A theoretical study of transition metal complexes of C_{60} and C_{70} and their ring-opened alternatives

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Ring opened structures of C_{60} and C_{70} are shown to be stabilized by complexation with transition metal fragments of the form C_nH_nM, where n = 3 to 6 and M = Cr, Mn, Fe, Co, and Rh. The ring opening of C_{60} and C_{70} is compared with the reverse process of the well-known catalytic conversion of acetylene into benzene. Calculations at the semi-empirical PM3(tm) level show that the 6-membered ring in C_{60} and C_{70} can be opened up in different ways through complexation with transition metal fragment. The mode of ring opening depends on the number of external 5- and 6-membered rings around the 6-membered ring being cleaved. The structures and energetics of the various ring-opened structures are discussed. © 2001 by Elsevier Science Inc.

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INTRODUCTION

The fullerenes have always been at the center stage of chemistry since the synthesis of their first member, C_{60} (Structure **1**). The high symmetry, the contiguous unsaturation spreading over 60 carbon atoms, and the possibility of endohedral and exohedral chemistry imparted a special status to C_{60}. It was natural to anticipate extensive organometallic chemistry with the fullerenes because of their large unsaturation. In the initial days, these were mostly of the endohedral variety.[1–5] The exohedral organometallic chemistry[6–21] of fullerenes began with the synthesis of $C_{60}Pt(PPh_3)_2$, an η^2-complex.[7] This relative ease of formation of η^2-complexes has been analyzed in detail; its driving force is the strain energy release involved in the process.[22–24] On the other hand, no η^6-transition metal complex of fullerene has been reported so far.[25] The decreased overlap of the splayed-out orbitals of five- and six-membered rings of C_{60} and C_{70} with the frontier orbitals of transition

metal fragments makes transition-metal fullerene complexes with higher hapticity unfavorable.[23,26] An apparently similar structure observed experimentally contains corannulene, the surface curvature of which is much less than that of the fullerenes.[27] The splayed-out orbitals of C_{60} have been optimally utilized in the formation of trinuclear C_{60} complexes in which a six-membered ring is bound to the M_3L_n unit with each metal atom binding to a C–C double bond.[8]

We studied the possibility of complexation of transition metal fragments in η^6- and η^5-fashions to C_{60} and C_{70}, using the knowledge that the Fragment Molecular Orbitals (FMO) of a C_nH_nM fragment become more diffuse with decreasing value of n.[28] During these studies, it occurred to us that the rigid structures of C_{60} and C_{70} could be useful templates to model details of the synthesis of benzene from acetylene discovered by Berthelot[29] and the mechanism of which was studied in detail by the groups of Reppe and Maitlis.[30–33]

The rigid skeleton of C_{60} may preclude the formation of the tris-acetylenic structure (Structure **2**) when the 6 carbon atoms are held in proximity. However, we reasoned that a ring-opened structure might possibly be stabilized by transition-metal fragments.

Another important reason for our interest in the ring opening of the fullerenes was that it might provide a method to open fullerenes in a controlled manner to introduce metal atoms inside the fullerene cage. There is an example of ring opening of a diene-adduct of C_{60} by $CpCo(CO)_2$ through consecutive pericyclic reactions and oxidative addition. This yields a 15-membered ring.[34] However, there is no report where a 6-membered ring of C_{60} is opened up to give rise to the tris-acetylenic arrangement discussed above, through its capping to a single transition metal fragment. The complexation of the acetylenic bonds to transition metal fragments must stabilize the ring-opened structures and thus should make their synthesis possible. A pathway for ring opening of fullerenes should be helpful in the endohedral metal chemistry of fullerenes. Other experimental reports of the opening of the 6-membered ring in C_{60} involve hydrogenation of the carbon atoms of the 6-membered ring being cleaved.[35,36] There is no such report altogether for C_{70} systems. Here, we report a theoretical study of the ring opening of the 6-membered rings of C_{60} and C_{70},

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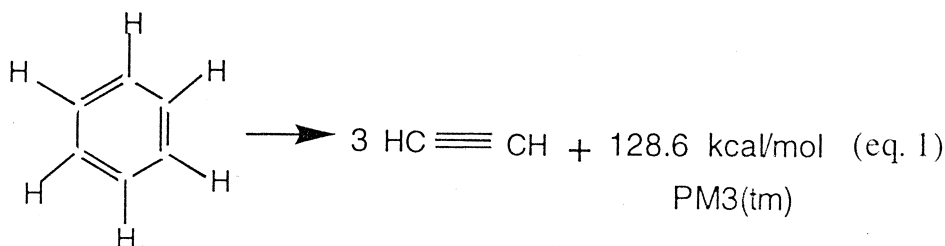
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$$\text{C}_6\text{H}_6 \longrightarrow 3\ \text{HC} \equiv \text{CH} + 128.6\ \text{kcal/mol} \quad \text{(eq. 1)}$$
$$\text{PM3(tm)}$$
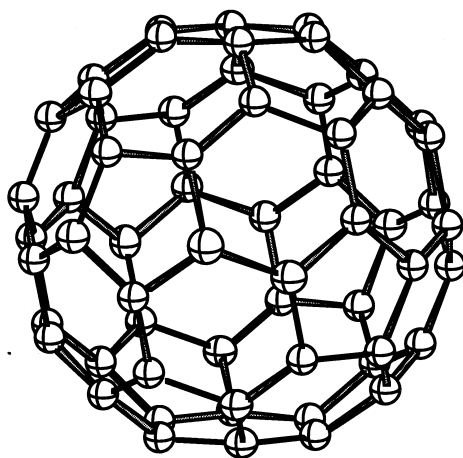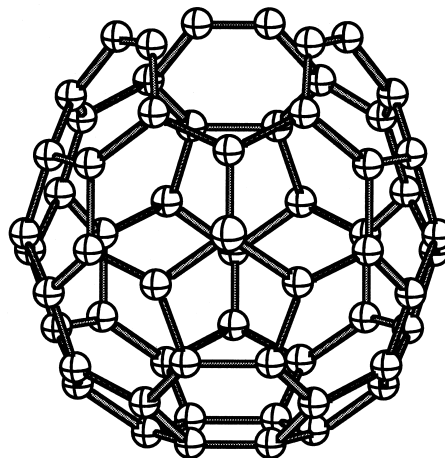
assisted by the capping of metal-ligand fragments and the stability of the resulting retro cycloaddition products. We considered $\text{C}_6\text{H}_6\text{CrC}_{60}$, $\text{C}_5\text{H}_5\text{MnC}_{60}$, $\text{C}_4\text{H}_4\text{FeC}_{60}$, $\text{C}_3\text{H}_3\text{CoC}_{60}$, $\text{C}_3\text{H}_3\text{RhC}_{60}$, and $\text{C}_6\text{H}_6\text{CrC}_{70}$, $\text{C}_5\text{H}_5\text{MnC}_{70}$, $\text{C}_4\text{H}_4\text{FeC}_{70}$, $\text{C}_3\text{H}_3\text{CoC}_{70}$, and $\text{C}_3\text{H}_3\text{RhC}_{70}$ with opened six-membered rings (Structures **7**, **8**, **14–18**) in this study.

METHOD OF COMPUTATION

Considering the number and size of the structures involved, we selected the semi-empirical PM3(tm) method with parameters given in the SPARTAN Software package.[37,38] This method has been employed earlier in several studies involving organometallic systems.[39–44] In spite of the general apprehension about the reliability of the PM3(tm) method, we have seen that it yields reasonably reliable results for organometallic complexes of fullerenes.[28] For example, model calculations involving distorted geometries of C_6H_6 and its complexes showed that the relative energies obtained at PM3(tm), HF/LANL2DZ, and B3LYP/ LANL2DZ were comparable (Table 3 in Ref. 28). All structures

were optimized at the PM3(tm) level and the energetic comparisons were made using isodesmic equations wherever possible. Here we have calculated equation 7 at the B3LYP/LANL2DZ level. A comparison of the reaction energy obtained from single-point calculations at the B3LYP/LANL2DZ level on PM3(tm) optimized geometries, with that at the PM3(tm) level shows that PM3(tm) results for such systems are reasonable and agree well with B3LYP/LANL2DZ results qualitatively.

RESULTS AND DISCUSSION

We begin with the unsubstituted benzene-trisacetylene equilibrium (Equation 1). It is endothermic by 128.6 kcal/mol at the PM3(tm) level. It may be thought to proceed through an intermediate step involving the formation of an acetylene and a didehydrobutadiene molecule (Equation 2), catalyzed by transition metals. The reaction energy without any metal fragment is 109.9 kcal/mol at the same level. Thus, the reaction of 3 HC≡CH to give HC≡CH and didehydrobutadiene is

$$\text{C}_6\text{H}_6 \longrightarrow \text{HC} \equiv \text{CH} + \quad + 109.9\ \text{kcal/mol} \quad \text{(eq. 2)}$$
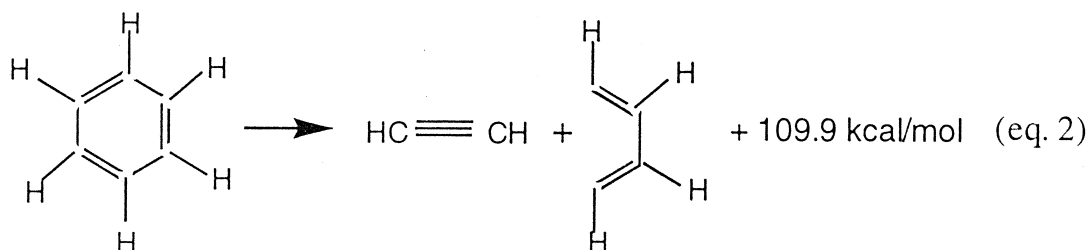
exothermic by 18.7 kcal/mol. Energy goes down further by 109.9 kcal/mol in forming benzene.

Transition metal fragments must reduce the energetics of Equations 1 and 2. Complexation with $Cr(CH)_6$ brings down the energy difference to 93.4 kcal/mol, while the corresponding values for Mn, Fe, Co, and Rh are 68.9, 68.2, 48.3, and 49.7 kcal/mol respectively (Equation 3). The letters **a–e** is taken to have the same significance throughout the text.
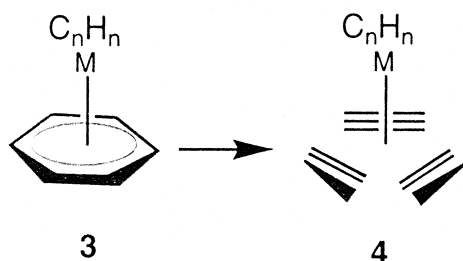
that are part of adjacent 6-membered rings are much shorter (1.384 Å) than those forming part of adjacent 5-membered rings (1.458Å). It is thus naturally expected that the C-C bonds that are part of the external 5-membered rings should be easier to break. The resulting structures should have three disconnected 6-membered rings capped by a transition-metal fragment. We obtained ring-opened structures corresponding to each of the transition-metal fragment mentioned above.

		n	ΔE, kcal/mol	
a)	Cr	6	93.4	
b)	Mn	5	68.9	
c)	Fe	4	68.2	(eq. 3)
d)	Co	3	48.3	
e)	Rh	3	49.7	

Transition metals affect Equation 2 in a similar fashion. Here the two fragments, didehydrobutadiene and acetylene, are held together by the transition metal fragment. Though some of the partially opened-up structures with transition metal fragments become distorted on optimization, the reaction energies (21.0, 45.1, 29.5, 35.9, and 47.6 kcal/mol for Cr, Mn, Fe, Co, and Rh, respectively) do not vary by large amount (Equation 4).

The difference in energy between the normal C_{60} (Structure **1**) and the ring-opened bare C_{60} (Structure **2**) is 225.4 kcal/mol at the PM3(tm) level. This is expected from the tremendous advantage of a closed structure for C_{60}, with 60 π-orbitals and the extremely strained geometry of three acetylene units in the ring-opened structure. The closeness of the atoms involved, along with the considerable amount of strain, should push these back to form a
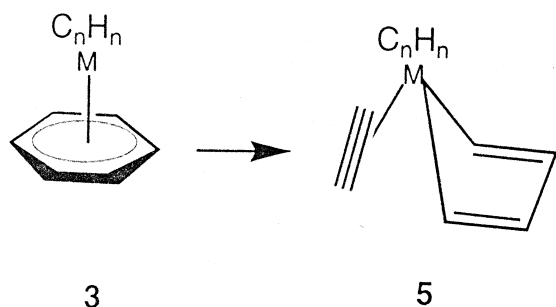
		n	ΔE, kcal/mol	
a)	Cr	6	21.0	
b)	Mn	5	45.1	
c)	Fe	4	29.5	(eq. 4)
d)	Co	3	35.9	
e)	Rh	3	47.6	

The decrease in the reaction energies (Equations 3 and 4 versus Equations 1 and 2) can be interpreted to be due to the stability imparted by complexation of the transition metal fragment to the three acetylenes or the C_4H_4 and the acetylene. The rigid structure of C_{60} should present a totally different picture of the ring-opened acetylenic units. With this in mind, we carried out studies on the ring-opened transition-metal-capped C_{60} and C_{70} systems.
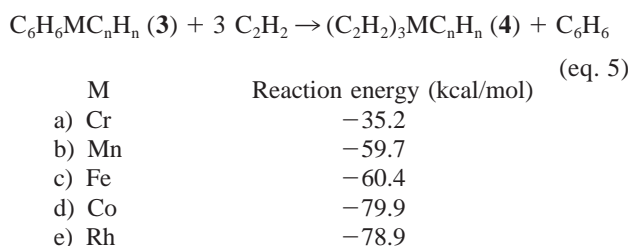
Complexes of C_{60}

In principle, there are two different (2 + 2 + 2) cycloreversion pathways for the 6-membered rings in C_{60}. The C—C bonds

closed structure for C_{60}. The transition-metal fragments should reduce the strain of the open system and also would hold, through effective capping, the acetylenes from falling back into the closed structures. Calculations show that the metal complexes of the open structures of $C_nH_nMC_{60}$ (Structures **7a–7e**) are higher in energy than their closed counterparts (Structures **6a–6e**) by much lower magnitudes than the parent systems; the values are 31.1 (Structure **7a**), 16.1 (Structure **7b**), 8.3 (Structure **7c**), 23.5 (Structure **7d**), and 26.2 (Structure **7e**) kcal/mol (Table 1). This clearly establishes the unusual stabilization of the tris-acetylene unit in C_{60} by complexation in comparison with the similar complexation of three bare acetylenes (Equation 3).
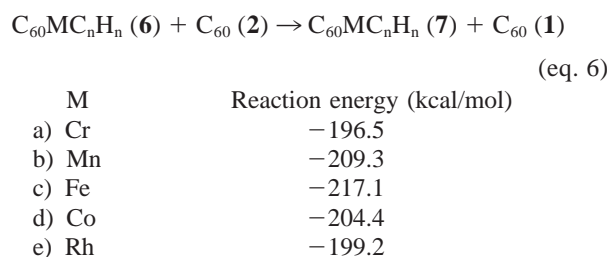
Table 1. Heat of formation values of 1-18 in kcal/mol. The relative energies of the ring-opened structures 2, 7-8, 10, 14, 15, 16-18 (kcal/mol) in comparison to their closed counterparts, 1, 6, 9, 11, 12 and 13 respectively are given in parentheses.

Structure	Heat of Formation (Rel. Energy) in kcal/mol	Structure	Heat of Formation (Rel. Energy) in kcal/mol	Structure	Heat of Formation (Rel. Energy) in kcal/mol
1	811.7	**7a**	1008.5 (31.1)	**13c**	749.6
2	1037.1 (225.4)	**7b**	785.5 (16.1)	**13d**	−676.4
3a	158.0	**7c**	708.2 (8.3)	**13e**	652.4
3b	−39.7	**7d**	−717.8 (23.5)	**14a**	1082.7 (33.3)
3c	−117.0	**7e**	611.1 (26.2)	**14b**	861.6 (19.3)
3d	−1530.8	**8a**	1002.0 (24.6)	**14c**	784.0 (12.2)
3e	−191.8	**8b**	798.0 (28.6)	**14d**	−640.9 (27.3)
4a	251.4	**8d**	−690.6 (48.3)	**14e**	688.4 (30.5)
4b	29.27a	**8e**	661.9 (74.0)	**15a**	1078.7 (25.3)
4c	−48.8	**9**	884.2	**15b**	873.5 (28.7)
4d	1482.1	**10**	1154.2 (270.0)	**15d**	−617.0 (48.6)
4e	−142.1	**11a**	1049.5	**15e**	725.5 (65.3)
5a	179.4	**11b**	842.3	**16a**	1121.9 (91.0)
5b	5.4	**11c**	771.8	**16d**	−605.2 (71.2)
5c	−87.5	**11d**	−668.2	**16e**	726.2 (73.8)
5d	−1494.9	**11e**	657.9	**17a**	1033.8 (2.9)
5e	−144.2	**12a**	1053.4	**17b**	827.6 (2.2)
6a	977.4	**12b**	844.8	**18a**	1040.1 (9.7)
6b	769.4	**12d**	−665.6	**18b**	823.2 (−2.2)
6c	699.9	**12e**	660.2	**18c**	734.7 (−14.9)
6d	−741.3	**13a**	1030.9	**18d**	−678.6 (−2.2)
6e	584.9	**13b**	825.4	**18e**	664.6 (12.2)

We have calculated the energetics of Equations 5 and 6 that would, to a certain extent, cancel the errors involved in the parameterization of the transition metals.
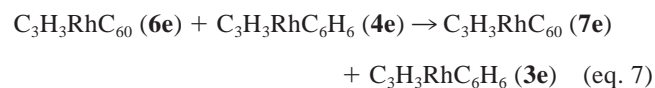
$$C_6H_6MC_nH_n \text{ (3)} + 3 \text{ } C_2H_2 \rightarrow (C_2H_2)_3MC_nH_n \text{ (4)} + C_6H_6$$

(eq. 5)

	M	Reaction energy (kcal/mol)
a)	Cr	−35.2
b)	Mn	−59.7
c)	Fe	−60.4
d)	Co	−79.9
e)	Rh	−78.9

Equation 5 is exothermic, ranging from −35.2 to −78.9 kcal/mol. The exothermicity of the corresponding equation involving C_{60} (Equation 6) is higher by 130 kcal/mol on the average.

$$C_{60}MC_nH_n \text{ (6)} + C_{60} \text{ (2)} \rightarrow C_{60}MC_nH_n \text{ (7)} + C_{60} \text{ (1)}$$

(eq. 6)

	M	Reaction energy (kcal/mol)
a)	Cr	−196.5
b)	Mn	−209.3
c)	Fe	−217.1
d)	Co	−204.4
e)	Rh	−199.2

We have calculated equation 5e, involving $Rh(C_2H_2)_3$ at the B3LYP/LANL2DZ level and found that it is exothermic by 7.5 kcal/mol. Though this is 71.4 kcal/mol lower than the PM3(tm) value, the large exothermicity of Equation 6 (196.5 to 217.1

kcal/mol) assures that even at higher levels of theory these reactions will be exothermic by substantial magnitudes.

In addition to the model systems mentioned earlier in the text, we have considered the following equation (Equation 7) using single-point calculations at the B3LYP/LANL2DZ level on the PM3(tm) optimized geometry. Even though there are differences in energy, they are not very large (−31.5 kcal at the B3LYP/PANL2DZ level versus −23.5 kcal at the PM3(tm) level).

$$C_3H_3RhC_{60} \text{ (6e)} + C_3H_3RhC_6H_6 \text{ (4e)} \rightarrow C_3H_3RhC_{60} \text{ (7e)}$$

$$+ C_3H_3RhC_6H_6 \text{ (3e)} \quad \text{(eq. 7)}$$

PM3(tm)	−23.5 kcal/mol
B3LYP/LANL2DZ	−31.5 kcal/mol

The transition metal capped C_{60} systems can open up in a different fashion where 4 carbon atoms of the 6-membered ring of C_{60} are connected to the transition-metal fragments similar to Equation 4. We obtained structures **8a**– **8e** corresponding to this for $C_nH_nMC_{60}$, with all the metal fragments except C_4H_4Fe under consideration. The relative energy values of these structures compared with Structure **6** increase monotonically as one moves from Cr to Rh, the values being 24.6 (Structure **8a**), 28.6 (Structure **8b**), 48.3 (Structure **8d**), and 74.2 (Structure **8e**) kcal/mol. This can be understood in terms of the orbital steering of the transition-metal fragments mentioned earlier. The atomic radii of the transition metal atoms considered in this study do not vary by large amounts. Thus the extent of effec-
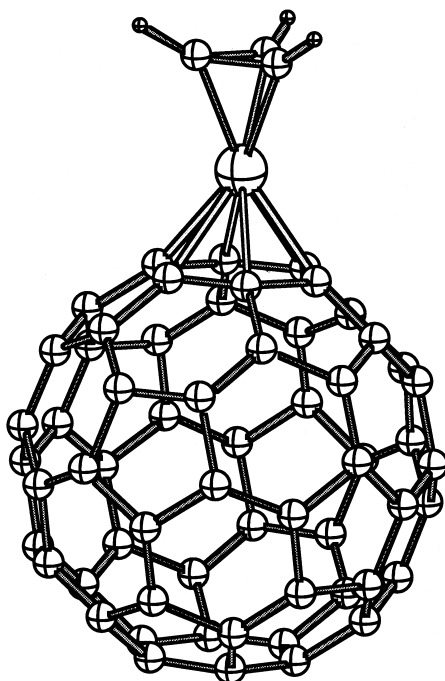
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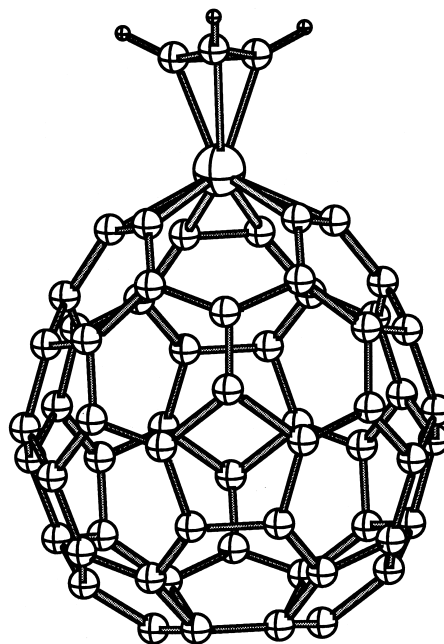
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tive overlap of the transition-metal fragment with the fullerene should depend mainly on the orientation of the transition-metal fragment. This, in turn, is dictated by the orbital steering it experiences, depending on the ring-size of the C_nH_n unit attached to it. The Cr atom with its benzene ligand is steered optimally for capping with a 4-membered ring and hence it shows the minimum change in relative energy while going from the closed system. The efficiency of the overlap decreases as the ring size of the C_nH_n unit decreases. Consequently, the relative energy values of Structure **8** increase monotonically as one moves from Cr to Rh via Mn and Co (Table 1).

The C—C nonbonded distances between the acetylenic carbons in Structure **2**, Structure **4**, and Structure **7** show the effect of metal complexation dramatically. The C—C non-bonded distance of 2.641Å in Structure **2** goes to 2.346Å in Structure **7a**. Thus the metal brings the acetylenic carbons close to each other. Structures **7b–7e** have similar distances. On the other hand, the C—C nonbonding distances for the partially opened-up structures (Structures **8a–8e**), vary to a much lesser extent. For example, the distance between the acetylenic and the butadiene-like fragments of the 6-membered ring are: 2.574Å (Structure **8a**), 2.534Å (Structure **8b**), 2.565Å (Structure **8d**), and 2.644Å (Structure **8e**).

Complexes of C_{70}

The presence of three distinct 6-membered rings in C_{70} makes the situation more involved. The 6-membered rings can be differentiated by the number of external 5- and 6-membered rings. Among the various possibilities, only one ring-opened structure of C_{70}, Structure **10**, could be located. This is structurally similar to the C_{60} fragments in Structures **8a–8e**. The difference in energy between the normal C_{70} (Structure **9**), and
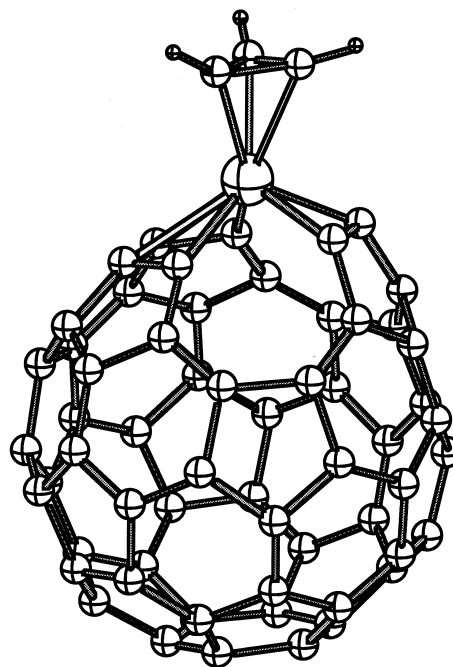

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the ring-opened C_{70} (Structure **10**) is 270.0 kcal/mol at the PM3(tm) level. Ring-opened structures of C_{70} involving the other 6-membered rings fall back to C_{70} on optimization. η^6-complexes are calculated with each of the 6-membered rings (Structure **11**, Structure **12** and Structure **13**), corresponding to

the nomenclature for the different six membered rings (1,2,12,11,10,9), (7,8,25,24,23,22) and (21,22,23,42,41,40) as defined by Taylor.[45]

One of the 6-membered rings in C_{70} is surrounded by three 5-membered and three 6-membered rings and is similar to the 6-membered ring in C_{60}. Tris-acetylenic ring-opened structures of $C_nH_nMC_{70}$ corresponding to this ring, Structures **14a–14e** were calculated with each of the metal fragments.

As with the transition-metal-capped C_{60} systems, the relative energies between the closed $C_nH_nMC_{70}$ systems, Structures **11a–11e**, and the opened-up structures, Structures **14a–14e**, fall from 33.3 (**14a**) kcal/mol to a minimum of 12.2 kcal/mol (Structure **14c**) and then rises to 30.5 kcal/mol (Structure **14e**) (Table 1).
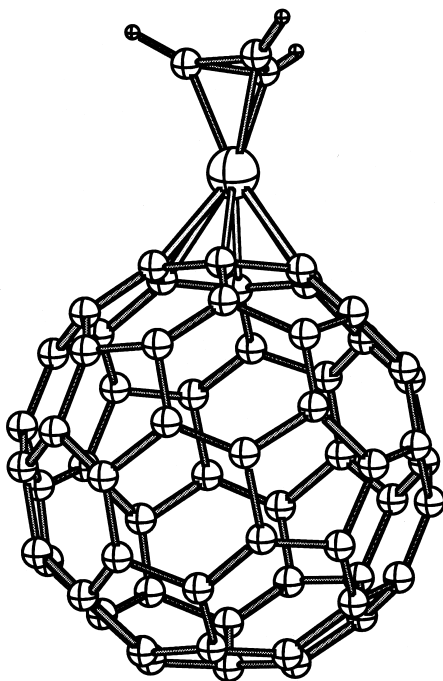
Structures similar to Structures **8a–8e** for the above ring could not be obtained. However, similar structures, Structures **15a–15e**, are calculated from Structure **12**. The relative energy
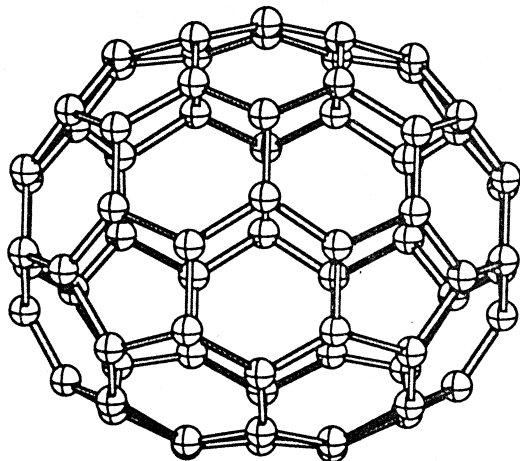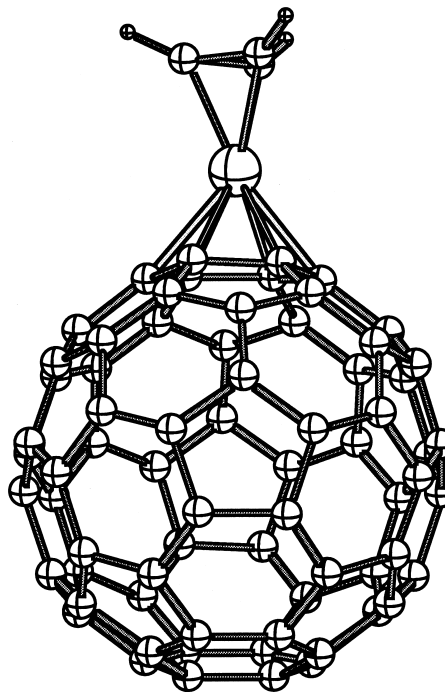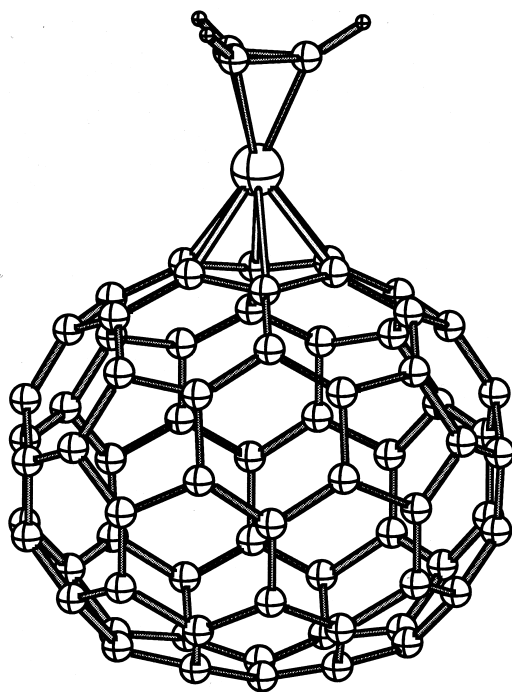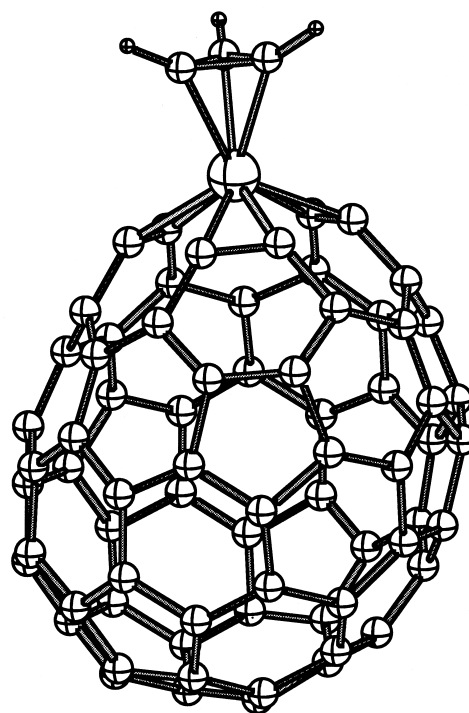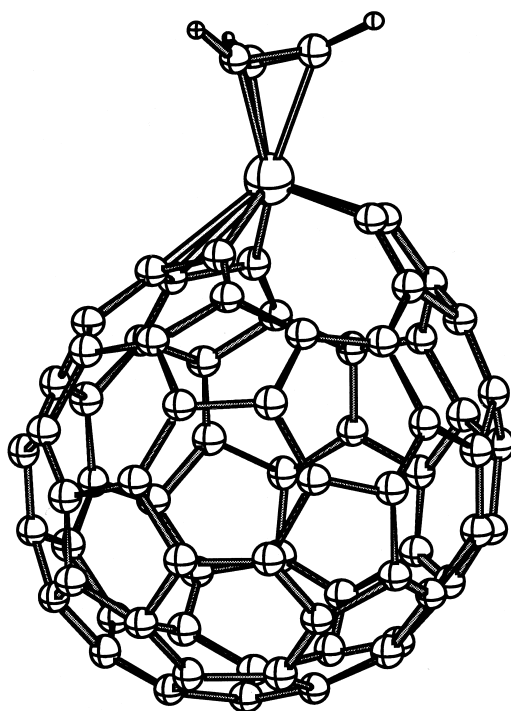
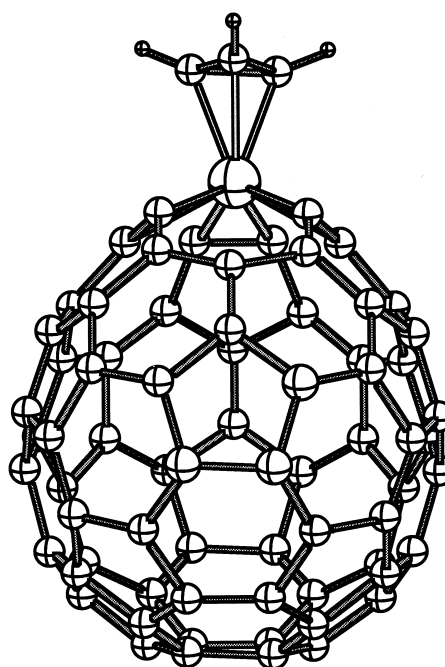

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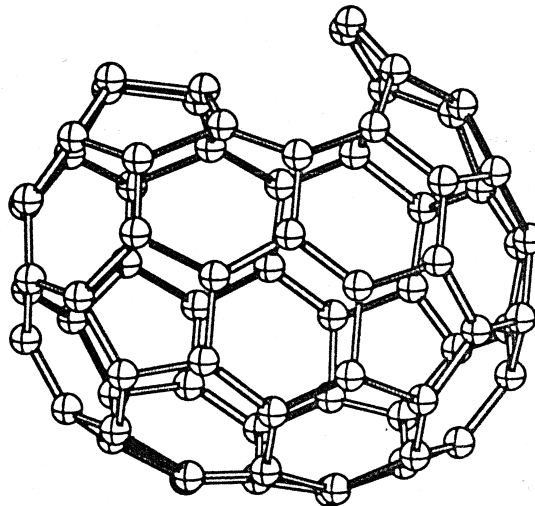
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values of these structures compared with the corresponding closed $C_nH_nMC_{70}$ systems (Structures **12a**–**12e**) show a mono-

tonic increase: 25.3 (Structure **15a**), 28.7 (Structure **15b**), 48.6 (Structure **15d**), and 65.4 (Structure **15e**) kcal/mol.


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The ring opening of $C_nH_nMC_{70}$ corresponding to Structure **13** becomes even more interesting. Tris-acetylenic ring-opened Structures, **16a**, **16d**, and **16e** were calculated. We could also obtain Structures **17a** and **17b**, which are similar to Structure **15**. The ring-opened $C_nH_nMC_{70}$ Structures **16** and **17** are higher in energy than the corresponding closed structures (Structures **13a**–**13e**). The relative energy values are 91.0 (Structure **16a**), 71.2 (Structure **16d**), 73.8 (Structure **16e**), 2.9 (Structure **17a**), and 2.2 (Structure **17b**) kcal/mol. Thus some of the ring-opened structures are very close to the η^6-complexes.

We also could obtain another set of ring-opened structures (Structures **18a**–**18e**). These structures have the metal atom connected to 4 of the 6-membered ring carbon atoms in a symmetric fashion. The relative energy pattern for these structures is interesting. While Structures **18a** and **18e** are higher in energy by 9.7 and 12.2 kcal/mol compared with their closed counterparts Structures **13a** and **13e**,

$$C_{70}MC_nH_n\ (\mathbf{12}) + C_{70}\ (\mathbf{10}) \rightarrow C_{70}MC_nH_n\ (\mathbf{15}) + C_{70}\ (\mathbf{9})$$

(eq. 8)
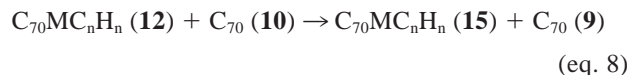
M	Reaction energy (kcal/mol)
a) Cr	−235.7
b) Mn	−241.3
c) Fe	
d) Co	−221.4
e) Rh	−204.7

CONCLUSIONS

Benzene is more favorable than 3 C_2H_2 by 128.6 kcal/mol. This difference increases to 225.4 kcal/mol for C_{60} (Structure **1**) and the ring-opened C_{60} (Structure **2**). The corresponding energy difference for C_{70} systems (Structure **10** versus Structure **9**) is 270.0 kcal/mol. Transition metals bring this difference down to 93.4 kcal/mol (Structure **3a**), 68.9 kcal/mol (Structure **3b**), 68.2
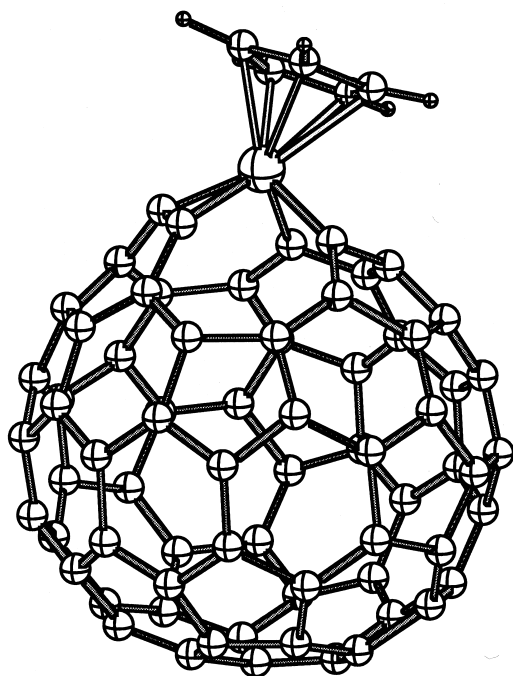
17
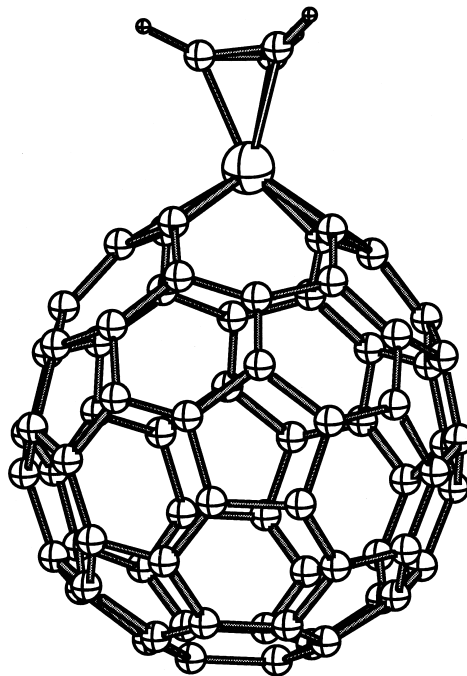
18

Structures **18b**, **18c**, and **18d** are more stable than their closed counterparts, Structures **13b**, **13c**, and **13d** by 2.2, 14.9, and 2.2 kcal/mol, respectively. The higher stability of Structure **18**, where a six-membered ring is broken by stretching two opposite C-C bonds over Structure **16**, indicates the unusually large strain relief involved in this mode of opening the ring and complexation.

Equation 8, calculated for C_{70}, which is similar to Equation 6, is exothermic by 204.7 to 241.3 kcal/mol. This high exothermicity observed at the semiempirical PM3(tm) level gives us confidence that higher levels of theory should show similar trends, even if the magnitudes may change.

kcal/mol (Structure **3c**), 48.3 kcal/mol (Structure **3d**), and 49.7 kcal/mol (Structure **3e**). The ease and the pattern of the ring opening depends on the number of 5- and 6-membered rings that surround the 6-membered ring being cleaved. Thus, different rings of C_{70} open up in different fashions as is evident from Structures **14**–**18**. However, the same 6-membered ring in C_{70} can open up in different ways for different transition metal fragments. Thus, the 6-membered ring of Structure **13** can open up in the tris-acetylenic fashion with transition metal fragments like C_6H_6Cr, C_3H_3Rh, or C_3H_3Co (Structures **16a**, **16d**, and 16e), while with C_5H_5Mn, the same ring cleaves to produce Structure **17b**.

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