a lattice that is slightly enlarged. If we dilate the lattice yet keep the geometries of the fullerenes and the metal clusters the same, the energy minimizes at a value of 14.37 Å for the lattice constant of the fcc phase. This rather small change leads to a Co–C distance of 1.99 Å (and a fullerene–fullerene C–C contact of 3.22 Å). The total DOS and projection of the Co d orbitals of this optimized C<sub>60</sub>(Co<sub>4</sub>)<sub>2</sub> phase are depicted in Figure 3.

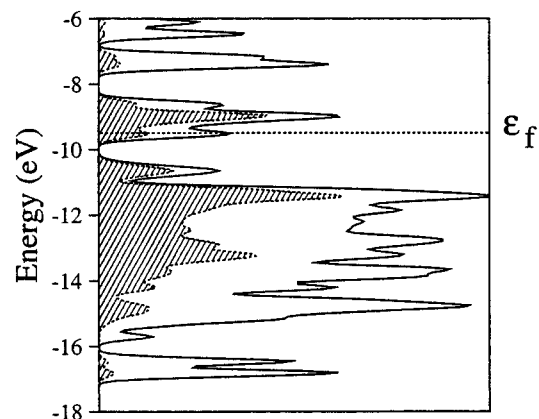
The Fermi level is found to lie in a region of high DOS at –10.98 eV. A projection of the DOS of the C<sub>60</sub> frontier orbitals (not shown) indicates that the levels around the Fermi level are mainly comprised both of Co d orbitals and the C<sub>60</sub> LUMO. There is significant electron transfer from the C<sub>60</sub> to the Co clusters, which manifests itself in an average net charge of –0.49 per Co atom. It would take an additional 8 electrons per C<sub>60</sub>(Co<sub>4</sub>)<sub>2</sub> unit to fill all the levels below the gap in the DOS just above the Fermi level.

Variation of the lattice constant for the rhodium analogue, C<sub>60</sub>(Rh<sub>4</sub>)<sub>2</sub>, shows that incorporation of rhodium clusters leads to an even larger expansion of the host lattice. An energy minimum is found for a lattice constant of 15.41 Å. This swelling of the phase leads to a Rh–C distance of 2.14 Å, compared to 1.85 Å in the geometry taken from the alkali-metal C<sub>60</sub> structure. In this dilated lattice, the inter-C<sub>60</sub> C–C short contact is now much longer, 3.96 Å. This is outside the van der Waals contact region for π-bonded carbon systems, so substantial loss of cohesive energy would be expected (extended Hückel calculations of course do not reproduce van der Waals minima). This is worrisome. The total DOS as well as the projections of the Rh d orbitals is shown in Figure 4. The Fermi level is found to fall in a region of high DOS at –9.49 eV, still significantly higher than for the cobalt phase. A value of 0.032

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**Figure 3.** Total DOS and projected DOS of the Co d orbitals (lined area) in  $C_{60}(Co_4)_2$  (lattice constant 14.37 Å).



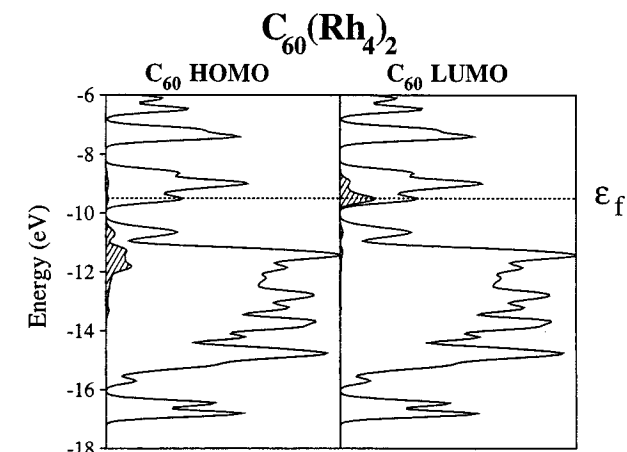
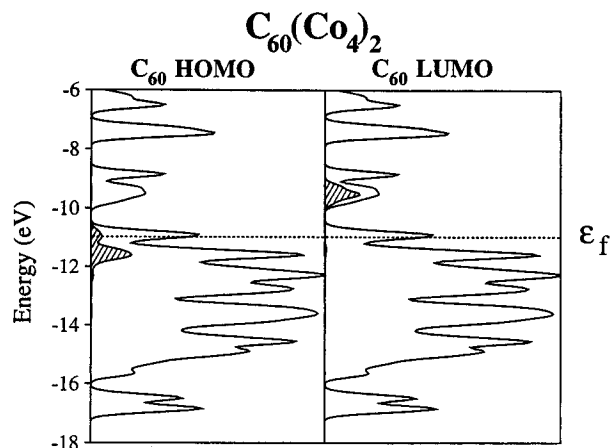
**Figure 4.** Total DOS and projected DOS of the Rh d orbitals (lined area) in  $C_{60}(Rh_4)_2$  (lattice constant 15.41 Å).

for the Rh–C OP indicates a weak bonding interaction between the rhodium clusters and the  $C_{60}$  arene units.

The average net charge of +0.18 on the Rh metal atoms indicates that, as in the case of the alkali-metal fullerene systems (but not the Co system), significant electron transfer from the metal to the  $C_{60}$  molecules takes place in this phase. A projection of the Rh d orbitals and of the  $C_{60}$  frontier orbitals (not depicted) shows that the levels around the Fermi energy are mainly composed of Rh d orbitals as well as the  $C_{60}$  LUMO: this is quite different from the case of the alkali-metal phases. This  $C_{60}(Rh_4)_2$  phase possesses an excess of 4 electrons per  $C_{60}(Rh_4)_2$  above the clear gap below the Fermi level.

The analysis of the bonding and electron transfer can be pursued to the orbital level. Figure 5 shows the contribution of the  $h_u$  (HOMO) and  $t_{1u}$  (LUMO)  $C_{60}$  fragment molecular orbitals (FMOs) to the total DOS of  $C_{60}(M_4)_2$ . In the Co case (Figure 5, top),  $h_u$  is occupied by 8.79 electrons (out of 10 possible) and  $t_{1u}$  by 0.54 (out of 6). For Rh, the occupation of  $h_u$  is 9.17 and that of  $t_{1u}$  is 3.19, consistent with the charges found.

The  $Rh_4$  case is thus calculated by us to be very different from the  $Co_4$  case; the direction of electron transfer between metal and carbon polyhedra is reversed. One reason for this different behavior of the two metals is the relative positions of their d levels. The cobalt d orbitals are approximately 1 eV lower than those of Rh (and those of Ir, which is expected to show bonding features similar to those of Rh), a difference large enough to reverse the electron transfer upon going from Co to Rh. However, that is not the only reason for the different behavior of these metals. We will analyze the origins of this important effect in more detail below.



**Figure 5.** Contributions of the  $C_{60}$  frontier orbitals (lined areas) to the total DOS (solid lines) of  $C_{60}(Co_4)_2$  (top) and  $C_{60}(Rh_4)_2$  (bottom).

What happens if we change the orientation of the  $C_{60}$  in the solid lattice? So far we have only looked at solids where the  $C_6$  rings of the fullerene molecules are all directly facing the tetrahedral holes. If we rotate all fullerenes in the solid simultaneously around the  $z$  axis (see structure **1**) the energy is found to increase steadily. The contacts between the metal and carbon atoms become too small to be realistic (as short as 1.5 Å). This suggests that the initial geometry we used in our calculations is in fact a reasonable one. It must be said, however, that we did not allow a dilation of the fcc lattice to accommodate the rotated tetrahedra. In any case, the rotation of the metal tetrahedra in a frozen  $C_{60}$  matrix is strongly hindered.

### Metal Clusters in the Octahedral Holes

Another point we have not addressed so far is the possible binding of metal clusters in the octahedral holes. What about the capabilities for metal–carbon bonding at these sites?

The octahedral interstices are surrounded by 6,6-ring junctures (or fulvalenoid double bonds). The distance between the center of such a C–C bond and the center of the hole is 3.65 Å (for a lattice constant of 14.24 Å). We have calculated the  $C_{60}$  lattice with all of its octahedral holes filled with tetrahedral  $M_4$  clusters. The computations indicate that the bonding of the tetrahedra in such an environment is very weak and such clusters can rotate totally unhindered. Thus it is not very likely that tetrahedral clusters bind in these sites.

In principle, one can envision larger clusters, such as  $M_6$  octahedral fragments, in these holes, binding at each M in an  $\eta^2$  fashion to the fulvalenoid double bonds which all point to the center of these sites. In known  $M_6$  clusters of Co, Rh, and Ir,

the average M–M distance is known experimentally to lie around 2.50, 2.78, and 2.76 Å for Co, Rh, and Ir, respectively.<sup>19</sup> Thus we arrive at a reasonably realistic metal–carbon distance of 2.00, 1.82, and 1.83 Å for the compounds with octahedral M<sub>6</sub> clusters in the octahedral holes of the fcc lattice. The molecular compounds that are known have generally two to three ligands bound to each metal, as in Rh<sub>6</sub>(CO)<sub>12</sub>(P(OPh)<sub>3</sub>)<sub>4</sub>.<sup>20</sup> η<sup>2</sup>-Olefin complexes of the composition M<sub>6</sub>(olefin)<sub>6</sub> are not known; they would be *very* electron deficient. We leave the C<sub>60</sub>M<sub>6</sub> complexes for future study. Preliminary investigations of these C<sub>60</sub>M<sub>6</sub> compounds as well as of the mixed C<sub>60</sub>(M<sub>4</sub>)<sub>2</sub>M<sub>6</sub> phases (tetrahedra and octahedra in the tetrahedral and octahedral holes, respectively) indicate that the incorporation of metal octahedra should lead to metallic compounds, too.

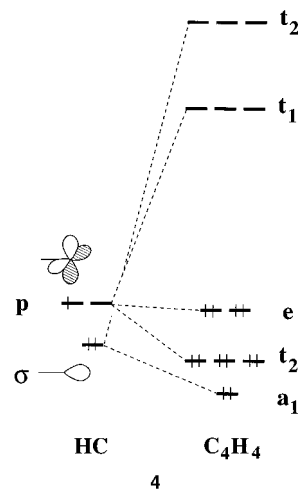
### General Aspects of Bonding in Tetrahedral Transition-Metal Clusters

The multitude of molecular levels in C<sub>60</sub> hampers a detailed analysis of the bonding in the metal-cluster fullerene compounds. Therefore, we choose to compare the bonding in these solids to that of a number of model compounds. This approach might also give some insight into the question of the high-lying Fermi level in the rhodium fullerene phase and the difference between Co and Rh.

If we substitute the C<sub>60</sub> by the smallest possible ligand which is η<sup>6</sup>-binding, benzene, we arrive at the class of hypothetical M<sub>4</sub>(C<sub>6</sub>H<sub>6</sub>)<sub>4</sub> molecules. These clusters should serve as ideal models for the postulated fullerene–M<sub>4</sub> phases, and, as it will turn out, there is a surprising aspect of their bonding.

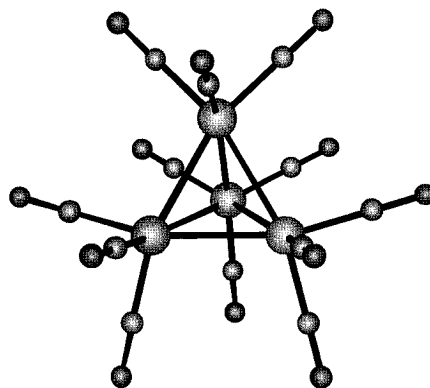
The relationship among C<sub>4</sub>H<sub>4</sub> (tetrahedrane), M<sub>4</sub>(CO)<sub>12</sub> (M = Co, Rh, Ir),<sup>21</sup> and M<sub>4</sub>(arene)<sub>4</sub> is instructive and important in understanding the electronic structure of the tetraarene clusters.<sup>22,23</sup> So we begin building these tetrahedral clusters.

Consider first tetrahedrane,<sup>24</sup> whose orbitals are constructed from four interacting HC units (4). Each CH brings to the molecule a σ-type hybrid orbital, radial with respect to the polyhedron, and two π-type p orbitals, tangential. The radial orbitals interact to give a low-lying a<sub>1</sub> combination and a strongly antibonding t<sub>2</sub>. The two degenerate tangential p orbitals form three C–C bonding combinations (t<sub>2</sub>), two nonbonding MOs (e), and three strongly carbon–carbon antibonding orbitals of t<sub>1</sub> symmetry. Mixing with still another CH orbital at lower energy complicates this simplistic picture of the bonding in tetrahedrane just a little. The six occupied cluster bonding orbitals (a<sub>1</sub> + t<sub>2</sub> + e) may also be generated from a starting point of six localized C–C σ bonds. These orbitals are the essence of localized tetrahedral cluster bonding.<sup>25</sup>



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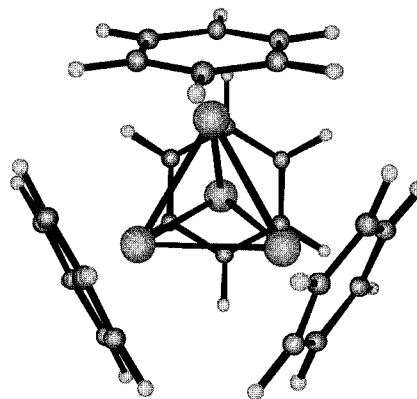
Next we consider M<sub>4</sub>(CO)<sub>12</sub>, 5, a well-known series of clusters. The bonding in these clusters may be constructed from



5

the interaction of four d<sup>9</sup> M(CO)<sub>3</sub> units, each isolobal with a CH. We do not present the interaction diagram here; the important result, consistent with the isolobal analogy, is that once again one sees a set of a<sub>1</sub> + t<sub>2</sub> + e cluster orbitals. Their ordering is different in energy from that of tetrahedrane, but their bonding characteristics are similar.

Now we proceed to the tetraarene clusters 6.<sup>26</sup> The d<sup>9</sup> M(arene) fragment is isolobal with the CH and d<sup>9</sup> M(CO)<sub>3</sub>;

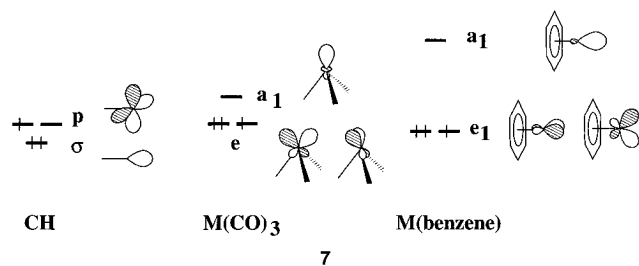


6

the relationship follows from the shape of the orbitals shown in 7.

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- (20) Note that this cluster only possesses 16 ligands. For details on this interesting topic of cluster chemistry, see: (a) Mingos, D. M.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1990; see also references therein. (b) Halet, J.-F. *Coord. Chem. Rev.* **1995**, 635, 637.
- (21) For recent extended Hückel calculations of [M<sub>4</sub>(CO)<sub>12</sub>] clusters (M = Co, Rh, Ir) in the context of a comparison of molecular and crystal structures of these species, see: Braga, D.; Grepioni, F.; Byrne, J. J.; Calhorda, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 3287.
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The interaction diagram for  $\text{Rh}_4(\text{C}_6\text{H}_6)_4$  and  $\text{Co}_4(\text{C}_6\text{H}_6)_4$  (Figure 6) has a surprise. First of all, the cluster bonding orbital of  $a_1$  symmetry in  $\text{Rh}_4(\text{C}_6\text{H}_6)_4$  ( $2a_1$ ) is rather high in energy. Still it is occupied, and one can pick out cluster  $a_1 + t_2 + e$  orbitals.

More importantly, the cobalt analogue is in real trouble. Here the totally symmetric cluster orbital ( $2a_1$ ) just does not come down low enough in energy. Instead the antibonding  $2t_1$  combination, descended from the  $e_1$  FMO, is filled. The metal–metal bonding in the Co cluster is much diminished, as the Co–Co OP of 0.081 shows (compare M–M OP's of 0.230 in  $\text{Co}_4(\text{CO})_{12}$ , 0.336 in  $\text{Rh}_4(\text{CO})_{12}$ , and 0.407 in  $\text{Rh}_4(\text{benzene})_4$ ). The ground state of this molecule, if it existed, would be a triplet. We have investigated the possibilities of off-center bonding ( $\eta^2$  or  $\eta^4$ ) and distortion of the arenes to a boat shape in these  $\text{M}_4(\text{benzene})_4$  clusters. All these distortions are found to be energetically unfavorable.

To summarize: (1)  $\text{M}_4(\text{CO})_{12}$  (M = Rh, Co) are metallatetrahedranes with reasonably strong M–M and M–CO bonds. (2)  $\text{Rh}_4(\text{C}_6\text{H}_6)_4$  is also a metallatetrahedrane, but with a high-lying HOMO;  $\text{Co}_4(\text{C}_6\text{H}_6)_4$  has much weaker metal–metal bonding and should be a high-spin molecule.

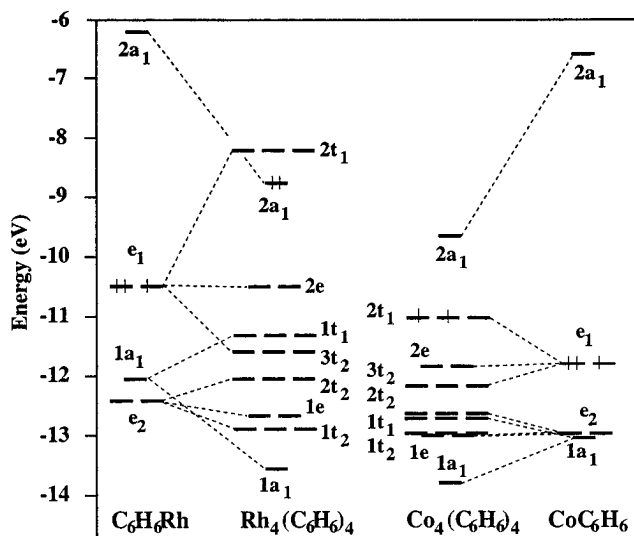
What is the problem for the M(arene) clusters? If we compare the bonding in the benzene and carbonyl clusters, we see that the two electrons which render the rhodium–benzene clusters unstable due to the fact that they occupy the high-lying  $2a_1$  orbital and which lead to the occupation of the  $2t_1$  HOMO in  $\text{Co}_4(\text{C}_6\text{H}_6)_4$  are found at considerably lower energy for the  $\text{M}_4(\text{CO})_{12}$  clusters. The  $2a_1$  is much lower in the carbonyl complexes. Why is this so? We can trace this phenomenon (see Appendix 2 for a detailed analysis) to the contribution of the CO  $\pi^*$  to the  $a_1$  FMO of the  $\text{M}(\text{CO})_3$  fragments. That contribution, really backbonding, is substantial and stabilizing.

We can now also understand why the Fermi level is raised to a value of  $-9.49$  eV in the  $\text{C}_{60}(\text{Rh}_4)_2$  compound. The same reasons that render the molecular model  $\text{Rh}_4(\text{C}_6\text{H}_6)_4$   $2a_1$  orbital unstable account for the high-lying Fermi energy in the extended structure.

In general, the metal to arene bonding in the tetranuclear clusters is quite weak. So whereas in  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$  the M–C(O) OPs are 0.88 and 0.70, respectively, the corresponding M–C( $\text{C}_6\text{H}_6$ ) OPs are only 0.06 and 0.08. The arene ligand is but weakly held, according to our calculations. This fact is the next focus of our analysis.

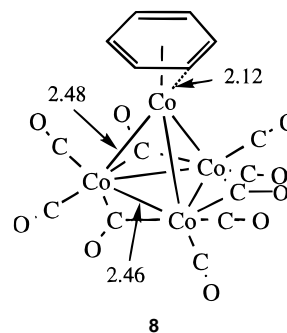
### Implications for the Existence of Molecular $\text{M}_4(\text{arene})_4$ Complexes

While we started thinking about the M–arene bonding in  $\text{C}_{60}(\text{M}_4)_2$ , we have come to an interesting point about a molecular problem, namely the  $\eta^6$  bonding of an arene to discrete transition-metal clusters. The conclusion we reach in the previous section is that while  $\text{M}_4(\text{CO})_{12}$  (M = Co, Rh, Ir) complexes are reasonably strongly bound, the seemingly innocent substitution of three carbonyls by an  $\eta^6$ -benzene leads



**Figure 6.** FMO diagram for the construction of the frontier orbitals of the  $\text{M}_4(\text{C}_6\text{H}_6)_4$  clusters (M = Rh, Co).

to substantial loss of bonding, both metal–metal and metal–arene for M = Co, just metal–arene for M = Rh. What is in fact known about  $\eta^6$ -arene complexes of these clusters?<sup>27</sup> There are rather few examples of group 9 molecules which contain arene molecules described in the literature. For cobalt, one compound related to our models has been synthesized some time ago.<sup>28</sup> This tetrahedral cobalt arene cluster (**8**) has been



obtained by replacement of three carbonyl groups in  $\text{Co}_4(\text{CO})_{12}$  by one benzene molecule. The metal–C<sub>arene</sub> bond distance of 2.12 Å in this tetranuclear cluster is quite similar to that of other known mononuclear clusters such as  $(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Co}(\text{C}_6\text{F}_5)_2$ <sup>29</sup> and  $\eta^6\text{-C}_6\text{H}_6\text{Co}(\eta^2\text{-H}_3\text{CCCCCH}_3)$ ,<sup>30</sup> where Co–C<sub>arene</sub> was found to lie between 2.12–2.18 and 2.08–2.16 Å, respectively. In two other tetranuclear cobalt clusters with an  $\eta^6$ -binding toluene as a ligand, the metal–carbon bond distances are slightly shorter: in  $(\eta^6\text{-toluene})\text{Co}_4(\text{CO})_6[\text{HC}(\text{PPh}_2)_3]$ ,<sup>31</sup> they were found to lie between 2.09 and 2.17 Å; in  $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Co}_4(\text{CO})_9$ , where the substituent R is a ferrocenylcarbinol derivative, the Co–C distance lies between 2.15 and 2.13 Å.<sup>32</sup>

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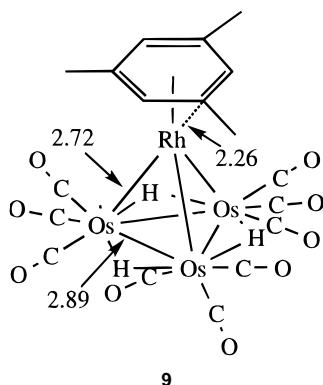
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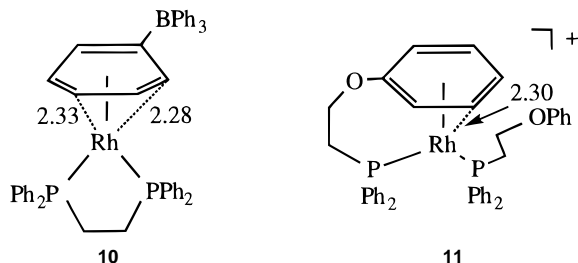
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The rhodium analogue of this compound seems not to have been synthesized. In fact we are aware of only one polynuclear metal cluster that displays an  $\eta^6$ -bound Rh–arene unit (**9**).<sup>33</sup> In



this compound, a Rh–mesitylene unit is bound to a trinuclear osmium–carbonyl frame which is additionally bridged by three hydrogen atoms.

There have been some reports of mononuclear Rh–arene compounds. The first crystallographic study of a rhodium–arene complex was carried out by Muettterties and co-workers.<sup>34</sup> The authors reported an  $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Rh}[\eta^4\text{-C}_6\text{H}_2(\text{CH}_3)_6]^+$  cation with a metal–C<sub>arene</sub> bond length between 2.28 and 2.32 Å; the mesitylene ring was found to be slightly off-center. This compound decomposes between 75 and 100 °C. Two other reported Rh–arene complexes are depicted in **10** and **11**.<sup>35</sup> In



compound **10** the C<sub>6</sub>-ring ligand actually distorts slightly in the direction of a boat, deviating from  $\eta^6$  bonding. A similar effect has been observed in  $[\text{Rh}(\text{diolfin})(\eta^6\text{-arene})]^+$  complexes.<sup>36</sup> In these complexes the arene has been found to adopt a boat form with the long Rh–C distances ranging between 2.29 and 2.37 Å and the short ones between 2.24 and 2.32 Å.<sup>37</sup> Compound **11**, on the other hand, has been shown to undergo facile intramolecular exchange of the two phenoxyarene units at room temperature. A similar and surprising facility with

which arene ligands exchange has been reported for the neutral arene–rhodium complexes  $[\text{Rh}(\eta^6\text{-toluene})(\eta\text{-cyclooctene})\text{-SnR}_3]$ .<sup>38</sup>

Thus group 9 cluster arene complexes are not very common in the literature. Even monometallic arene compounds of these metals display a significant degree of instability. Yet, there are some Rh<sub>4</sub> and Ir<sub>4</sub> clusters reported in the literature which display unexpected behavior: The M<sub>4</sub>( $\eta^5\text{-Cp}^*$ )<sub>4</sub>H<sub>4</sub><sup>2+</sup> clusters<sup>39</sup> (M = Rh, Ir; Cp\* = C<sub>5</sub>Me<sub>5</sub>) are not 60-electron complexes as would have been anticipated but are unusual 58-electron compounds. X-ray and electron diffraction studies reveal that the Rh<sub>4</sub> 58-electron complex has a slightly distorted metal tetrahedron. The hydrogen atoms cap the four faces of the metal cluster which possesses two different types of Rh–Rh bonds (2.83 and 2.61 Å). Related to these species are a number of interesting clusters of group 8 elements such as M<sub>4</sub>(arene)<sub>4</sub>H<sub>4</sub><sup>2+</sup> (M = Ru, Os).<sup>40</sup>

Unfortunately there seem to be no X-ray structures of these compounds. The fact that they are 58-electron complexes just like the clusters mentioned above, however, supports our argument about the instability of the 60-electron M<sub>4</sub>(benzene)<sub>4</sub> group 9 clusters. In fact, our calculations indicate that 2-electron oxidation of the 60-electron model Rh<sub>4</sub>(benzene)<sub>4</sub> should lead to significant stabilization. The high-lying singly degenerate HOMO of this model would be depopulated, and a large HOMO–LUMO gap would be created; this is what is presumably found in the experimentally observed 58-electron complexes mentioned above.

We think that our finding of the lability of the rhodium–arene bond is reflected in these experimental observations. As indicated by our calculations, sequential substitution of three carbonyl groups in the [M(CO)<sub>3</sub>]<sub>4</sub> tetrahedra to form the corresponding arene–carbonyl clusters M<sub>4</sub>[(CO)<sub>3</sub>]<sub>4-x</sub>(benzene)<sub>x</sub> (x = 0–4) is expected to lead to a substantial loss of stabilization. We believe total substitution of the carbonyl ligands by arenes will not lead to isolable molecular entities; their oxidized 58-electron counterparts, however, could be experimentally feasible species.

## Summary and Conclusions

Our calculations indicate that group 9 metal tetrahedra intercalated in the tetrahedral holes of a C<sub>60</sub> lattice are geometrically and electronically reasonable phases. The tetrahedra are not just guests in the lattice but are  $\pi$ -bonded (albeit weakly) to the C<sub>60</sub> arene rings. Experiments aimed at generating such compounds, perhaps by co-condensing preformed metal carbonyl clusters and C<sub>60</sub> molecules and then activating them, need to be done.

Incorporation of tetrahedral or smaller metal clusters into the octahedral holes formed by the face-centered cubic host lattice of solid C<sub>60</sub> is not very likely. These cavities are rather large, and the tetrahedral metal clusters will not bond very well in them. From geometrical considerations, however, these sites should be able to accommodate octahedral metal clusters.

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**Table 1.** Parameters Used in the Extended Hückel Calculations<sup>14,47</sup>

atom	orbital	$H_{ii}$ (eV)	$\zeta_{i1}$	$c_1$	$\zeta_{i2}$	$c_2$
Rh	5s	-8.09	2.135			
	5p	-4.57	2.10			
	4d	-12.50	4.29	0.5807	1.97	0.5685
Co	4s	-9.21	2.0			
	4p	-5.29	2.0			
	3d	-13.18	5.55	0.5680	2.10	0.6060
C	2s	-21.4	1.625			
	2p	-11.4	1.625			
O	2s	-32.3	2.275			
	2p	-14.8	2.275			
H	1s	-13.6	1.3			

Interactions between the transition-metal clusters and the fullerene molecules in these hypothetical phases are expected to be rather different from those in the well-known alkali-metal fullerenes. Whereas in the latter systems the valence electrons of the metal atoms are pretty much fully transferred to the C<sub>60</sub> LUMO and the metal-C<sub>60</sub> bonding appears to be ionic, the transition-metal clusters we predict are involved in actual carbon-metal bonding; the levels around the Fermi energy are formed by carbon as well as metal d orbitals.

The partially filled bands around the Fermi level indicate that these compounds should be conducting. Will they be superconductors? We do not know. Two further points we have not addressed in our calculations, but which could be consequences of the partial filling of these bands, are potential distortion of the tetrahedra to lower symmetry and/or interesting magnetic properties of the phases.

There is a molecular bonus from these extended-structure calculations. There are indications in the calculations of instability in the bonding of four arenes to either Co<sub>4</sub> or Rh<sub>4</sub> clusters. In fact, such clusters are not known, and really very few single  $\eta^6$ -arene ligands bound to M<sub>4</sub> clusters exist. There are signs of lability even in mononuclear arene-ML<sub>n</sub> complexes. We trace the differences between Co- and Rh-arene bonding to the diffuseness of the d orbitals of rhodium compared to first-row transition metals and the large energy difference between the d and p levels in this second-row transition metal.

**Acknowledgment.** N.G. thanks especially Greg Landrum and Hugh Genin as well as all other members of the group for their assistance in the use of the programs and for many helpful discussions. N.G. is also grateful to the Deutsche Forschungsgemeinschaft (DFG) for the award of a research fellowship. We are indebted to the National Science Foundation for supporting our work through Research Grant CHE-9408455.

## Appendix 1: Computational Details

Extended Hückel calculations were performed using the YAeHMOP package (see Table 1 for parameters).<sup>41</sup> Bond lengths and angles used in the calculations are given in Table 2. For the calculations of the three-dimensional systems a primitive unit cell was used and 10K points were sampled.<sup>42</sup> The CACAO program<sup>43</sup> was used for the visualization of the molecular orbitals.

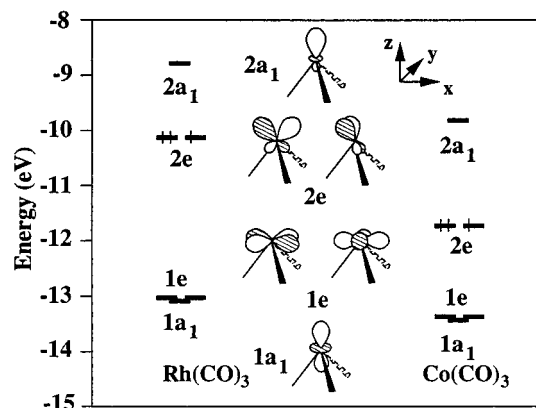
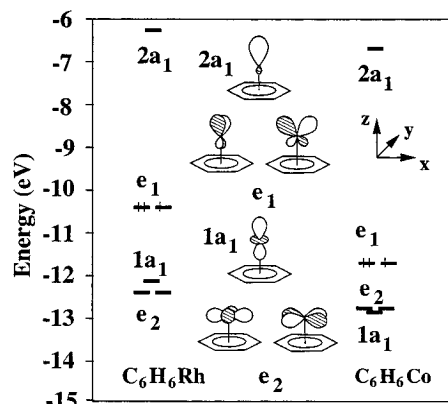
## Appendix 2: Comparison of M(CO)<sub>3</sub> and M(arene) Fragments

The orbitals of the M(CO)<sub>3</sub> unit are well-known.<sup>44</sup> We note in Figure 7 the familiar ML<sub>3</sub> set of higher-lying hybrid orbitals of a<sub>1</sub> and e symmetries above the remnant "t<sub>2g</sub>" set of the octahedron. The detailed

**Table 2.** Bond Lengths Used in the Calculations

type	bond length (Å)	type	bond length (Å)
C-C (C <sub>60</sub> )	1.453	Rh-C <sub>carbonyl</sub>	1.86
C=C (C <sub>60</sub> )	1.382	C=O <sub>carbonyl</sub> <sup>d</sup>	1.14
Co-Co in the Co <sub>4</sub> tetrahedra	2.54	C-C <sub>benzene</sub>	1.40
Rh-Rh in the Rh <sub>4</sub> tetrahedra	2.72	C-H <sub>benzene</sub>	1.10
Co-C <sub>carbonyl</sub>	1.78		

<sup>a</sup> The C-metal-C angle for the calculations on the metal carbonyl compounds was chosen to be 93°.

**Figure 7.** Frontier orbitals of the M(CO)<sub>3</sub> fragments (M = Rh, Co). Only the electrons in the HOMO are shown.**Figure 8.** Frontier orbitals of the M(C<sub>6</sub>H<sub>6</sub>) fragments (M = Rh, Co).

composition of these orbitals is important in the sequel, so we proceed to discuss it in some detail here.

In the C<sub>3v</sub> symmetry of the fragment both (d<sub>xy</sub>, d<sub>x<sup>2</sup>-y<sup>2</sup>) and (d<sub>xz</sub>, d<sub>yz</sub>) transform as e. These orbitals will mix slightly with each other (and with p<sub>x</sub>, p<sub>y</sub>), but the lower 1e set of Figure 7 (the remnant of the octahedral t<sub>2g</sub> set) is largely d<sub>xy</sub>, d<sub>x<sup>2</sup>-y<sup>2</sup>) and the upper one, 2e, is mainly d<sub>xz</sub>, d<sub>yz</sub>. Significant contributions of the d<sub>z<sup>2</sup></sub> orbital are found in two a<sub>1</sub> fragment orbitals—one (1a<sub>1</sub>) orbital at approximately the same energy as the e set formed by d<sub>xy</sub> and d<sub>x<sup>2</sup>-y<sup>2</sup>) and the other (2a<sub>1</sub>) at higher energy. Both of these a<sub>1</sub> orbitals will be crucial for metal-metal bonding in the clusters. That several MOs contain substantial d<sub>z<sup>2</sup></sub> character is the result of an interaction of three fragment orbitals within M(CO)<sub>3</sub>: first an a<sub>1</sub> combination from the CO lone pairs, the d<sub>z<sup>2</sup></sub> orbital, and finally an a<sub>1</sub> set from the π\* CO orbitals. This a<sub>1</sub> set is the bonding combination of the three π\* orbitals, a crucial combination as we will see later. The net outcome is that the lower-lying 1a<sub>1</sub> orbital is 71% d<sub>z<sup>2</sup></sub> and the higher-lying 2a<sub>1</sub> 21% d<sub>z<sup>2</sup></sub> (in Rh(CO)<sub>3</sub>).</sub></sub></sub>

In general, the cobalt fragment levels are found at lower energies compared to those of Rh(CO)<sub>3</sub> and display a weaker splitting of the levels. This is caused by the diffuseness of the 4d orbitals as compared with the 3d orbitals and the lower lying d levels as well as the smaller energy difference among s, p, and d levels in cobalt.

(41) Landrum, G. YAeHMOP—Yet Another Extended Hückel Molecular Orbital Package, version 1.1; Cornell University: Ithaca, NY, 1995. This great freeware package is available on the World Wide Web: <http://overlap.chem.cornell.edu:8080/yaehmop.html>.

(42) Ramirez, R.; Böhm, M. C. *Int. J. Quantum Chem.* **1988**, *34*, 571.

(43) Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 3399.

(44) An analysis of the M(CO)<sub>3</sub> fragment is given in: Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.



The orbitals of the M(arene) fragment<sup>45,46</sup> are in many ways similar to, yet also different from, those of M(CO)<sub>3</sub>, which is what one would expect from the isolobal connection between the two. The frontier orbitals of this fragment are shown in Figure 8. The 6-fold symmetry of the isolated fragments allows a complete separation of the (d<sub>xy</sub>, d<sub>x<sup>2</sup>-y<sup>2</sup></sub>) and (d<sub>xz</sub>, d<sub>yz</sub>) sets. The d<sub>xy</sub> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbitals (e<sub>2</sub>) interact most weakly with the benzene ring; these molecular orbitals are found at low energy in the metal d block. Now there is less ambiguity about which molecular orbital "is" the d<sub>z<sup>2</sup></sub>; 1a<sub>1</sub> is 93% d<sub>z<sup>2</sup></sub> and 2a<sub>1</sub> only 0.02% d<sub>z<sup>2</sup></sub>

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(45) For a more detailed comparison of the bonding of conical fragments, see: Elian, M.; Chen, M. L. C.; Mingos, M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

(46) The bonding of arenes to metal centers has been reviewed in: Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(47) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(in Rh(benzene)). The e<sub>1</sub> FMO consists of the d<sub>xz</sub> and d<sub>yz</sub> orbitals; π bonding with the HOMO of the benzene ring pushes these orbitals highest. In Figure 8 we have also included the high-lying 2a<sub>1</sub>, an sp<sub>z</sub> hybrid orbital. This orbital does in fact contribute to the metal-metal bonding of the polynuclear clusters.

The cobalt-benzene fragment shows a similar splitting pattern, the only difference being that the 1a<sub>1</sub> orbital (d<sub>z<sup>2</sup></sub>) is slightly lower in energy than the e<sub>2</sub> set. This is due to the contraction of the d orbitals on cobalt as compared to rhodium and the fact that the s and p orbitals are closer to the d levels for cobalt (which in turn leads to a stronger mixing of these orbitals into the a<sub>1</sub> molecular orbital and hence a relative stabilization).

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