Strategies to stabilize exohedral η^5- and η^6-fullerene transition metal organometallic complexes: A molecular orbital treatment

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Transition metal fragments are designed to overcome the unfavourable interaction arising from the splayed-out π-orbitals of the five- and six-membered rings of C_{60} in complex formation. Semiemprical studies at the PM3(tm) level on a series of $C_{60}MC_nH_n$ complexes suggest that, with the appropriate transition metal fragment, it is possible to stabilize η^6-complexes of C_{60}. Isodesmic equations of the type $C_mH_mMC_nH_n + C_{60} \rightarrow C_{60}MC_nH_n + C_mH_m$ indicate that C_3H_3Co and C_3H_3Rh are ideal fragments in stabilizing η^6-C_{60} complexes. In comparison, η^5-complexes are less favourable; structural modifications such as those in the recently synthesized $C_{60}Ph_5^-$ should readily help η^5-bonding.

WITH their five- and six-membered rings, it is tempting to speculate a rich organometallic chemistry for fullerenes along the same lines as ferrocene $(C_2H_5)_2Fe$ and dibenzene chromium $(C_6H_6)_2Cr$. However, the transition metal organometallic chemistry of fullerenes, so far, is dominated by η^2-bonding[1–14] akin to olefin complexes. η^5- and η^6-complexes involving the five- and six-membered rings of fullerenes are unknown[15–18]. The propensity for η^2-complexes is readily understood from the strain energy release involved in the complex formation; the geometry around carbon in C_{60} is remarkably close to that in the olefin complex[19,20]. On the other hand, the decreased overlap of the splayed out orbitals of five- and six-membered rings of C_{60} with the frontier orbitals of transition metal fragments makes η^5- and η^6-complexes unfavourable[20,21]. The only η^6-organometallic complex reported for a curved polyaromatic hydrocarbon involved corannulene which is much less curved than C_{60} (ref. 22). We present here ways to enhance the overlap of transition metal fragment orbitals with the five- and six-membered rings of C_{60} and predict viable targets for synthesis based on theoretical studies.

The rigid structure of C_{60} (refs 23–25) cluster does not permit many avenues to enhance exohedral η^5- and η^6-bonding without dramatic alterations in the structure. Therefore, we concentrate on the metal fragment first. If the frontier orbitals of the transition metal fragments can be made more diffuse, the overlap with the splayed out orbitals of five- and six-membered rings can be improved. The frontier orbitals of transition metal fragments can be controlled to a large extent by the ligands around it. For example, the diffuse nature of the fragment orbitals increases on going from η^6-C_6H_6M to η^3-C_3H_3M (Figure 1)[26]. In any such exercise, the electron count that is necessary to form a stable electronic structure has to be maintained. Hence, we selected the complexes of C_{60} and $C_{60}H_5^-$ (refs 27, 28) with metal fragments C_nH_nM (n = 3–6; M = transition metal) for theoretical study. The structures (**1–14**) studied here are given in Figure 2.

In view of the number and size of the molecules involved, the semiempirical MO method PM3(tm) with the parameters for transition metal provided by Hehre *et al.* is used for all calculations[29,30]. The reliability of the method is tested for both geometry and energy of experimentally known complexes. Figure 3 shows crucial geometric parameters computed using PM3(tm) and found experimentally for $C_3H_3Co(CO)_3$, $C_4H_4Fe(CO)_3$, $C_5H_5Mn(CO)_3$ and $C_6H_6Cr(CO)_3$ or its derivatives[31–34]. These are in reasonable agreement. A check on the reliability of energetics at this level is made by comparing the experimental value of the energy of the following reaction with the computed value (eq. 1)[35]. The calculated value of 6.1 kcal/mol is in good accordance with the experimental value of 4.5 kcal/mol (ref. 36). This is also comparable to the estimate of 2.1 kcal/mol made using the PRDDO method[21]. Similar isodesmic equations[37] are used to estimate the improvements brought by various transition metal fragments in binding to fullerene.

$$C_6H_6Cr(CO)_3 + C_6H_5Cl \rightarrow \eta^6\text{-}C_6H_5ClCr(CO)_3 + C_6H_6; \quad \Delta E = 6.1 \text{ kcal/mol} \qquad (1)$$

Let us consider the isodesmic eqs (2)–(5) that involve η^6-C_{60} complex. As anticipated, dibenzenechromium is considerably more favourable than η^6-$C_{60}CrC_6H_6$(**1**) (eq. 2). The endothermicity of the reactions decreases from 30.8 kcal/mol with η^6-C_6H_6M to 1.6 kcal/mol with η^3-C_3H_3M. Evidently, the diffuse frontier orbitals of η^3-C_3H_3Co help in increasing the interaction with C_{60}. Additional enhancement of diffuse nature of the metal fragment orbitals is achieved by going down the periodic

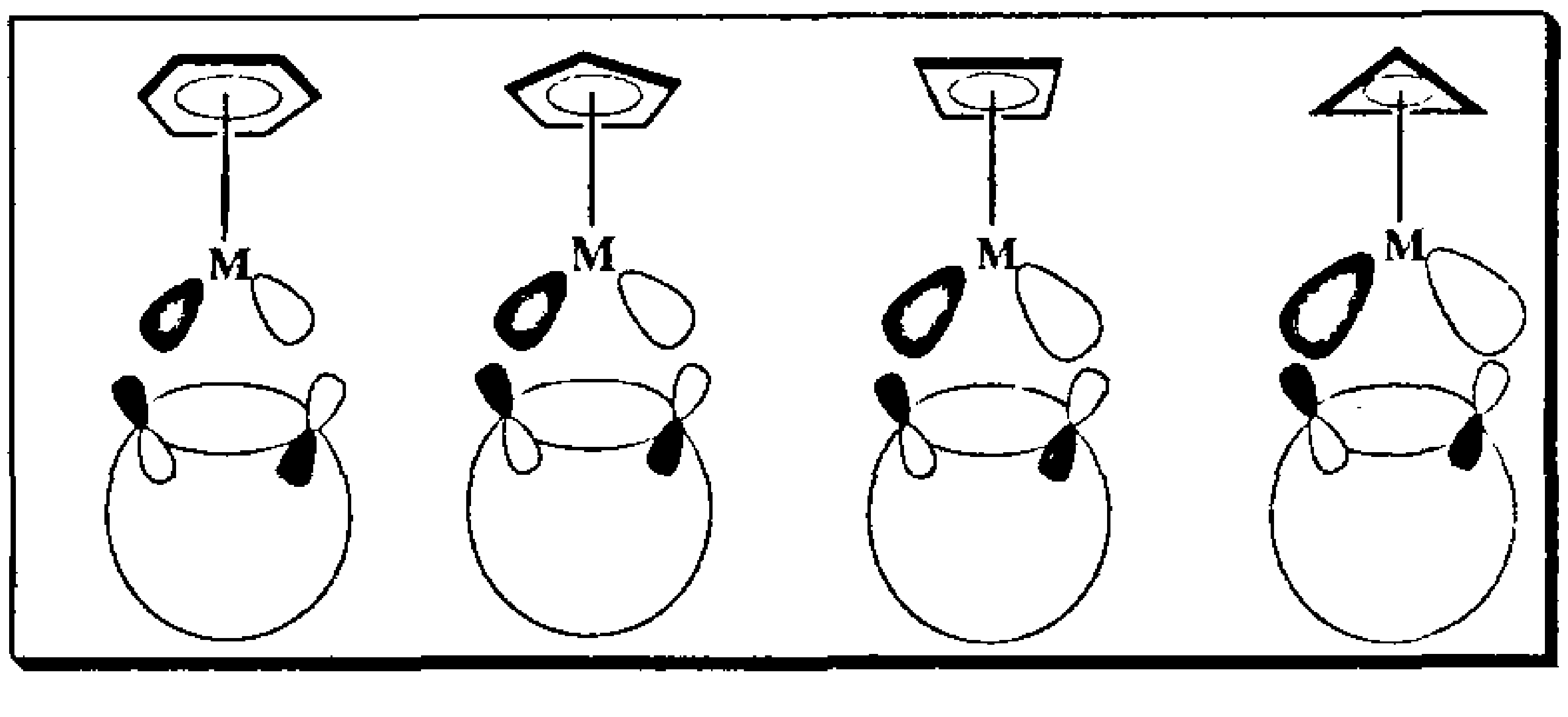

Figure 1. Schematic representation of the variation in the diffuse nature of the C_nH_nM fragment as a function of n.

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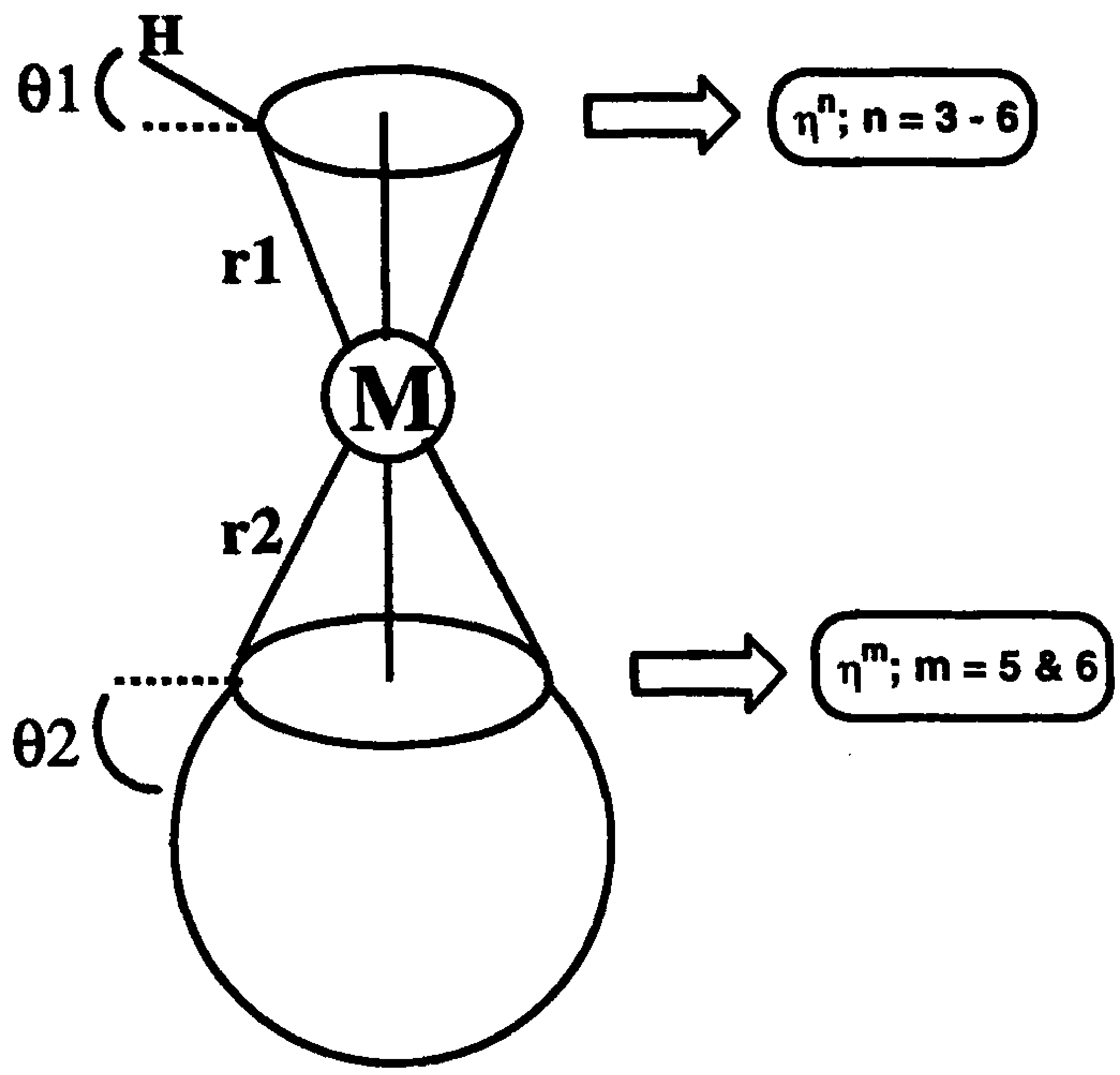


Structure no.	M	n	m	ΔH_f (kcal/mol)	r_1 (Å)	r_2 (Å)	θ_1 (deg.)	θ_2 (deg.)
1	Cr	6	6	977.2	2.213	2.246	3.2	35.5
2	Mn	5	6	769.4	2.118	2.196	4.1	34.3
3	Fe	4	6	699.9	2.005	2.151	9.6	35.1
4	Co	3	6	−741.3	1.985	2.170	27.6	35.6
5	Rh	3	6	584.9	2.105	2.256	28.2	35.8
6	Cr	6	5	1003.1	2.209	2.182	1.2	35.2
7	Mn	5	5	795.5	2.115	2.139	3.1	33.9
8	Fe	6	5	637.8	2.110	2.119	3.1	31.3
9	Co	5	5	−802.8	2.083	2.147	4.9	32.6
10	Mn	6	5	619.5	2.153	2.144	0.6	19.3
11	Fe	5	5	498.7	2.086	2.077	2.6	18.7
12	Co	4	5	−917.7	2.032	2.119	13.5	20.8
13	Ni	3	5	383.2	2.002	2.167	21.0	20.9
14	Pd	3	5	688.3	2.085	2.238	32.5	21.1

Figure 2. ΔH_f and selected geometric parameters of $(\eta^n\text{-C}_n\text{H}_n)M(\eta^m\text{-C}_{60})$[**1–9**] and $(\eta^n\text{-C}_n\text{H}_n)$M $(\eta^m\text{-C}_{60}\text{H}_5)$[**10–14**] at PM3(tm) level.

table to Rh; eq. 6 (Figure 4) is calculated to be exothermic by 11.4 kcal/mol. The possibility of increasing the metal–C_{60} interactions using heavier metals had been suggested by Marynick[21]. This is indeed an encouraging result and is to be compared to the reactions that are acknowledged to be

$$\mathrm{C_6H_6CrC_6H_6 + C_{60} \rightarrow \eta^6\text{-}C_{60}CrC_6H_6[1] + C_6H_6;}\quad \Delta E = 30.8 \text{ kcal/mol} \qquad (2)$$

$$\mathrm{C_6H_5MnC_6H_6 + C_{60} \rightarrow \eta^6\text{-}C_{60}MnC_5H_5[2] + C_6H_6;}\quad \Delta E = 20.8 \text{ kcal/mol} \qquad (3)$$

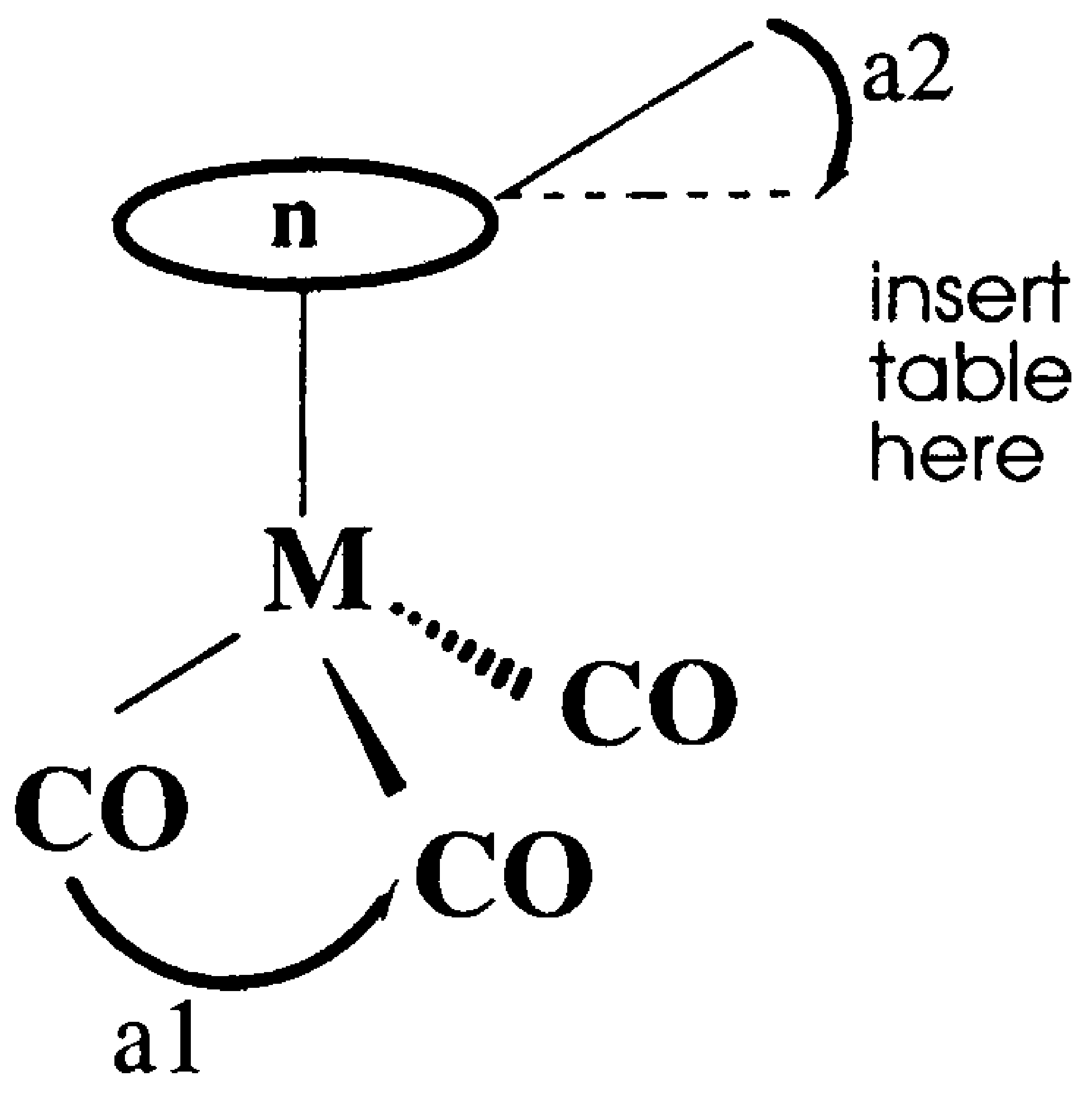
$$\mathrm{C_4H_4FeC_6H_6 + C_{60} \rightarrow \eta^6\text{-}C_{60}FeC_4H_4[3] + C_6H_6;}\quad \Delta E = 28.7 \text{ kcal/mol} \qquad (4)$$

$$\mathrm{C_3H_3CoC_6H_6 + C_{60} \rightarrow \eta^6\text{-}C_{60}CoC_3H_3[4] + C_6H_6;}\quad \Delta E = 1.6 \text{ kcal/mol} \qquad (5)$$

$$\mathrm{C_3H_3RhC_6H_6 + C_{60} \rightarrow \eta^6\text{-}C_{60}RhC_3H_3[5] + C_6H_6;}\quad \Delta E = -11.4 \text{ kcal/mol} \qquad (6)$$

favourable experimentally. For example, eq. (7) which compares an ethylene complex to the η^2-C_{60} complex is exothermic by 22.1 kcal/mol. Thus, transition metal fragments of the type η^3-C_3R_3M

$$\mathrm{\eta^2\text{-}C_2H_4Ni(PH_3)_2 + C_{60} \rightarrow \eta^2\text{-}C_{60}Ni(PH_3)_2 + C_2H_4;}\quad \Delta E = -22.1 \text{ kcal/mol} \qquad (7)$$



n	3	4	5	6
M	Co	Fe	Mn	Cr
a1, PM3(tm)	102.5	97.7	91.9	88.7
exp.	104.0	97.0	92.0	88.0
a2, PM3(tm)	29.0	11.7	7.1	3.7
exp.	26.0	10.8	0.0	−1.7

Figure 3. Selected bond angles of $C_nH_nM(CO)_3$ complexes computed at PM3(tm) level and corresponding experimental values.

should be able to support η^6-complexes of C_{60}. The structure of η^6-$C_{60}RhC_3H_3$(**5**) shown in Figure 4 presents an interesting conformational problem. The C–C bonds of a six-membered ring in C_{60} are not equal in length[38]. This leads to three distinct arrangement **a**, **b** and **c** (Figure 4). The conformation **a** is calculated to be more favourable than **b** by 2.8 kcal/mol. This is true with the qualitative results available on $C_6H_6M(CO)_3$ complexes[39]. Conformation **c** goes to **a** on optimization. The geometric parameters (Figure 2) calculated for various structures follow expected trends.

From the point of view of ring-size and π-metal orbital-overlap alone η^5-C_{60} should be better than η^6-C_{60} in binding to transition metal fragments. The angle subtended by a C–C bond with the plane of five- and six-membered rings are found to be 31.7° and 35.3° respectively[38]. Thus, the π-orbitals of the five-membered face should be less unfavourable than those of the six-membered face. However, η^5-C_{60} binding brings in some constraints of electron counting. If the C_5 ring in C_{60} forms an η^5-complex, the remaining C_{55} atoms will be left as an open shell system. This was not so with the η^6-C_{60} complexes. A closed shell C_{55} unit can be obtained by forcing the η^5-C_{60} to bind either as a 4-electron donor leaving a formal C_{55}^- unit or as a 6-electron donor with a formal C_{55}^+ unit. η^5-$C_{60}CrC_6H_6$(**6**) and η^5-$C_{60}MnC_5H_5$(**7**) constitute examples for C_{60} as an η^5-six-electron ligand. These complexes are calculated to have the 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 hence the C_{55} unit in these complexes are calculated to have −0.495 and −0.167 charge respectively. None of these complexes are favourable in relation to the isolated C_{60} and the corresponding metallocene; eqs (8)–(11) are all endothermic, by larger magnitudes than those of comparable eqs (2) and (3) involving η^6-C_{60}.

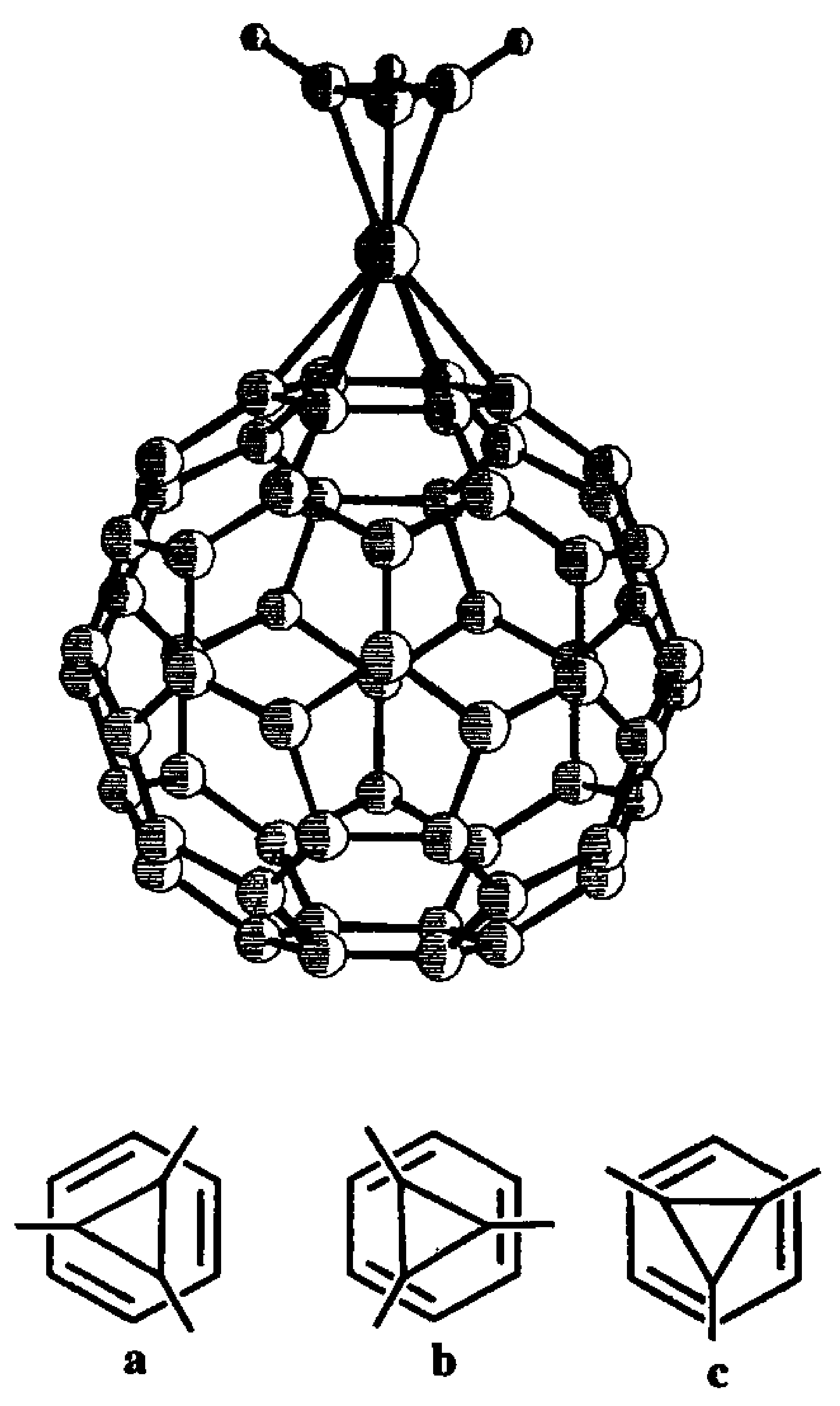


Figure 4. Computed structure of η^6-$C_{60}RhC_3H_3$ complex (**5**). The structures **a**, **b** and **c** represent the orientation of C_3H_3 in relation to the six-membered ring of C_{60}; **a** is found to be lower in energy than **b** by 2.8 kcal/mol.

$$C_6H_6CrC_6H_6 + C_{60} \rightarrow \eta^5\text{-}C_{60}CrC_6H_6[\mathbf{6}] + C_6H_6; \quad \Delta E = 56.7 \text{ kcal/mol} \tag{8}$$

$$C_5H_5MnC_6H_6 + C_{60} \rightarrow \eta^5\text{-}C_{60}MnC_5H_5[\mathbf{7}] + C_6H_6; \quad \Delta E = 46.9 \text{ kcal/mol} \tag{9}$$

$$C_6H_6FeC_4H_4 + C_{60} \rightarrow \eta^5\text{-}C_{60}FeC_6H_6[\mathbf{8}] + C_4H_4; \quad \Delta E = 42.2 \text{ kcal/mol} \tag{10}$$

$$C_5H_5CoC_4H_4 + C_{60} \rightarrow \eta^5\text{-}C_{60}CoC_5H_5[\mathbf{9}] + C_4H_4; \quad \Delta E = 52.0 \text{ kcal/mol} \tag{11}$$

Obviously, the overlap factor alone cannot explain these results. A possible explanation comes from the electronic structure of C_{60} itself[40–45]; the delocalization of electrons in C_{60} is dominated by the C_6 rings[25,46–48]. The pentagon isolation rule is a direct consequence of the meagre contribution of the valence bond configurations involving double bonds within the five-membered rings to the electronic structure of C_{60} (refs 40–45). The five-membered ring is not naturally available to participate in bonding as a conventional cyclopentadienyl unit. Forcing the C_5 unit to act a penta-hapto ligand perturbs the electronic structure considerably and hence the complexes are not favourable. One of the ways of overcoming the dilemma of the open shell C_{55} unit faced above is to form derivatives of C_{60} such as the recently synthesized η^5-$C_{60}Ph_5Tl$ (ref. 28). This has a regular five-membered ring which can act as an isolated cyclopentadienyl anion. We have examined the η^5-complexes of $C_{60}H_5^-$(**10–14**). Equations (12)–(16) are endothermic, but this is more due to the extra stabilization anticipated for a large ion vs a small ion. However, even here the advantage of using metal fragments with more diffuse orbitals is clear as found in η^6-C_{60} complexes. A heavier metal reduces the endothermicity; eq. (16) is almost thermoneutral.

$$\mathrm{C_6H_6MnC_5H_5 + C_{60}H_5^- \rightarrow \eta^5\text{-}C_{60}H_5MnC_6H_6[\mathbf{10}] + C_5H_5^-;}\quad \Delta E = 32.6\ \mathrm{kcal/mol} \tag{12}$$

$$\mathrm{C_5H_5FeC_5H_5 + C_{60}H_5^- \rightarrow \eta^5\text{-}C_{60}H_5FeC_5H_5[\mathbf{11}] + C_5H_5^-;}\quad \Delta E = 38.1\ \mathrm{kcal/mol} \tag{13}$$

$$\mathrm{C_4H_4CoC_5H_5 + C_{60}H_5^- \rightarrow \eta^5\text{-}C_{60}H_5CoC_4H_4[\mathbf{12}] + C_5H_5^-;}\quad \Delta E = 23.7\ \mathrm{kcal/mol} \tag{14}$$

$$\mathrm{C_3H_3NiC_5H_5 + C_{60}H_5^- \rightarrow \eta^5\text{-}C_{60}H_5NiC_3H_3[\mathbf{13}] + C_5H_5^-;}\quad \Delta E = 20.7\ \mathrm{kcal/mol} \tag{15}$$

$$\mathrm{C_3H_3PdC_5H_5 + C_{60}H_5^- \rightarrow \eta^5\text{-}C_{60}H_5PdC_3H_3[\mathbf{14}] + C_5H_5^-;}\quad \Delta E = 7.0\ \mathrm{kcal/mol} \tag{16}$$

The effect of the inherent extra stability of the larger ion, $C_{60}H_5^-$, can be removed 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 $C_5H_5^-$, the reactions (eqs (17)–(21)) are found to be more favourable. Similar estimates can also be made by using η^5-$C_{60}H_5Li$ and η^5-C_5H_6Li (eqs (22)–(26)) with comparable results.

$$\mathrm{C_6H_6MnC_5H_5 + C_{60}H_6 \rightarrow \eta^5\text{-}C_{60}H_5MnC_6H_6[\mathbf{10}] + C_5H_6;}\quad \Delta E = -5.4\ \mathrm{kcal/mol} \tag{17}$$

$$\mathrm{C_5H_5FeC_5H_5 + C_{60}H_6 \rightarrow \eta^5\text{-}C_{60}H_5FeC_5H_5[\mathbf{11}] + C_5H_6;}\quad \Delta E = 0.1\ \mathrm{kcal/mol} \tag{18}$$

$$\mathrm{C_4H_4CoC_5H_5 + C_{60}H_6 \rightarrow \eta^5\text{-}C_{60}H_5CoC_4H_4[\mathbf{12}] + C_5H_6;}\quad \Delta E = -14.3\ \mathrm{kcal/mol} \tag{19}$$

$$\mathrm{C_3H_3NiC_5H_5 + C_{60}H_6 \rightarrow \eta^5\text{-}C_{60}H_5NiC_3H_3[\mathbf{13}] + C_5H_6;}\quad \Delta E = -17.3\ \mathrm{kcal/mol} \tag{20}$$

$$\mathrm{C_3H_3PdC_5H_5 + C_{60}H_6 \rightarrow \eta^5\text{-}C_{60}H_5PdC_3H_3[\mathbf{10}] + C_5H_6;}\quad \Delta E = -30.9\ \mathrm{kcal/mol} \tag{21}$$

$$\mathrm{C_6H_6MnC_5H_5 + \eta^5\text{-}C_{60}H_5Li \rightarrow \eta^5\text{-}C_{60}H_5MnC_6H_6[\mathbf{10}] + C_5H_5Li;}\quad \Delta E = -12.2\ \mathrm{kcal/mol} \tag{22}$$

$$\mathrm{C_5H_5FeC_5H_5 + \eta^5\text{-}C_{60}H_5Li \rightarrow \eta^5\text{-}C_{60}H_5FeC_5H_5[\mathbf{11}] + C_5H_5Li;}\quad \Delta E = -6.4\ \mathrm{kcal/mol} \tag{23}$$

$$\mathrm{C_4H_4CoC_5H_5 + \eta^5\text{-}C_{60}H_5Li \rightarrow \eta^5\text{-}C_{60}H_5CoC_4H_4[\mathbf{12}] + C_5H_5Li;}\quad \Delta E = -21.1\ \mathrm{kcal/mol} \tag{24}$$

$$\mathrm{C_3H_3NiC_5H_5 + \eta^5\text{-}C_{60}H_5Li \rightarrow \eta^5\text{-}C_{60}H_5NiC_3H_3[\mathbf{13}] + C_5H_5Li;}\quad \Delta E = -24.1\ \mathrm{kcal/mol} \tag{25}$$

$$\mathrm{C_3H_3PdC_5H_5 + \eta^5\text{-}C_{60}H_5Li \rightarrow \eta^5\text{-}C_{60}H_5PdC_3H_3[\mathbf{14}] + C_5H_5Li;}\quad \Delta E = -37.8\ \mathrm{kcal/mol} \tag{26}$$

We conclude that C_3H_3M fragments would provide largely diffuse frontier orbitals to stabilize the η^6-C_{60} transition metal complexes. Isodesmic equations indicate that η^6-$C_{60}RhC_3H_3$ (Figure 4) should be one of the best possibilities. η^5-C_{60} complexes are more unfavourable. Structural modifications such as the recently synthesized $C_{60}Ph_5^-$ would help to form η^5-complexes.

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1. Balch, A. L., Hao, L. and Olmstead, M. M., *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 188.
2. Fagan, P. J., Calabrese, J. C. and Malone, B., *Science*, 1991, **252**, 1160.
3. Fagan, P. J., Calabrese, J. C. and Malone, B., *Acc. Chem. Res.*, 1992, **25**, 134.
4. Balch, A. L., Catalano, V. J., Lee, J. W. and Olmstead, M. M., *J. Am. Chem. Soc.*, 1992, **114**, 5455.
5. Bhasilov, V. V., Petrovskii, P. V., Sokolov, C. I., Linderman, S. V., Guzey, I. A. and Struchkov, Y. T., *Organometallics*, 1993, **12**, 991.
6. Balch, A. L., Lee, J. W., Noll, B. C. and Olmstead, M. M., *Inorg. Chem.*, 1993, **32**, 3577.
7. Schreiner, S., Gallaher, T. N. and Parsons, H. K., *Inorg. Chem.*, 1994, **33**, 3021.
8. Park, T. J., Cho, J. and Song, H., *Chem. Commun.*, 1995, 15.
9. Mavunki, I. J., Chi, Y., Peng, S. and Lee, G., *Organometallics*, 1995, **14**, 4454.
10. Hsu, H. and Shapley, J. R., *J. Am. Chem. Soc.*, 1996, **118**, 9192.
11. Lee, K., Hsu, H. and Shapley, J. R., *Organometallics*, 1997, **16**, 3876.

12. Chernega, A. N., Green, M. L. H., Haggitt, J. and Stephens, H. H., *J. Chem. Soc., Dalton Trans.*, 1998, 755.
13. Park, J. T., Song, H., Cho, J., Chung, M., Lee, J. and Suh, I., *Organometallics*, 1998, **17**, 227.
14. Maggini, M., Guldi, D. M., Mondini, S. and Scorrano, G., *Chem. Eur. J.*, 1998, **4**, 1992.
15. Roth, L. M., Huang, Y., Schwedler, J. T., Cassady, J. C., Ben-Amotz, D., Kahn, B. and Freiser, B. S., *J. Am. Chem. Soc.*, 1991, **113**, 6298.
16. Huang, Y. and Freiser, B. S., *J. Am. Chem. Soc.*, 1991, **113**, 8186.
17. Huang, Y. and Freiser, B. S., *J. Am. Chem. Soc.*, 1991, **113**, 9418.
18. Nagao, S., Kurikawa, T., Miyajima, K., Nakajima, A. and Kaya, K., *J. Phys. Chem.*, 1998, **A102**, 4495.
19. Koga, N. and Morokuma, K., *Chem. Phys. Lett.*, 1993, **202**, 330.
20. Haddon, R. C., *J. Comp. Chem.*, 1998, **19**, 139.
21. Rogers, J. R. and Marynick, D. S., *Chem. Phys. Lett.*, 1993, **205**, 197.
22. Seiders, T. J., Baldridge, K. K., O'Connor, J. M. and Siegel, J. S., *J. Am. Chem. Soc.*, 1997, **119**, 4781.
23. Billups, E. D. and Ciufolini, M. A., in *Buckminsterfullerene*, VCH Publishers, Weinheeim, 1993.
24. Hirsch, A., in *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994.
25. Haddon, R. C., *Science*, 1993, **261**, 1545.
26. Jemmis, E. D., *J. Am. Chem. Soc.*, 1982, **104**, 7017 and references therein.
27. Sawamura, M., Iikura, H. and Nakamura, E., *J. Am. Chem. Soc.*, 1996, **118**, 12850.
28. Iikura, H., Mori, S., Sawamura, M. and Nakamura, E., *J. Org. Chem.*, 1997, **62**, 7912.
29. Yu, J. and Hehre, W. J., *J. Comp. Chem.*, in press.
30. SPARTAN 4.1, Wavefunction Inc., California, 1993.
31. Rees, B. and Coppens, P., *Acta Crystallogr.*, 1973, **B29**, 2515.
32. Berndt, A. F. and Marsh, R. E., *Acta Crystallogr.*, 1963, **16**, 118.
33. Dolge, R. P. and Schomaker, V., *Acta Crystallogr.*, 1965, **18**, 614.
34. Elian, M., Chen, M. M. L., Mingos, D. M. P. and Hoffmann, R., *Inorg. Chem.*, 1976, **15**, 1148.
35. Other ΔH_f values (kcal/mol) at PM3(tm) involved in the isodesmic equations are $C_6H_6 = 23.5$, $C_5H_5^- = 15.9$, $C_4H_4 = 99.1$, $C_5H_6Cl = 16.7$, $C_5H_6 = 31.8$, $C_2H_4 = 16.6$, $C_5H_5Li = 35.9$, $C_2H_4Ni(PH_3)_2 = -350.0$, $C_6H_6CrC_6H_6 = 158.1$, $C_6H_6MnC_5H_5 = -39.7$, $C_6H_6FeC_4H_4 = -117.2$, $C_6H_6CoC_3H_3 = -1531.2$, $C_6H_6RhC_3H_3 = -192.1$, $C_5H_5FeC_5H_5 = -166.0$, $C_5H_5CoC_4H_4 = -1568.0$, $C_5H_5NiC_3H_3 = -264.1$, $C_5H_5PdC_3H_3 = 54.6$, $C_6H_6Cr(CO)_3 = -45.2$, $C_6H_5ClCr(CO)_3 = -45.9$, $C_{60} = 811.8$, $C_{60}H_5^- = 642.5$, $C_{60}H_6 = 696.3$, $C_{60}Li = 707.3$, $C_{60}Ni(PH_3)_2 = 423.0$.
36. Muetterties, E. J., Bleeke, J. R. and Sievert, A. C., *J. Organomet. Chem.*, 1979, **178**, 197.
37. Hehre, W. J., Radom, L., Schleyer, P. V. R. and Pople, J. A., in *Ab initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986.
38. Burgi, H., Blanc, E., Schwarzenbach, D., Liu, S., Lu, Y., Kappes, M. M. and Ibe, J. A., *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 640.
39. Albright, T. A., Hoffmann, P. and Hoffmann, R., *J. Am. Chem. Soc.*, 1977, **99**, 7546.
40. Kroto, H. W., *Nature*, 1987, **329**, 529.
41. Curl, R. F. and Smalley, R. E., *Science*, 1988, **242**, 1017.
42. Kroto, H. W., *Science*, 1988, **242**, 1139.
43. Schmalz, T. G., Seitz, W. A., Klein, D. J. and Hite, G. E., *J. Am. Chem. Soc.*, 1988, **110**, 1113.
44. Kroto, H. W., *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1578.
45. Smalley, R. E., *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1594.
46. Haddon, R. C., *Nature*, 1995, **378**, 249.
47. Zanasi, R., Lazzeretti, P. and Fowler, P. W., *Chem. Phys. Lett.*, 1997, **278**, 251.
48. Ruud, K., Agren, H., Helgaker, T., Dahle, P., Kock, H. and Taylor, P. R., *Chem. Phys. Lett.*, 1998, **285**, 205.

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A neurotransmitter role for methionine enkephalin in causing hyperglycemia in the freshwater crab, *Oziotelphusa senex senex*

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Injection of methionine enkephalin caused a significant increase in the hemolymph glucose and total sugar level of intact crabs in a dose-dependent manner, apparently by triggering release of the hyperglycemic hormone.

EVER since the first report of presence of leucine enkephalin in the red swamp crayfish, *Procambarus clarkii* and in the spiny lobster, *Panulirus interruptus* by Mancillas *et al.*[1], there have been sporadic reports of occurrence of opioids in different crustacean species[2–6]. Though the status of opioid research in crustaceans is fragmentary, there are several interesting questions pertaining to demonstration of these peptides and the diverse functions they perform, which are very different from what they do in mammals[7,8].

Since the discovery of a 'diabetogenic factor' in the crustacean eyestalk[9], work has been carried out on its chemical nature, mode and site of action[10–14]. In view of the fact that opioid peptides act as neurotransmitters[6,15], it is conceivable that these peptides could help in the secretion of the hyperglycemic hormone from the neurosecretory cells that synthesize it. The present investigation was undertaken to determine, whether methionine enkephalin can indeed produce an increase in the hemolymph sugar level of the crab *Oziotelphusa senex senex* and if so whether it might involve stimulation of the release of hyperglycemic hormone.

Freshwater rice field crabs *Oziotelphusa (Paratelphusa) senex senex* Fabricius were collected

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