Exohedral η^5 and η^6 Transition-Metal Organometallic Complexes of C_{60} and C_{70}: A Theoretical Study

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Suitable transition-metal fragments are proposed to overcome the unfavorable interaction arising from the splayed out π-orbitals of the five- and six-membered rings of C_{60} and C_{70} in complex formation. Computations carried out at the semiempirical PM3(tm) level on a series of $C_{60}MC_nH_n$ and $C_{70}MC_nH_n$ complexes suggest that it is possible to stabilize η^6 complexes of C_{60} and C_{70} using appropriate transition-metal fragments. Isodesmic equations of the type $C_mH_mMC_nH_n + C_k \rightarrow C_kMC_nH_n + C_mH_m$, where $k = 60$, 70, $m = 5$, 6, and $n = 3-6$, indicate that C_3H_3Co and C_3H_3Rh are ideal fragments for stabilizing η^6-C_{60} complexes. Model studies at HF/LANL2DZ and B3LYP/LANL2DZ levels on $C_6H_6ML_n$ complexes with C_6H_6 constrained so as to mimic the C_{60} geometry support these results. Single-point calculations at these same levels on complexes of sumanene ($C_{21}H_{12}$) using geometry optimized at the PM3(tm) method also lead to similar conclusions. η^5 complexes are less favorable in comparison; structural modifications such as those in the recently synthesized $C_{60}Ph_6$ should readily help in η^5 bonding. However, the difficulty of formation of the mononuclear η^5-$C_{60}ML_n$ complex is reduced considerably if all 12 five-membered rings are used in η^5 bonding as in $C_{60}(NiC_3H_3)_{12}$. For C_{70}, however, the stability of the exohedral complexes depends on the position and curvature of the five- and six-membered rings. Capping on the flattest six-membered face leads to maximum stability.

Introduction

The fullerenes, with their rapid expansion and continuous growth into almost all branches of chemistry, are fascinating subjects.[1] With 12 5-membered and 20 6-membered rings, and 30 double bonds in contiguous conjugation, the parent fullerene, C_{60}, possesses the potential for varied organometallic chemistry. The dominant initial organometallic chemistry of the fullerenes was of the endohedral variety, where one or more metal atoms were trapped inside the cage.[2] The metal atoms obviously attach themselves to the endohedral surface of the fullerenes with varying degrees of bonding. Several studies have been directed toward elucidating the details of such interactions.[3] The conventional exohedral organometallic chemistry began with the synthesis of $C_{60}Pt(PPh_3)_2$ by Fagan, Calabrese, and Malone (Figure 1).[4] Since then, several complexes, most of which have the transition-metal fragment bonded to the fullerene in an η^2 fashion, have been reported.[5] This relative ease of formation of η^2 complexes have been analyzed in detail.[6] The driving force for η^2-complex formation is the strain energy release involved

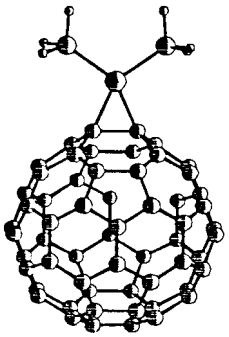

Figure 1. Schematic diagram of $C_{60}Pt(PH_3)_2$.

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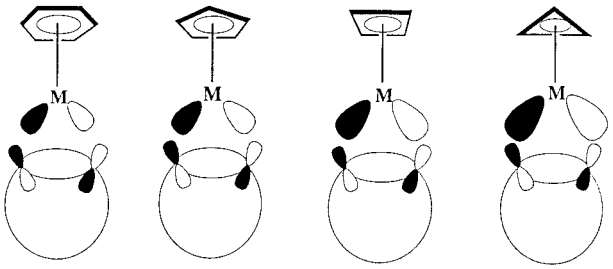

Figure 2. Schematic representation of the variation in the diffuse nature of the C_nH_nM fragment as a function of n.

in the process. The geometry around the carbon atoms in C_{60} and C_{70} is remarkably close to that in olefin complexes;[6a,b] the organometallic chemistry of C_{60} is considered to be similar to that of electron-deficient alkenes.[6c] On the other hand, no η^5 or η^6 transition-metal complex of fullerene has been reported so far.[7] 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 η^5 and η^6 complexes unfavorable (Figure 2).[6b,8] Though an X-ray structure with C_{60} and $(C_5H_5)_2Fe$ in the unit cell has been reported,[9] we have not come across any well-characterized η^5 or η^6 transition-metal complex of fullerene so far. The closest structure observed experimentally is an η^6 organometallic complex reported for the curved polyaromatic hydrocarbon, corannulene.[10a] The surface curvature of this complex, however, is much less than that of C_{60} or C_{70}. The splayed out orbitals of C_{60} have been optimally utilized in the formation of trinuclear C_{60} complexes where a six-membered ring is bound to the M_3L_n unit with each metal atom binding to a C−C double bond.[5a] The η^5 complexes have been synthesized by starting with derivatives of C_{60} such as $C_{60}Ph_5$.[11] Here, the five-membered ring is isolated from the rest of the fullerene by sp^3 hybrid carbons. Similar complexes are also reported for C_{70} derivatives such as $C_{70}(C_6H_4CF_3)_3$ with K, Tl, and $Cu(C_6H_4CF_3)$.[12] The changes in geometry brought here by the saturated carbon centers help in bonding. We present here ways to get five- and six-membered rings of parent C_{60} and C_{70} to bind to transition-metal fragments and predict viable targets based on theoretical studies.

The fullerenes, with their rigid geometry, do not leave much scope for chemical manipulations to force exohedral η^5 or η^6 bonding. Therefore, the orbital steering should be achieved from the metal end. The large number of studies reported on the exohedral metal complexes mostly involve a single atom or ion attached

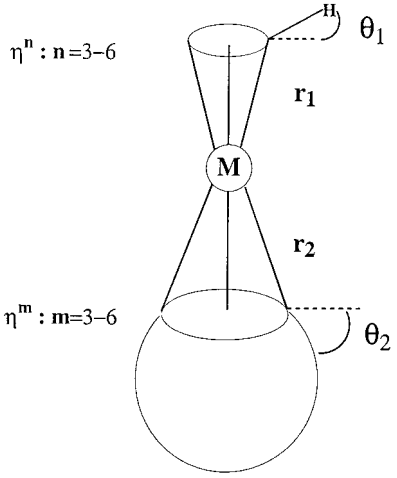

Figure 3. Schematic representation of structures **1**−**9** and **11**−**23** of transition-metal complexes $C_nH_nMC_{60}$ and $C_nH_nMC_{70}$ computed in this study. Details are given in Table 4.

to the external surface of the fullerene.[5a,13] While the hapticity of these bindings could vary from 1 to 6, no specific orbital steering is possible without additional attachments of other groups/ligands to the metal atom. Thus, the natural extent of the orbitals on the atom alone should decide the hapticity. However, with additional ligands on the metal atom, it should be possible to orient the metal orbitals in a splayed out fashion so that the interaction with the fullerenes becomes more favorable.[14]

It has been established many times that the Fragment Molecular Orbitals (FMO) of a C_nH_nM fragment become more diffuse with decreasing value of n. For example, C_3H_3Co will provide considerably more diffuse orbitals than those provided by C_6H_6Cr (Figure 2). An additional way of increasing the size of the orbitals is to use heavier metals. Thus, we selected C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, C_3H_3Co, and C_3H_3Rh as possible fragments to complex C_{60} and C_{70} in η^6 and η^5 fashion so that a gradation in stability can be noticed.

In any such fullerene−ML_n combination, the electron count around the metal has to be carefully controlled. All metal complexes, $C_{60}MC_nH_n$ and $C_{70}MC_nH_n$ (n = 3−6, M = transition metal; Figure 3) considered in this paper have 18 electrons around the metal (**1**−**9**, **11**−**23**). Preliminary results on the C_{60} complexes have been published.[15] The η^6 complexes do not bring in any unusual distribution of charge. However, the five-membered ring in the η^5 complexes (**6**−**9**) is forced to behave either as a 4-electron donor or a 6-electron donor so that the C_{55} unit will be a closed-shell system. An exact η^5 arrangement will be obtained if all the 12 pentagons of C_{60} are brought into bonding.[16] Therefore, we have also studied $C_{60}(NiC_3H_3)_{12}$ as a possible realistic complex with pseudo-icosahedral symmetry, **10**. C_{70} poses more complexity due to the presence of five- and

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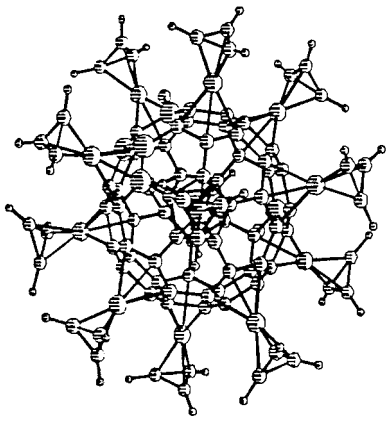

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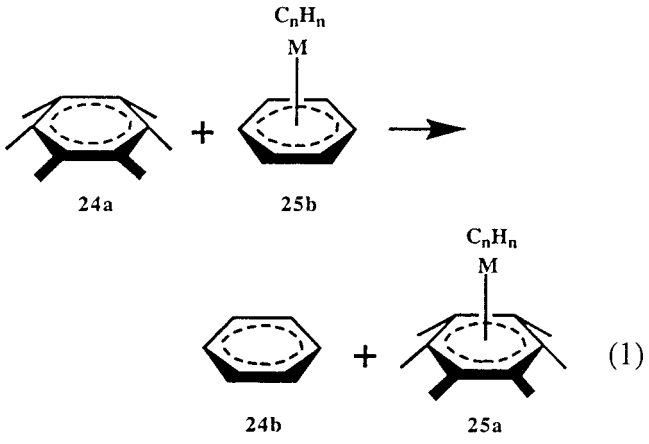
six-membered rings with varying curvature. We have selected structures **11**−**13** for the complexes of C_{70}. We also report studies on models for the η^5 complexes of C_{60} and C_{70} derivatives: viz., $C_{60}H_5ML_n$ (**14**−**18**), $C_{60}Cl_5Pd(C_3H_3)$ (**19**), $C_{70}H_5ML_n$ (**20**, **21**), and $C_{70}H_3ML_n$ (**22**, **23**) (Table 4).

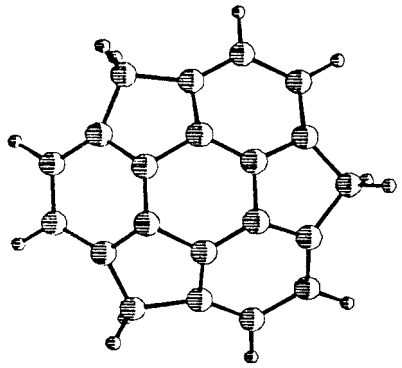
Method of Calculations

In view of the number and size of the molecules involved in this study, it was clear from the beginning that extensive ab initio computations were not practical with the facilities available. Therefore, we selected the semiempirical method PM3(tm) of Hehre et al. for this study after the following considerations. Several theoretical studies of transition-metal systems using PM3(tm) have been reported recently.[17] The method is shown to be reasonably reliable in relation to the computational time involved. We studied the structures of a series of $(C_nH_n)M(CO)_3$ complexes (n = 3−6, M = Cr, Mn, Fe, Co) using PM3(tm) and found that the geometric parameters are comparable to the related experimental structures (Table 1). We also compared the PM3(tm) results with those obtained from B3LYP/LANL2DZ computations on a closely related model system to decide the appropriateness of the method to study the complexes of C_{60} and C_{70}. For this purpose, two models were used. In the first model, benzene (**24a** and **25a**)



(1)

is used in constrained geometry by bending the six C−H bonds, retaining the C_{6v} symmetry so that the geometry parallels the η^6-C_{60} complexes. In the second model, the curved molecule sumanene (**26**), which can be treated as a fragment of C_{60}, is used to replace C_{60}. The results obtained at the HF/LANL2DZ, B3LYP/LANL2DZ, and PM3(tm) methods showed similar trends (Table 3).



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We also studied an isodesmic reaction, used previously to gauge the results of PRDDO calculation on fullerene complexes,[8] to compare PM3(tm), HF/LANL2DZ and B3LYP/LANL2DZ results (eq 3). Results from all these model studies encouraged us to use the PM3(tm) method for the fullerene complexes in this study. All PM3(tm) calculations were carried out using the Spartan software[23] and the HF and B3LYP calculations using the GAUSSIAN94 program.[24]

Results and Discussion

Structures of $C_nH_nM(CO)_3$ (n = 3−6, M = Cr, Mn, Fe, and Co): PM3(tm) vs Experiment. The structures were optimized without any geometry constraints using the PM3(tm) method. All the structures were found to be minima. Selected geometric parameters are compared to the corresponding values from the experimental structures and are found to be in reasonable agreement (Table 1). This has given us confidence to

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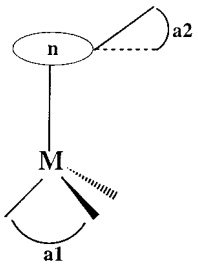
Table 1. Selected Bond Angles (deg) of $C_nH_nM(CO)_3$ Complexes Computed at the PM3(tm) Level and the Corresponding Experimental Values[a]



	n, M			
	3, Co[b]	4, Fe[c]	5, Mn[d]	6, Cr[e]
a1				
PM3(tm)	102.5	97.7	91.9	88.9
exptl	105.0	97.0	91.8	88.8
a2				
PM3(tm)	29.0	13.7	7.1	3.0
exptl	19.1	10.9	0.4	−2.5
M−CO				
PM3(tm)	1.804	1.744	1.766	1.894
exptl	1.797	1.751	1.789	1.833
M−C_nH_n				
PM3(tm)	2.001	2.073	2.226	2.238
exptl	1.980	2.067	2.136	2.221
C−C				
PM3(tm)	1.469	1.489	1.446	1.438
exptl	1.426	1.459	1.420	1.404

[a] Some of the experimental structures have groups other than H in the C_nH_n fragments. [b] Reference 21a. [c] Reference 21b [d] Reference 21c. [e] Reference 21d.

use geomteries obtained at the PM3(tm) level for ab initio calculations without geometry optimization for comparison of models.

Model Systems using C_{6v} Constrained C_6H_6. The splayed out orbitals of C_{60} and C_{70} were simulated using the C_{6v} constrained C_6H_6. The increasing preference of C_nH_nM for splayed out orbitals with decreasing value of *n* can be observed in the variation of the reaction energies obtained at PM3(tm), HF/LANL2DZ, and B3LYP/LANL2DZ levels (eq 1; Tables 2 and 3). All geometric parameters except the C−H out-of-plane bending of the C_6H_6 of the structures used in eq 1 were optimized at HF/LANL2DZ and B3LYP/LANL2DZ. The C−H out-of-plane bendings in **24a** and **25a** were taken from C_{60} and the $C_{60}MC_nH_n$ complexes optimized at the PM3(tm) level. It may be mentioned here that the rigid structure of C_{60} does not change considerably after complexation. The energy values of this equation were also obtained at the PM3(tm) level through single-point calculations carried out on the B3LYP/LANL2DZ-optimized structures obtained above (Table 3).

Ab initio calculations indicate that it is indeed better for the C_nH_nM fragment to interact with an unconstrained C_6H_6 ring. However, this preference decreases as *n* goes down. The equation is least endothermic for C_3H_3Rh, where fragment molecular orbitals are maximally diffuse. While PM3(tm) shows eq 1 to be exothermic for all C_nH_nM fragments except when M = Mn, the maximum exothermicity is obtained for C_3H_3M, as expected. We have also checked these trends with a more realistic model, sumanene (**26**).

Model Studies Using Sumanene as the Curved Ligand. Sumanene[10b] ($C_{21}H_{12}$, **26**) is considered as a model in place of constrained C_6H_6 (eq 2). Here, all

$$C_{21}H_{12} + \eta^5\text{-}C_nH_nMC_6H_6 \rightarrow (\eta^5\text{-}C_nH_n)MC_{21}H_{12} + C_6H_6 \quad (2)$$

26

structures involved were fully optimized at the PM3-(tm) level, and single-point calculations on PM3(tm) optimized structures were carried out at the HF/LANL2DZ and B3LYP/LANL2DZ levels (Table 3). Clearly, the η^6 complex with benzene, $C_nH_nMC_6H_6$, is favored by large magnitudes at all of these levels. As the value of *n* decreases, the endothermicity decreases. With the most favorable fragment C_3H_3Rh, the equation is still endothermic by 15.2 kcal/mol (HF/LANL2DZ) and 13.7 kcal/mol (B3LYP/LANL2DZ) but marginally exothermic at PM3(tm). Though the quantitative agreement is lacking, the trends are reproduced well. It should be possible to vary substituents on the C_3H_3 ring to further favor the bent complexes. It should also be kept in mind that sumanene is much less curved than C_{60}.

Table 2. Total Energy (au) of the Compounds in Eqs 1−3

	total energy	
compd[a]	HF/LANL2DZ	B3LYP/LANL2DZ
$C_6H_6Cr(CO)_3$	−654.208 61	−658.491 88
$(\eta^6\text{-}C_6H_5)ClCr(CO)_3$	−668.312 04	−672.821 91
C_6H_6	−230.640 93	−232.213 34
C_6H_5Cl	−244.752 09	−246.551 23
$C_6H_6CrC_6H_6$ (**a**)	−546.585 49	−550.597 77
$C_6H_6CrC_6H_6$ (**b**)	−546.706 37	−550.706 57
$C_5H_5MnC_6H_6$ (**a**)		−529.496 34
$C_5H_5MnC_6H_6$ (**b**)	−525.813 37	−529.615 37
$C_4H_4FeC_6H_6$ (**a**)	−506.554 07	−510.241 64
$C_4H_4FeC_6H_6$ (**b**)	−506.535 72	−510.356 42
$C_3H_3CoC_6H_6$ (**a**)	−489.615 73	−493.153 08
$C_3H_3CoC_6H_6$ (**b**)	−489.733 17	−493.257 97
$C_3H_3RhC_6H_6$ (**a**)	−454.331 97	−457.623 91
$C_3H_3RhC_6H_6$ (**b**)	−454.443 84	−457.721 52
$C_6H_6(Cr)$[b]	−230.534 78	−232.124 13
$C_6H_6(Mn)$[b]	−230.537 13	−232.126 09
$C_6H_6(Fe)$[b]	−230.535 72	−232.124 92
$C_6H_6(Co)$[b]	−230.535 17	−232.124 45
$C_6H_6(Rh)$[b]	−230.533 05	−232.122 67
$C_{21}H_{12}$ (**c**)	−801.951 90	−807.286 49
C_6H_6 (**c**)	−230.638 66	−232.211 36
$C_6H_6CrC_{21}H_{12}$ (**c**)	−1 117.938 97	−1 125.717 33
$C_6H_6CrC_6H_6$ (**c**)	−546.689 47	−550.702 88
$C_5H_5MnC_{21}H_{12}$ (**c**)	−1 097.038 60	−1 104.629 75
$C_5H_5MnC_6H_6$ (**c**)	−525.782 81	−529.611 32
$C_4H_4FeC_{21}H_{12}$ (**c**)	−1 077.881 48	−1 085.363 35
$C_4H_4FeC_6H_6$ (**c**)	−506.632 49	−510.347 58
$C_3H_3CoC_{21}H_{12}$ (**c**)	−1060.978 84	−1068.295 11
$C_3H_3CoC_6H_6$ (**c**)	−489.688 45	−493.249 97
$C_3H_3RhC_{21}H_{12}$ (**c**)	−1 025.678 66	−1 032.751 17
$C_3H_3RhC_6H_6$ (**c**)	−454.389 71	−457.697 83

[a] Structures **a** are optimized with bent C−H out of plane constraint. Structures **b** are fully optimized. Structures **c** are the result of single-point calculations performed on PM3(tm) optimized geometries. [b] The C_6H_6 systems with the metal atom in parentheses indicate the partially optimized C_6H_6 with the bent C−H out of plane fixed at the value obtained from the corresponding metal complex.

Study of the Experimentally Known Reactions. The exchange reaction of $C_6H_6Cr(CO)_3$ with C_6H_5Cl (eq 3) was used to see the correctness of the PRDDO method.[8] We found that HF/LANL2DZ, B3LYP/LANL-

Table 3. Comparison of Reaction Energies (in kcal/mol) Computed at PM3(tm), HF/LANL2DZ, and B3LYP/LANL2DZ for Reactions Involving Complexes of C_6H_6 (Eq 1) and $C_{21}H_{12}$ (26, Eq 2) Modeled after PM3(tm) Optimized Structures of $C_nH_nMC_{60}$ (M = Cr, Mn, Fe, Co, Rh) with Those Obtained at PM3(tm) for Eqs 5−9

	$C_nH_nMC_6H_6$ (eq 1)			$C_nH_nMC_{21}H_{12}$ (eq 2)			$C_nH_nMC_{60}$
C_nH_nM	PM3(tm)	HF/LANL2DZ	B3LYP/LANL2DZ	PM3(tm)	HF/LANL2DZ	B3LYP/LANL2DZ	PM3(tm)
C_6H_6Cr	11.3	9.2	12.3	50.5	40.0	38.1	30.8
C_5H_5Mn	18.4	*a*	19.9	37.0	36.1	35.6	20.8
C_4H_4Fe	*a*	11.6	16.5	41.0	40.3	37.2	28.7
C_3H_3Co	8.3	7.3	10.1	10.2	14.3	18.8	1.6
C_3H_3Rh	-0.8	2.5	4.4	−2.5	15.2	13.7	−11.4

[a] Optimization (at HF/LANL2DZ) on $C_5H_5MnC_6H_6$ (**a**) and single point calculation (at PM3(tm)) on $C_4H_4FeC_6H_6$ (**a**) did not lead to SCF convergence.

$$C_6H_6Cr(CO)_3 + C_6H_5Cl \rightarrow (\eta^6\text{-}C_6H_5Cl)Cr(CO)_3 + C_6H_6 \quad (3)$$

experimental:[20] 4.5 kcal/mol

PRDDO:[8] 2.2 kcal/mol

PM3(tm): 6.1 kcal/mol

HF/LANL2DZ: 4.5 kcal/mol

B3LYP/LANL2DZ: 4.7 kcal/mol

2DZ, and PM3(tm) methods also give results comparable to the experimental one. Obviously, these are isodesmic equations.

It may be argued that here the metal−C_6H_6 interactions cancel totally, and hence, the PM3(tm) result agrees well with the experiment. By the same token, all energetic comparisons made using eqs 1 and 2 also had essentially similar ligands: C_6H_6 and constrained C_6H_6 in eq 1 and $C_{21}H_{12}$ in eq 2. Another example that we have calculated to see the validity of the PM3(tm) method is given in eq 4. Experimentally, η^2 complexes

$$(\eta^2\text{-}C_2H_4)Ni(PH_3)_2 + C_{60} \rightarrow (\eta^2\text{-}C_{60})Ni(PH_3)_2 + C_2H_4 \quad (4)$$

$$\Delta E = -22.1 \text{ kcal/mol}$$

of C_{60} are well-known. Equation 4 is calculated to be highly exothermic by PM3(tm), supporting the overall suitability of the PM3(tm) method for this group of molecules.

η^6 and η^5 Complexes of C_{60}. We have used isodesmic equations to estimate the thermodynamic stabilities of various metal complexes of C_{60} (eqs 5−9 and 10−13). The transition metal complexes $C_6H_6CrC_6H_6$, $C_5H_5MnC_6H_6$, $C_4H_4FeC_6H_6$, $C_3H_3CoC_6H_6$, $C_3H_3RhC_6H_6$, $C_5H_5FeC_5H_5$, $C_5H_5CoC_4H_4$, $C_3H_3NiC_5H_5$, and $C_3H_3PdC_5H_5$ are calculated for using in isodesmic equations. The stability of these complexes is estimated in relation to the traditional benzene complexes with the same metal fragments using eqs 5−9.

$$C_6H_6CrC_6H_6 + C_{60} \rightarrow (\eta^6\text{-}C_{60})CrC_6H_6 + C_6H_6 \quad (5)$$
1

$$\Delta E = 30.8 \text{ kcal/mol}$$

$$C_5H_5MnC_6H_6 + C_{60} \rightarrow (\eta^6\text{-}C_{60})MnC_5H_5 + C_6H_6 \quad (6)$$
2

$$\Delta E = 20.8 \text{ kcal/mol}$$

$$C_4H_4FeC_6H_6 + C_{60} \rightarrow (\eta^6\text{-}C_{60})FeC_4H_4 + C_6H_6 \quad (7)$$
3

$$\Delta E = 28.7 \text{ kcal/mol}$$

$$C_3H_3CoC_6H_6 + C_{60} \rightarrow (\eta^6\text{-}C_{60})CoC_3H_3 + C_6H_6 \quad (8)$$
4

$$\Delta E = 1.6 \text{ kcal/mol}$$

$$C_3H_3RhC_6H_6 + C_{60} \rightarrow (\eta^6\text{-}C_{60})RhC_3H_3 + C_6H_6 \quad (9)$$
5

$$\Delta E = -11.4 \text{ kcal/mol}$$

As anticipated, dibenzenechromium is considerably more favorable than $(\eta^6\text{-}C_{60})CrC_6H_6$ (**1**) (eq 5). The endothermicity of the reactions decreases from 30.8 kcal/mol with $(\eta^6\text{-}C_6H_6)Cr$ (eq 5) to 1.6 kcal/mol with $(\eta^3\text{-}C_3H_3)Co$ (eq 8). Evidently, the diffuse frontier orbitals of $(\eta^3\text{-}C_3H_3)Co$ help in increasing the interaction with C_{60} (Table 4). Additional enhancement of the diffuse nature of the metal fragment orbitals is achieved by going down the periodic table to Rh; eq 9 is calculated to be *exothermic* by 11.4 kcal/mol. This also emphasizes the possibility of increasing the metal−C_{60} interactions using heavier metals as suggested by Marynick.[8]

Because of the C−C bonds of unequal length in the six-membered rings of C_{60},[25] the structure of $(\eta^6\text{-}C_{60})RhC_3H_3$ (**5**) presents an interesting conformational problem. This leads to three distinct arrangements, **a**−**c** (Figure 4), among which **a** is calculated to be more favorable than **b** by 2.7 kcal/mol. This is similar to the qualitative results available on $C_6H_6M(CO)_3$ complexes.[26] Conformation **c** goes to **a** on optimization. An overlap-based explanation is available for the present example as well.[26] As expected, the geometric parameters of **a** and **b** are, however, very similar. A similar result is obtained for $C_{60}CoC_3H_3$ (**4**) with an energy difference of 2.5 kcal/mol between conformers **a** and **b**.

η^5 coordination of C_{60} presents additional problems. The consideration of ring size and π-metal orbital overlap alone does not suffice to explain and predict the relative stability of such systems. For example, the angles subtended by a C−C bond of C_{60} with the plane of five- and six-membered rings are found to be 31.7 and 35.3°, respectively.[25] Thus, the π orbitals of the five-membered face should be less unfavorable than those of the six-membered face and so η^5 coordination should be better than η^6 coordination in binding to transition-

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Table 4. ΔH_f Values and Selected Geometric Parameters of (η^n-C_nH_n)M(η^m-C_{60}) (1−9), $C_{60}(Ni(C_3H_3)_{12})$ (10), (η^6-C_{70})RhC_3H_3 (11−13), (η^n-C_nH_n)M(η^m-$C_{60}H_5$) (14−18), (η^5-$C_{60}Cl_5$)PdC_3H_3 (19), (η^5-$C_{70}H_5$)PdC_3H_3 (20, 21), and (η^5-$C_{70}H_3$)PdC_3H_3 (22, 23) Computed at the PM3(tm) Level

no.	M	n	m	ΔH_f (kcal/mol)	r_1 (Å)	r_2 (Å)	θ_1 (deg)	θ (deg)	pyr angle[a] (deg)
1	Cr	6	6	977.2	2.213	2.246	3.2	35.5	17.8
2	Mn	5	6	769.4	2.118	2.196	4.1	34.3	17.2
3	Fe	4	6	699.9	2.005	2.151	9.6	35.1	17.6
4	Co	3	6	−741.3	1.985	2.170	27.6	35.6	17.8
5	Rh	3	6	584.9	2.105	2.256	28.2	35.8	17.9
6	Cr	6	5	1003.1	2.209	2.182	1.2	35.2	17.6
7	Mn	5	5	795.5	2.115	2.139	3.1	33.9	17.0
8	Fe	6	5	637.8	2.110	2.119	3.3	31.3	15.7
9	Co	5	5	−802.8	2.083	2.147	4.9	32.6	16.3
10	Ni	3	5	−3007.4	2.000	2.160	20.6	31.5	15.8
11	Rh	3	6	652.4	2.109	2.254	28.3	32.5	16.3
12	Rh	3	6	660.2	2.103	2.264	28.2	30.5	15.3
13	Rh	3	6	657.9	2.104	2.257	28.2	37.2	18.6
14	Mn	6	5	619.5	2.153	2.144	0.6	19.3	9.7
15	Fe	5	5	498.7	2.086	2.077	2.6	18.7	9.4
16	Co	4	5	−917.7	2.032	2.119	13.5	20.8	10.4
17	Ni	3	5	383.2	2.002	2.167	21.0	20.9	10.5
18	Pd	3	5	688.3	2.085	2.238	32.5	21.1	10.6
19	Pd	3	5	657.3	2.086	2.246	31.4	19.9	10.0
20	Pd	3	5	761.6	2.085	2.237	31.5	21.8	10.9
21	Pd	3	5	783.2	2.085	2.240	32.5	20.1	10.1
22	Pd	3	5	815.1	2.087	2.243	31.7	26.8	13.4
23	Pd	3	5	803.7	2.087	2.243	31.9	24.1	12.1

[a] Calculated following: Haddon, R. C. *Science* **1993**, *261*, 1545.

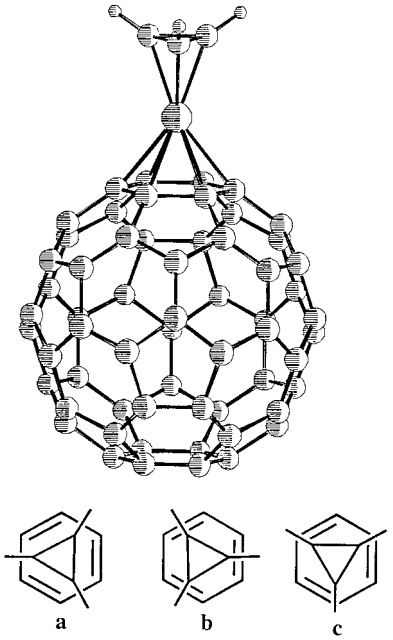

Figure 4. Computed structure of (η^6-C_{60})RhC_3H_3 (**5**). The structures **a**−**c** represent the orientation of C_3H_3 in relation to the six-membered ring of C_{60}; **a** is found to be lower in energy than **b** by 2.7 kcal/mol.

metal fragments (Figure 5). However, η^5-C_{60} binding brings in some constraints on electronic structure. If the C_5 ring of C_{60} acts as a five-electron η^5-complex, the remaining C_{55} fragment will be an open-shell system. This was not the case with the η^6−C_{60} complexes. A closed-shell C_{55} unit can be obtained by forcing the η^5-C_{60} group to bind either as a four-electron donor, leaving a formal C_{55}^- unit, or as a six-electron donor, with a formal C_{55}^+ unit. (η^5-C_{60})CrC_6H_6 (**6**) and (η^5-C_{60})MnC_5H_5

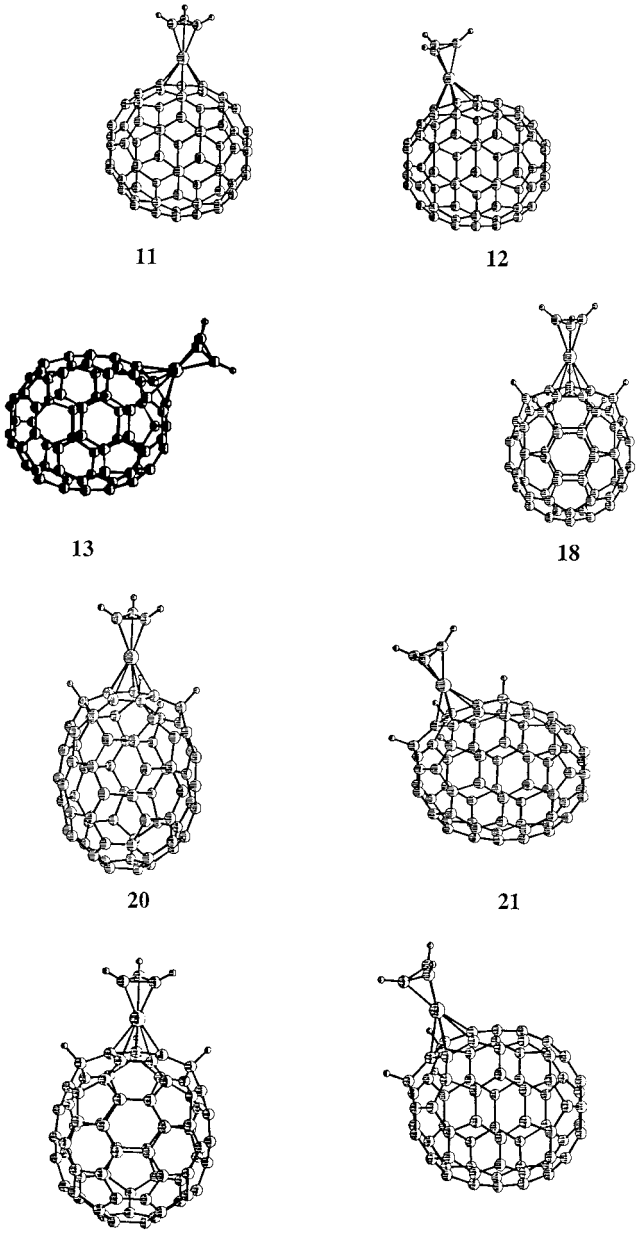

Figure 5. PM3(tm) optimized structures of (η^6-C_{70})RhC_3H_3 (**11**−**13**), (η^5-$C_{60}H_5$)PdC_3H_3(**18**), (η^5-$C_{70}H_5$)PdC_3H_3 (**20**, **21**), and (η^5-$C_{70}H_3$)PdC_3H_3 (**22, 23**).

(**7**) constitute examples of C_{60} as an η^5 six-electron ligand with charges of +0.144 and +0.077, respectively, in the C_{55} unit. C_{60} is forced to be an η^5 four-electron donor in (η^5-C_{60})FeC_6H_6 (**8**) and (η^5-C_{60})CoC_5H_5 (**9**), and the C_{55} units in these complexes are calculated to have charges of −0.495 and −0.167, respectively. None of these complexes are favorable in relation to the isolated C_{60} and the corresponding metallocene; eqs 10−13 are all *endothermic*, by larger magnitudes than those of the comparable eqs 5−8 involving η^6-C_{60}.

$$C_6H_6CrC_6H_6 + C_{60} \rightarrow (\eta^5\text{-}C_{60})CrC_6H_6 + C_6H_6 \quad (10)$$
6

$$\Delta E = 56.7 \text{ kcal/mol}$$

$$C_5H_5MnC_6H_6 + C_{60} \rightarrow (\eta^5\text{-}C_{60})MnC_5H_5 + C_6H_6 \quad (11)$$
7

$$\Delta E = 46.9 \text{ kcal/mol}$$

$$C_6H_6FeC_4H_4 + C_{60} \rightarrow (\eta^5\text{-}C_{60})FeC_6H_6 + C_4H_4 \quad (12)$$
8

$$\Delta E = 42.2 \text{ kcal/mol}$$

$$C_5H_5CoC_4H_4 + C_{60} \rightarrow (\eta^5\text{-}C_{60})CoC_5H_5 + C_4H_4 \quad (13)$$
9

$$\Delta E = 52.0 \text{ kcal/mol} \quad (?)$$

A possible explanation for this comes from the fact that the delocalization of electrons in C_{60} is dominated by the C_6 rings.[1,27] The five-membered ring is not naturally available for participation in bonding as a conventional cyclopentadienyl unit; the C_5 unit cannot be forced to act as an η^5 ligand without considerable perturbation to the electronic structure of C_{60}. This is in tune with the pentagon isolation rule found in C_{60}. In addition, the large charge separation should also make these less favorable.

The problem of η^5-C_{60} complexes can also be solved by the formation of multinuclear $C_{60}(NiC_3H_3)_{12}$ (**10**). The detailed structure of $C_{60}(NiC_3H_3)_{12}$ is revealing. Instead of the pentagon isolation rule,[28] it is the hexagon isolation rule that is applicable here. The electronic structure of $C_{60}(NiC_3H_3)_{12}$ is best described in the following way. The hypothetical C_{60}^{12-} would have the hexagon isolation rule where 12 cyclopentadienyl anions with their delocalized π systems are interconnected by C−C bonds that define the 6-membered rings. Complexation of the C_5 rings of C_{60} by 12 Ni(C_3H_3) groups increases the C−C distances of the 5-membered rings to 1.467 Å. These are comparable to the C−C distances of the Cp ring in $C_5H_5NiC_3H_3$ and also to those calculated for $C_{60}Li_{12}$,[16] indicating the similarity of the η^5 binding in these two complexes. The six-membered rings do not have the delocalized π system any more; the bonds are considerably longer than that in C_{60} (1.384 vs 1.462 Å). The net result is that all the C−C distances of C_{60} in $C_{60}(NiC_3H_3)_{12}$ become nearly equal. The advantage of the simultaneous interaction of 12 pentagons with Ni(C_3H_3) is shown by the energetics of the interactions. The interaction of C_{60} with Ni(C_3H_3) to give $C_{60}Ni(C_3H_3)$ is exothermic by 137.7 kcal/mol (Table 4). However, the simultaneous interaction of 12 Ni(C_3H_3) with C_{60} to give $C_{60}(Ni(C_3H_3))_{12}$ is exothermic by 1760.5 kcal/mol, much more than 12 × 137.7 kcal/mol. $C_{60}(Ni(C_3H_3)_{12})$ is an extremely attractive synthetic target.

Complexes of C_{70}. The lower symmetry of C_{70} provides many interesting possibilities for η^5 and η^6 coordination. On the basis of the degree of curvature, three types of six-membered and two types of five-membered rings are present in C_{70}. The varying curvatures of different rings of C_{70} determine the stability of the isomeric transition-metal complexes.[28] We studied the effect of complexation of transition-metal fragments to each of these varieties of rings and estimated their stability using the best transition-metal fragment (C_3H_3-Rh) for the purpose, obtained from the previous study on C_{60} (Figure 4). Capping C_3H_3Rh onto the different six-membered rings[29] of C_{70} leads to stabilization of different degrees:

$$C_3H_3RhC_6H_6 + C_{70} \rightarrow (\eta^6(21,22,23,42,41,40)\text{-}C_{70})RhC_3H_3 + C_6H_6 \quad (14)$$
11

$$\Delta E = -16.4 \text{ kcal/mol}$$

$$C_3H_3RhC_6H_6 + C_{70} \rightarrow (\eta^6(7,8,25,24,23,22)\text{-}C_{70})RhC_3H_3 + C_6H_6 \quad (15)$$
12

$$\Delta E = -8.4 \text{ kcal/mol}$$

$$C_3H_3RhC_6H_6 + C_{70} \rightarrow (\eta^6(1,2,12,11,10,9)\text{-}C_{70})RhC_3H_3 + C_6H_6 \quad (16)$$
13

$$\Delta E = -10.4 \text{ kcal/mol}$$

The increased flatness of the ring enhances the stability of the complex, as shown by the values of reaction energy above in relation to (η^6-C_{60})RhC_3H_3 (eq 9 vs eq 14).

Complexes of $C_{60}H_5$, $C_{70}H_5$, and $C_{70}H_3$. The problem of the open-shell C_{55} unit faced above can be overcome by forming derivatives of C_{60} similar to the recently synthesized (η^5-C_{60})Ph_5Tl.[30] This has a regular five-membered ring capable of acting as an isolated cyclopentadienyl anion. We have examined the η^5 complexes of $C_{60}H_5^-$ (**14**−**18**). Equations 17−21 are all

$$C_6H_6MnC_5H_5 + C_{60}H_5^- \rightarrow (\eta^5\text{-}C_{60}H_5)MnC_6H_6 + C_5H_5^- \quad (17)$$
14

$$\Delta E = 32.6 \text{ kcal/mol}$$

$$C_5H_5FeC_5H_5 + C_{60}H_5^- \rightarrow (\eta^5\text{-}C_{60}H_5)FeC_5H_5 + C_5H_5^- \quad (18)$$
15

$$\Delta E = 38.1 \text{ kcal/mol}$$

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(29) The standard numbering scheme is followed to differentiate the six-membered rings in C_{70} in our discussion. See: Taylor, J. *J. Chem. Soc., Perkin Trans. 2* **1993**, 813.

(30) (a) Birkett, P. A.; Avent, A. G.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans.* **1997**, 1121. (b) Birkett, P. A.; Avent, A. G.; Darwish, A. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1230. (c) Chistyakov, A. L.; Nesmeyanov, A. N.; Stankevich, I. V. *Fullerene Sci. Technol.* **1998**, *6*, 1069.

$$C_4H_4CoC_5H_5 + C_{60}H_5^- \rightarrow (\eta^5\text{-}C_{60}H_5)CoC_4H_4 + C_5H_5^- \quad (19)$$
16

$$\Delta E = 23.7 \text{ kcal/mol}$$

$$C_3H_3NiC_5H_5 + C_{60}H_5^- \rightarrow (\eta^5\text{-}C_{60}H_5)NiC_3H_3 + C_5H_5^- \quad (20)$$
17

$$\Delta E = 20.7 \text{ kcal/mol}$$

$$C_3H_3PdC_5H_5 + C_{60}H_5^- \rightarrow (\eta^5\text{-}C_{60}H_5)PdC_3H_3 + C_5H_5^- \quad (21)$$
18

$$\Delta E = 7.0 \text{ kcal/mol}$$

endothermic, but this is more due to the extra stabilization anticipated for a large ion vs a small ion. However, the advantage of using metal fragments with more diffuse orbitals, as was observed with the η^6-C_{60} complexes, is clearly present here as well. A heavier metal reduces the endothermicity considerably (eq 21).

For a more accurate and realistic estimate of the stability of such complexes, the effect of the inherent extra stability of the larger ion, $C_{60}H_5^-$, has to be taken into account. This can be achieved by employing the corresponding protonated species in the equations. For example, when these reactions are calculated with $C_{60}H_6$ and C_5H_6 instead of $C_{60}H_5^-$ and $C_5H_5^-$, these (eqs 22−26) are found to be more favorable. While $C_{60}H_6$ is only a model, we have calculated the energy of reaction for its hexachloro derivative, $C_{60}Cl_6$, known experimantally (eq 27).[30] The increase in exothermicity by more than 25 kcal/mol over eq 26 points to the possibility of substituent effects in these molecules.

$$C_6H_6MnC_5H_5 + C_{60}H_6 \rightarrow (\eta^5\text{-}C_{60}H_5)MnC_6H_6 + C_5H_6 \quad (22)$$
14

$$\Delta E = -5.4 \text{ kcal/mol}$$

$$C_5H_5FeC_5H_5 + C_{60}H_6 \rightarrow (\eta^5\text{-}C_{60}H_5)FeC_5H_5 + C_5H_6 \quad (23)$$
15

$$\Delta E = 0.1 \text{ kcal/mol}$$

$$C_4H_4CoC_5H_5 + C_{60}H_6 \rightarrow (\eta^5\text{-}C_{60}H_5)CoC_4H_4 + C_5H_6 \quad (24)$$
16

$$\Delta E = -14.3 \text{ kcal/mol}$$

$$C_3H_3NiC_5H_5 + C_{60}H_6 \rightarrow (\eta^5\text{-}C_{60}H_5)NiC_3H_3 + C_5H_6 \quad (25)$$
17

$$\Delta E = -17.3 \text{ kcal/mol}$$

$$C_3H_3PdC_5H_5 + C_{60}H_6 \rightarrow (\eta^5\text{-}C_{60}H_5)PdC_3H_3 + C_5H_6 \quad (26)$$
18

$$\Delta E = -30.9 \text{ kcal/mol}$$

$$C_3H_3PdC_5H_5 + C_{60}Cl_6 \rightarrow (\eta^5\text{-}C_{60}Cl_5)PdC_3H_3 + C_5H_5Cl \quad (27)$$
19

$$\Delta E = -56.2 \text{ kcal/mol}$$

There is little change in stability of the complexes brought in by the capping of the transition-metal fragments to the different five-membered rings of the pentahydro derivatives of C_{70}. This is indicated by the heats of reaction values given in eqs 28 and 29.

$$C_3H_3PdC_5H_5 + C_{70}H_6 \rightarrow (\eta^5\text{-}C_{70}H_5)PdC_3H_3 + C_5H_6 \quad (28)$$
20

$$\Delta E = -30.8 \text{ kcal/mol}$$

$$C_3H_3PdC_5H_5 + C_{70}H_6 \rightarrow (\eta^5\text{-}C_{70}H_5)PdC_3H_3 + C_5H_6 \quad (29)$$
21

$$\Delta E = -29.9 \text{ kcal/mol}$$

There is just one report of transition-metal fragment η^5 coordinated to $C_{70}Ar_3$ (Ar = aryl).[12] With the trihydro derivative of C_{70} systems, the positional isomers (**22** and **23**) differ more in their stability (eqs 30 and 31).

$$C_3H_3PdC_5H_5 + C_{70}H_4 \rightarrow (\eta^5\text{-}C_{70}H_3)PdC_3H_3 + C_5H_6 \quad (30)$$
22

$$\Delta E = -20.2 \text{ kcal/mol}$$

$$C_3H_3PdC_5H_5 + C_{70}H_4 \rightarrow (\eta^5\text{-}C_{70}H_3)PdC_3H_3 + C_5H_6 \quad (31)$$
23

$$\Delta E = -25.7 \text{ kcal/mol}$$

Conclusions

It is possible to stabilize η^6 complexes of C_{60} and C_{70} with the appropriate transition-metal fragments. Fragments such as C_3H_3Co and C_3H_3Rh, with their highly diffuse frontier orbitals, are ideal for stabilizing η^6-C_{60} and η^6-C_{70} complexes. Orbital compatibility of the transition-metal fragments with that of C_{60} plays a major role in the stability of such molecules. In comparison to η^6 bonding, η^5 complexes are less favorable; structural modifications such as those in the recently synthesized $C_{60}Ph_6$ should readily help η^5 bonding. Substituent effects in these molecules are probed by studying $C_{60}Cl_6$ in addition to $C_{60}H_6$. Hexagon isolation of C_{60} can be attained by capping NiC_3H_3 on all the 12 5-membered rings of C_{60}. This leads to significant stability of the resulting complex, $C_{60}(NiC_3H_3)_{12}$. In the case of C_{70} fragments, however, the stabilities of the exohedral complexes differ, depending on the curvature of the 5- and 6-membered rings. Capping on the flattest 6-membered face leads to the maximum stability. The change is less dramatic in the case of capping to the 5-membered rings of $C_{70}H_5$. Experimental attempts to use the RhC_3H_3 fragment to complex fullerenes should yield attractive results.

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Supporting Information Available: Listings of all relevant heats of formation from the PM3(tm) calculations, compared with the available experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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