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Density Functional Study of Carbon−Carbon Bond Activation in Curved Polyaromatic Hydrocarbons by Transition-Metal Complexes

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Density functional calculations have been performed on the oxidative addition of a Pt(0) fragment, $Pt(PH_3)_2$, to one of the rim C−C bonds of semibuckminsterfullerene ($C_{30}H_{12}$), to give an η^2-σ-bonded Pt(II)−buckybowl complex. To evaluate the effect of the ring strain and of the hydrocarbon curvature on the C−C bond activation, analogous calculations have been performed on the oxidative addition of Pt(0) to the C−C bond in five-membered rings of less strained hydrocarbons, such as dihydro-3-fluorene ($C_{13}H_{10}$) and benzo[*ghi*]fluoranthene ($C_{18}H_{10}$). The optimized geometries of the η^2-σ-bonded Pt(II) buckybowl and dihydroanthracene complexes have been found to be in good agreement with the X-ray experimental data. Reliable values have been calculated for the energy of the Pt(0) oxidative addition to these hydrocarbons and compared with the corresponding energies of the C−C bond cleavage, allowing us to distinguish between strain energy within the five-membered ring and strain energy associated with the bowl-like curvature.

1. Introduction

The increasing interest recently attracted by fullerenes has led to a growing attention to curved polycyclic aromatic hydrocarbons (PAHs) composed of five- and six-membered rings organized in the same arrangement as those found on the surface of a fullerene.[1] The simplest PAH that exhibits a fullerene-like structure is corannulene, $C_{20}H_{10}$,[2] with a central five-membered ring surrounded by five hexagonal rings, which was synthesized as early as 20 years before the first isolation of C_{60}.[3] Larger representatives have begun to appear in recent years, such as cyclopentacorannulene ($C_{22}H_{10}$),[4] benzocorannulene ($C_{24}H_{14}$),[5] diindenochrysene ($C_{26}H_{10}$),[1d] $C_{30}H_{10}$,[1d] and several higher homologues.[6] Among them, semibuckminsterfullerene ($C_{30}H_{12}$), which represents half of the buckminsterfullerene molecule with the rim carbons capped by hydrogen atoms, has been intensively studied.[7] Substantial efforts have been recently directed toward the synthesis of transition-metal complexes of curved polyaromatic hydrocarbons, such as corannulene and other buckybowls, to compare the metal coordination chemistry of these PAHs and that of fullerenes. The metal coordination chemistry of fullerene has been the subject of intense investigation since the first isolation of C_{60}, and many transition-metal fullerene complexes have been synthesized and structurally characterized.[8] In all the characterized transition-metal fullerene complexes, C_{60} acts as an electron-deficient polyalkene and the metal atom is attached in an η^2 fashion to the carbon−carbon bond at the fusion of two six-membered rings. On the other hand, PAHs, with a readily accessible internal surface, show a different coordination chemistry with respect to C_{60}, giving rise to π-systems for the potential coordination of transition-metal complexes. For instance, corannulene forms with the (η^5C_5-Me_5)Ru^+ fragment a metal complex, where the ruthe-

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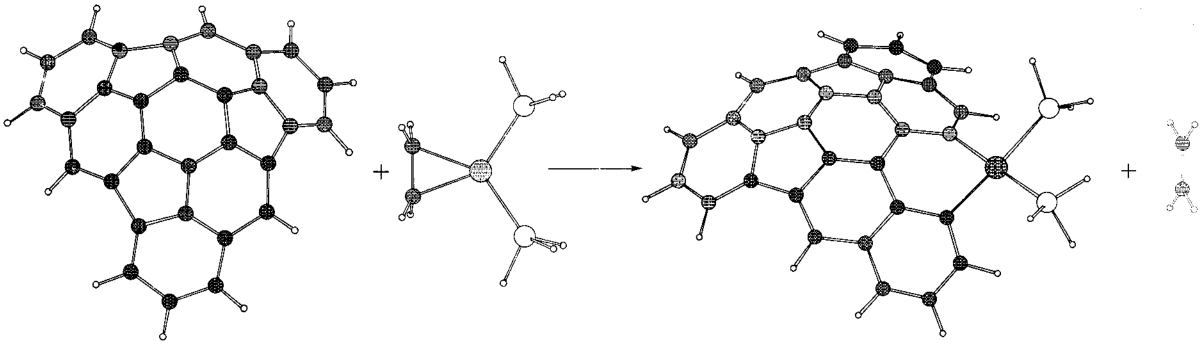
Scheme 1. Reaction Scheme for the Oxidative Addition of Pt(0) to the Semibuckminsterfullerene[a]



(1) **(2)**

[a] Ph_3 ligands have been replaced with H atoms for clarity.

nium atom is η^6 coordinated to one hexagonal ring of the corannulene moiety.[9] An unusual behavior has been observed for semibuckminsterfullerene, $C_{30}H_{12}$, whose reaction with $Pt(C_2H_4)(PPh_3)_2$ does not result in simple η^2 coordination of a $Pt(PPh_3)_2$ unit; rather, it accomplishes an insertion of the platinum into one of the C−C bonds on the edge of the hydrocarbon,[10] as shown in Scheme 1. Such unusual C−C bond breaking has been attributed to the relief of the strain present in the five-membered ring at the edge of this hydrocarbon.

An analogous model system, the 9,10-dihydroplatinaanthracene complex $Pt(\eta^2\text{-}\sigma\text{-}C_6H_4CH_2C_6H_4)(PR_3)_2$, has been prepared and structurally characterized.[11] However, such a compound was synthesized by starting from the acyclic bis(2-lithiophenyl)methane precursor and not from the parent dihydro-3-fluorene hydrocarbon through a C−C bond-breaking reaction. Indeed, C−C bond breaking is a quite difficult reaction and usually only occurs upon relief of ring strain,[12] attainment of aromaticity,[13] or forcing of the C−C bond in close proximity to the metal.[14] The easy C−C bond cleavage in semibuckminsterfullerene is probably related to the presence of unusual highly strained five-membered rings. These five-membered, formally nonaromatic ring sites are the source of the buckybowl curvature, and the breaking of the external C−C bond relieves not only the ring strain within the pentadienyl ring but also some of the steric strain connected with the curved structure of the buckybowl. In this paper we employ density functional theory (DFT) to investigate the thermodynamics and mechanistic aspects of the oxidative addition of Pt(0) to one of the rim C−C bonds of semibuckminsterfullerene. To evaluate the effects of the ring and curvature strain, DFT calculations have been performed also on the oxidative addition of Pt(0) to the C−C bonds of analogous less strained hydrocarbons, such as dihydro-3-fluorene and benzo[*ghi*]fluoranthene.

2. Computational Details

The calculations reported in this paper are based on the ADF (Amsterdam Density Functional) program package.[15] Its main characteristics are the use of a density fitting procedure to obtain accurate Coulomb and exchange potentials in each SCF cycle, the accurate and efficient numerical integration of the effective one-electron Hamiltonian matrix elements, and the possibility to freeze core orbitals. The molecular orbitals were expanded using a Slater-type orbital (STO) basis set. Double-ζ STO basis sets were used for carbon (2s, 2p), phosphorus (3s, 3p), and hydrogen (1s), augmented with a single 3d polarization function, except for hydrogen, where a 2p function was used. For platinum orbitals we used a double-ζ STO basis set for 5s and 5p and a triple-ζ STO basis set for 5d and (5 + 1)s. A single (5 + 1)p function was added as a polarization function on the platinum center. The inner-shell cores have been kept frozen, corresponding to 1s for carbon, 1s−2p for phosphorus, and 1s−4d for platinum.

The LDA exchange correlation potential and energy were used, together with the Vosko−Wilk−Nusair parametrization[16] for homogeneous electron gas correlation, including Becke's nonlocal correction[17] to the local exchange expression and Perdew's nonlocal correction[18] to the local expression of correlation energy.

Since the relativistic effects play an important role in describing the electronic structure and relative energetics of the species containing a heavy metal, such as platinum, they were taken into account by the Pauli formalism, the Pauli Hamiltonian including first-order scalar relativistic corrections (Darwin and mass velocity) while neglecting spin−orbit corrections.[19,20]

To make the calculations feasible, the PPh_3 ligand was modeled with the smaller PH_3 group. Molecular structures of all considered systems were optimized including nonlocal corrections. No symmetry constraints have been used on compounds **1** and **2** (see Scheme 1), whereas C_{2v} and C_s

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Table 1. Selected Bond Distances (Å) and Angles (deg) for $C_{30}H_{12}$ (1) and $C_{30}H_{12}-PtL_2$ (2)[a]

	$C_{30}H_{12}$ (**1**)		$C_{30}H_{12}-PtL_2$ (**2**)	
	BP86	B3LYP[b]	BP86 L = PH_3	exptl[c] L = PPh_3
C1−C2	1.430	1.435	1.426	1.37(2)
C2−C3	1.400	1.406	1.440	1.45(2)
C3−C4	1.422	1.428	1.462	1.49(2)
C4−C5	1.439	1.443	1.442	1.47(2)
C1−C5	1.506	1.513	2.900	2.84
C1−C6	1.385	1.385	1.394	1.44(2)
C5−C18	1.393	1.392	1.396	1.39(2)
Pt−C1			2.064	2.04(2)
Pt−C5			2.037	2.05(1)
Pt−P1			2.319	2.348(4)
Pt−P2			2.323	2.323(4)
∠C1−C2−C3	110.2		122.3	
∠C2−C3−C4	108.9		123.7	
∠C3−C4−C5	110.1		126.1	
∠P1−Pt−P2			93.0	96.0(1)

[a] Values in parentheses are esd's. [b] Reference 21. [c] Reference 10.

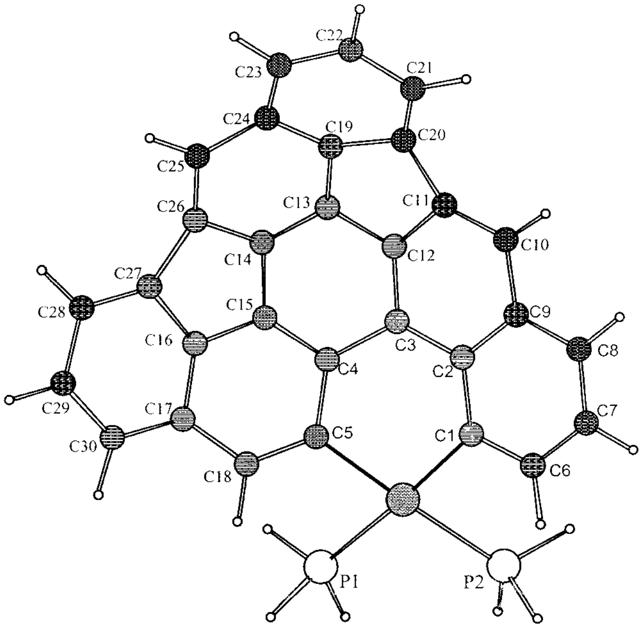

Figure 1. Optimized geometry for the Pt(η^2-σ-$C_{30}H_{12}$)(PH_3)$_2$ complex.

symmetry constraints have been imposed respectively on compounds **3** and **5** and on compounds **4** and **6** (see Figures 2 and 3).

3. Results and Discussion

Geometry Optimization. A geometry optimization has been performed on semibuckminsterfullerene (**1**) and on its platinum complex Pt(η^2-σ-$C_{30}H_{12}$)(PH_3)$_2$ (**2**) without any symmetry constraints. The optimized geometries are shown in Scheme 1, while selected bond distances and angles are reported in Table 1, together with the B3LYP structure for $C_{30}H_{12}$[21] and with the experimental data for the Pt(η^2-σ-$C_{30}H_{12}$)(PPh_3)$_2$ compound.[10] The numbering scheme for the molecule is shown in Figure 1. The calculated values for complex **2** compare quite well with the available experimental data. Particularly, the C−C bonds are reproduced with deviations of 0.01−0.06 Å, whereas the Pt−C and Pt−P bonds differ less than 0.03 Å. Part of these bond length deviations could be due to the use of model PH_3 ligands on the metal atoms, which are less electron releasing and much less sterically demanding than the actual PPh_3 ligands. In fact, a recent theoretical study has shown that the use of a PH_3 ligand in place of aryl- or alkyl-substituted phosphines could lead to significant differences in the geometrical structure of the corresponding complexes.[22]

The oxidative addition of Pt(PH_3)$_2$ causes a relief of the strain energy of the five-membered ring directly bound to the metal center and a release of the curvature of the buckybowl structure. The relaxing of the five-membered ring is accomplished through the increase of the inner ∠CCC angles by 12−16° (see Table 1). The Pt center does not lie in the broken ring plane, but it is folded 40° outward (from the mean plane defined by atoms C1−C5) to the exo surface, in good agreement with the experimental value of 42°. This is probably due to the fact that this folding allows us to reach a less strained partial boat conformation of the six-membered metallacycle. The geometrical parameters of **2** clearly indicate that the C1−C5 bond has been broken, the C−C bond distance passing from 1.506 Å in **1** to 2.900 Å in **2**, quite close to the X-ray value of 2.84 Å.

An analogous, less strained model compound for the semibuckminsterfullerene complex has been synthesized and structurally characterized, the 9,10-dihydroplatinaanthracene system Pt(η^2-σ-$C_6H_4CH_2C_6H_4$)(PR_3)$_2$.[11] A geometrical optimization has been performed on its hypothetical hydrocarbon precursor dihydro-3-fluorene (**3**) and on the model complex Pt(η^2-σ-$C_6H_4CH_2C_6H_4$)(PH_3)$_2$ (**4**), respectively, within C_{2v} and C_s symmetry constraints (see Figure 2). To simplify the comparison, we labeled the carbon atoms of compound **4** following the numbering scheme adopted for compound **2** (see Figure 1), rather than following the conventional anthracene sequence. As shown in Table 2, the calculated parameters compare rather well with the averaged experimental data. In particular, the description of the metal center is good, the deviations on the metal−ligand bond lengths being within 0.01 Å.

The five-membered ring in the dihydro-3-fluorene hydrocarbon is not strained enough to activate the C−C bond breaking, and indeed the platinum complex has been prepared from the acyclic bis(2-lithiophenyl)methane precursor, and not from the parent dihydro-3-fluorene hydrocarbon through a C−C bond-breaking reaction. The optimized structure of the compound **3** shows a C1−C5 bond distance of 1.461 Å, far shorter than the value of 1.506 Å for compound **1**, where the rim C1−C5 bond is the longest and most strained C−C bond on the buckybowl structure. The addition of the Pt center separates the C1 and C5 carbon atoms at a distance of 2.773 Å, a value much shorter than that in complex **2** (0.13 Å), still reflecting the higher strain in semibuckminsterfullerene. It is surprising that the Pt−C bond distances show almost the same values both in **2** and **4**, despite this shorter C1−C5 bond distance. This could be attributed to the higher flexibility of the dihydro-3-fluorene moiety. Indeed, the six-membered ring containing the platinum atom in complex **4** adopts

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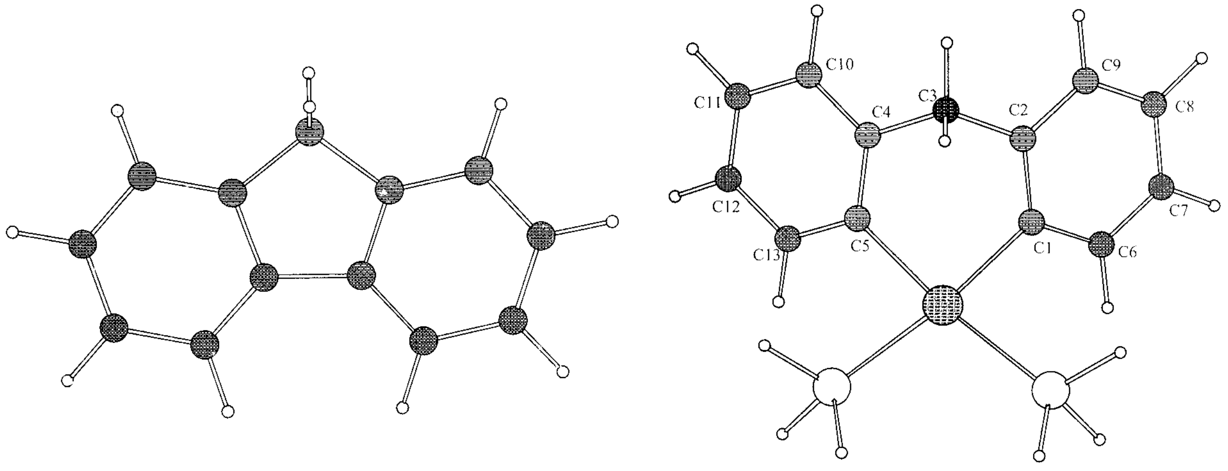

(3) **(4)**

Figure 2. Optimized geometry for the hypothetical precursor dihydro-3-fluorene $C_{13}H_{10}$ (**3**) and the Pt(η^2-σ-$C_6H_4CH_2C_6H_4$)-$(PH_3)_2$ product (**4**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $C_{13}H_{10}$ (3) and $C_{13}H_{10}$−PtL_2 (4)[a]

	$C_{13}H_{10}$ (**3**)	$C_{13}H_{10}$−PtL_2 (**4**)	
	BP86	BP86 L = PH_3	exptl[b] L = PEt_3
C1−C2	1.408	1.407	1.384(15), 1.415(15)
C2−C3	1.507	1.513	1.531(17), 1.512(14)
C1−C5	1.461	2.773	2.67
C1−C6	1.394	1.401	1.378(17), 1.399(15)
C2−C9	1.388	1.397	1.382(17), 1.348(17)
C6−C7	1.419	1.404	1.384(18), 1.380(18)
C8−C9	1.397	1.395	1.360(19), 1.374(20)
Pt−P		2.315	2.323(3), 2.303(3)
Pt−C		2.047	2.062(11), 2.038(11)
∠C1−C2−C3	110.0	119.4	
∠C2−C3−C4	102.9	110.2	
∠C−Pt−C		85.3	81.3(4)
∠P−Pt−P		97.4	98.8(1)

[a] Values in parentheses are esd's. [b] Reference 11.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $C_{18}H_{12}$ (5) and $C_{18}H_{12}$−$Pt(PH_3)_2$ (6)

	$C_{18}H_{12}$ (**5**) BP86	$C_{18}H_{12}$−$Pt(PH_3)_2$ (**6**) BP86
C1−C2	1.419	1.426
C2−C3	1.392	1.449
C1−C5	1.495	2.791
C1−C6	1.394	1.401
C2−C9	1.389	1.434
C6−C7	1.423	1.404
C8−C9	1.419	1.411
Pt−P		2.328
Pt−C		2.031
∠C1−C2−C3	110.2	123.5
∠C2−C3−C4	108.4	122.0
∠C−Pt−C		86.8
∠P−Pt−P		93.6

a boat conformation, where the Pt center is folded by 49° with respect to the mean plane containing the C1,-C2,C4,C5 carbon atoms, a value higher than in the semibuckminsterfullerene system (40°).

To investigate in detail which factors affect the C−C bond activation by the Pt center, we have performed a geometry optimization on a third model structure, the $C_{18}H_{10}$−$Pt(PH_3)_2$ complex **6**, hypothetically formed by oxidative addition on the benzo[*ghi*]fluoranthene ligand (**5**) (see Figure 3). The presence of four fused benzene rings in compound **5** makes the ring strain within the five-membered ring very similar to that in semibuckminsterfullerene. However, the benzo[*ghi*]fluoranthene molecule is a planar system, so that the C1−C5 bond activation is not related to the release of any bowl-like curvature, as in the semibuckminsterfullerene. As is shown in Table 3, the C1−C5 bond on the $C_{18}H_{10}$ fragment is slightly shorter (0.01 Å) than in the $C_{30}H_{12}$ fragment, showing a less strained C−C bond. The C−C bond breaking causes a distortion of the organic moiety from the planar structure, and the Pt atom is folded by 41° with respect to the mean plane defined by the C1−C5 carbon atoms, very close to the corresponding value found for the semibuckminsterfullerene complex, **2**.

Bonding Energies. The bond dissociation energies between the $Pt(PH_3)_2$ and the C_nH_m fragments, $D(Pt-C_nH_m)$, have been calculated according to

$$Pt(\eta^2\text{-}\sigma\text{-}C_nH_m)(PH_3)_2 \rightarrow Pt(PH_3)_2 + C_nH_m \qquad (1)$$

where both the complex and the two fragments have been considered in their ground-state equilibrium geometries. Using the fragment-oriented approach of the DFT computational scheme, implemented in the ADF program, the above bond dissociation energies are computed in two steps, as shown in Scheme 2. First we calculate the "snapping energies", $E^*(Pt-C_nH_m)$, i.e., the energies gained when snapping the metal−ligand bond, obtained by building $Pt(\eta^2\text{-}\sigma\text{-}C_nH_m)(PH_3)_2$ from the fragments with the conformation they assume in the equilibrium geometry of the overall complex. In the second step we compute the energies $E_{Pt(PH_3)_2}{}^R$ and $E_{C_nH_m}{}^R$, gained when the isolated fragments relax to their equilibrium geometries. This approach allows also the direct computation of the basis set superposition error (BSSE) by applying the counterpoise method.[23] Corrections for the zero-point vibrations were not included, since they are expected to give small contributions. Rosa et al.[24] have carried out an investigation of the effects of the basis set incompleteness on the bond dissociation energies of some metal−ligand and metal−metal bonds.

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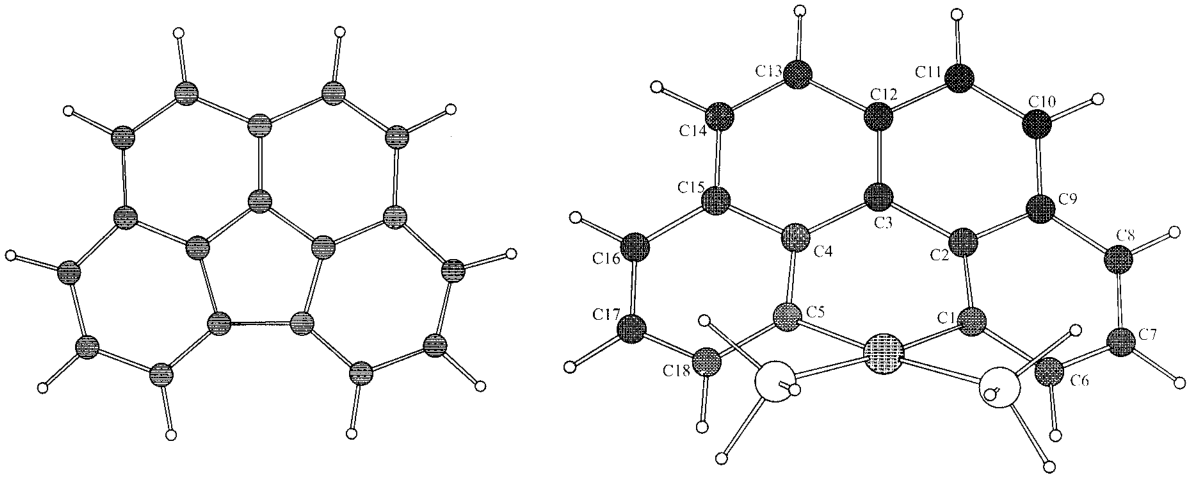

(5) (6)

Figure 3. Optimized geometry for the benzo[*ghi*]fluoranthene $C_{18}H_{12}$ model (**5**) and the $Pt(\eta^2\text{-}\sigma\text{-}C_{18}H_{10})(PH_3)_2$ product (**6**).

Scheme 2. Bonding Dissociation Energy Scheme

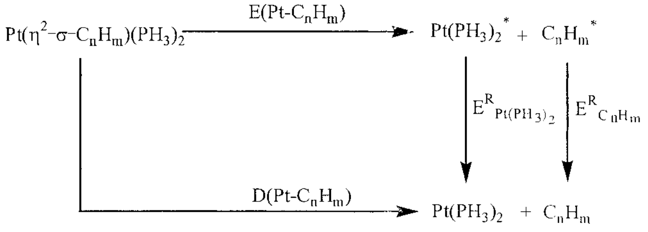

Table 4. Calculated Bond Dissociation Energies for the C_nH_m−$Pt(PH_3)_2$ Complexes (kJ mol^{-1})

	E^*	BSSE	E^a	$E_{Pt(PH_3)_2}{}^R$	$E_{C_nH_m}{}^R$	D	D(C−C)
$C_{30}H_{12}$−$Pt(PH_3)_2$ (**2**)	681	−25	656	−178	−331	147	316
$C_{13}H_{10}$−$Pt(PH_3)_2$ (**4**)	657	−25	632	−164	−485	−17	482
$C_{18}H_{10}$−$Pt(PH_3)_2$ (**6**)	641	−26	615	−178	−398	39	403

[a] $E = E^* + \text{BSSE}$.

This work has pointed out that double-ζ plus polarization basis sets give reasonably accurate bond energies for organometallic systems with sufficiently small BSSE corrections to warrant its neglect in most situation.

The results obtained for the bond dissociation energies $D(Pt-C_nH_m)$ are given in Table 4, together with all the various contributions, i.e. snapping energies, relaxation energies, and BSSEs. The calculated bond dissociation energies show that the oxidative addition of the Pt(0) fragment to the C−C bond, according to eq 1 written in the opposite sense:

$$\mathrm{Pt(PH_3)_2} + C_nH_m \rightarrow \mathrm{Pt}(\eta^2\text{-}\sigma\text{-}C_nH_m)(PH_3)_2 \qquad (1')$$

is strongly exothermic for the semibuckminsterfullerene (−147 kJ mol^{-1}), less exothermic for benzo[*ghi*]fluoranthracene (−39 kJ mol^{-1}), and even endothermic for 9,10-dihydroplatinaanthracene (+17 kJ mol^{-1}). A comparison with the experimental data is not possible, since no thermodynamic data have been reported for the oxidative addition of Pt(0) to the semibuckminsterfullerene. However, the theoretically predicted bonding energy of complex **2** (147 kJ mol^{-1}; see Table 4) is in agreement with the experiments, through which the $Pt(\eta^2\text{-}\sigma\text{-}C_{30}H_{12})(PPh_3)_2$ complex is obtained by the reaction of **1** with $Pt(CH_2{=}CH_2)(PPh_3)_2$. In a previous paper,[25] the interaction of olefins with metal diphosphines was investigated at the same level of theory and a bonding energy of 78 kJ mol^{-1} was found for the $Pt(C_2H_4)(PH_3)_2$ complex, thus suggesting that the displacement of ethylene by the buckybowl ligand is exothermic by 69 kJ mol^{-1}. Moreover, the endothermicity of the oxidative addition to the C−C bond in **3** is supported by the experimental difficulty in preparing the 9,10-dihydroplatinaanthracene complex $Pt(\eta^2\text{-}\sigma\text{-}C_6H_4CH_2C_6H_4)(PR_3)_2$, through a C−C bond-breaking reaction from the parent dihydro-3-fluorene hydrocarbon. The oxidative addition to the C−C bond in the benzo[*ghi*]fluoranthene **5** is favorable, the reaction being exothermic by −39 kJ mol^{-1}, a value intermediate between those for **1** and **3**.

The decomposition scheme used for the bonding energies allows us to evaluate the C−C bond strength in compounds **1**, **3**, and **5**. The relaxation energy $E_{C_nH_m}{}^R$, gained when the organic moiety relaxes from the conformation in the complex (i.e. with the broken C−C bond) to the equilibrium geometry, gives an estimation of the opposite of the C−C bond energy, D(C−C). For the sake of completeness, the C−C bond energies, D(C−C), have been calculated by optimizing the organic moieties with the broken C−C bond in their triplet ground state; the results are reported in Table 4. The rim C−C bond in the less strained $C_{13}H_{10}$ compound is the strongest among the three organic fragments, D(C−C) being equal to 482 kJ mol^{-1}. The C−C bond strength is much lower in $C_{18}H_{10}$, D(C−C) = 403 kJ mol^{-1}, and even more in $C_{30}H_{12}$, D(C−C) = 316 kJ mol^{-1}, in agreement with the higher degree of strain showed by these compounds, with respect to the dihydroanthracene system. This trend of the D(C−C) values is also in agreement with the geometrical parameters reported in Tables 1−3, since a higher C−C bond energy corresponds to a shorter C−C bond. It is worth noting that the endothermicity of the oxidative addition of $C_{13}H_{10}$ with respect to $C_{30}H_{12}$ is almost entirely due to the higher strength of the rim C−C bond (166 kJ mol^{-1}).

C−C Bond Activation. The approach through the model compounds **1**, **3**, and **5** allows us to examine in

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[25] Nunzi, F.; Sgamellotti, A.; Re, N.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1999**, 3487.

detail the molecular parameters affecting the C−C bond activation on the semibuckminsterfullerene. The addition of the metal fragment to the hydrocarbons leads to the formation of two relatively weak M−C bonds, because of the poor overlap between the molecular orbitals of the fragments.[26] This suggests that the hydrocarbon C−C bond activation is favored by particular structural characteristics of the organic substrate, such as (i) relief of the strain, (ii) attainment of aromaticity, and (iii) forcing the C−C bond into close proximity to the metal. All of these factors can, in principle, operate in the oxidative addition of Pt(0) to semibuckminsterfullerene and will be, in turn, analyzed below.

Two kinds of strain energy operating on the C−C rim bond can be distinguished in the semibuckminsterfullerene fragment, one due to the strain within the five-membered rings and one due to the nonplanarity of the carbon network. The C−C bond breaking through the oxidative addition of the platinum fragment allows a release of the strain energy of the system, by enlarging the ring size and by relaxing the bond angles on the two rim carbon atoms. The comparison of semibuckminsterfullerene with its model compounds **3** and **5** gives a quantitative estimate of the strain energy, pointing out a "ring" and "curvature" contribution to the total strain energy.

The energy decomposition scheme implemented in the ADF program has been employed, allowing us to divide the bond dissociation energy $D(\mathrm{Pt{-}C}_n\mathrm{H}_m)$ into a number of contributions:

$$D(\mathrm{Pt{-}C}_n\mathrm{H}_m) = -[E_{\mathrm{prep}} + E_{\mathrm{ster}} + E_{\mathrm{orb}}] \qquad (2)$$

The first term, E_{prep}, corresponds to the amount of energy required to deform the separated fragments, $\mathrm{Pt(PH_3)_2}$ and $\mathrm{C}_n\mathrm{H}_m$, from their equilibrium structures to the geometry they acquire in the optimized structure of the overall complex. Since the fragments have been considered in the same closed-shell state both in the complex formation and as free molecules, this term corresponds simply to the sum of the fragments relaxation energies, $E_{\mathrm{C_nH_m}}{}^{\mathrm{R}} + E_{\mathrm{Pt(PH_3)_2}}{}^{\mathrm{R}}$. E_{ster} represents the steric repulsion between the two fragments and consists of two components, E_{elstat} and E_{Pauli}. The first, E_{elstat}, is the electrostatic interaction of the nuclear charges and the unmodified electronic charge density of one fragment with those of the other fragment. The second component, E_{Pauli}, is the so-called Pauli repulsion, which is essentially due to the antisymmetry requirement on the total wave function. E_{orb}, known as the orbital interaction term, represents the attracting orbital interactions, which give rise to the energy lowering upon coordination.

This decomposition scheme is particularly useful in the considered complexes, since it allows us to outline the structural and electronic parameters affecting the Pt(0) oxidative addition to the semibuckminsterfullerene. The results of the energy decomposition for compounds **2**, **4**, and **6** are reported in Table 5. It can see from Table 5 that the steric repulsion term E_{ster} for compound **6** is higher by 38 kJ mol^{-1} with respect to compound **2**. Such a result suggests that the planar structure of benzo[*ghi*]fluoranthene gives rise to a stronger steric interaction with respect to the bowl-like curved structure of semibuckminsterfullerene. Moreover, Table 5 shows that the orbital interaction term, E_{orb}, is almost the same for complexes **2** and **6**, thus suggesting that the benzo[*ghi*]fluoranthene reproduces fairly well the electronic interactions between the molecular orbitals of the semibuckminsterfullerene and the metal fragment. Therefore, we can argue that the bowl-like curvature of the hydrocarbon plays an essential role in the C−C bond-breaking reaction, together with the strength of the rim C−C bond.

Table 5. Bond Dissociation Energy Decomposition for the $\mathrm{C}_n\mathrm{H}_m{-}\mathrm{Pt(PH_3)_2}$ Complexes (kJ mol^{-1})

	E_{prep}	E_{elstat}	E_{Pauli}	E_{ster}	E_{orb}
$\mathrm{C_{30}H_{12}{-}Pt(PH_3)_2}$ (**2**)	−554	−1411	1703	292	−973
$\mathrm{C_{13}H_{10}{-}Pt(PH_3)_2}$ (**4**)	−649	−1449	1724	275	−932
$\mathrm{C_{18}H_{10}{-}Pt(PH_3)_2}$ (**6**)	−576	−1465	1795	330	−971

A comparison of the bonding energies between compounds **4** and **6** allows us to estimate the effect of the presence of the four fused benzene rings on the strain energy within the five-membered ring in compound **3**. Such contribution is equal to 56 kJ mol^{-1} and shows that the surrounding fused structure remarkably increases the strain energy of the five-membered ring.

A second factor that plays an important role for the activation of C−C bonds in hydrocarbons is the possible attainment of aromaticity. The presence of the five-membered rings on the fullerene cage causes a localization of the double C−C bonds on each hexagon, thus preventing a conjugation of the π system. The C−C bond-breaking reaction on the semibuckminsterfullerene can lead to an increase of the aromatic character of the system by means of a relaxation of the five-membered ring. The possible enhancement of the aromaticity has been analyzed on the benzo[*ghi*]fluoroanthene **5**, reproducing the same topology of the semibuckminsterfullerene around the five-membered ring. Let us consider the isodesmic equations[27] for the benzo[*ghi*]fluoroanthene molecule, $\mathrm{C_{18}H_{10}}$, and for the corresponding molecule with the broken C−C bond, $\mathrm{C_{18}H_{12}}$, where the dangling bonds have been saturated with hydrogen atoms:

$$\mathrm{C_{18}H_{10} + 26CH_4 \rightarrow 13CH_3CH_3 + 9CH_2{=}CH_2} \qquad (3)$$

$$\mathrm{C_{18}H_{12} + 24CH_4 \rightarrow 12CH_3CH_3 + 9CH_2{=}CH_2} \qquad (4)$$

A comparison between the energies associated with eqs 3 and 4, ΔE, provides an estimate of the variation of the aromatic character as a consequence of the C−C bond cleavage. Density functional calculations for the ground state of the molecules involved in the isodesmic eqs 3 and 4 have been calculated at the same level of theory of compound **5**. The energies ΔE associated to eqs 3 and 4 are respectively equal to 892 and 896 kJ mol^{-1}, thus suggesting a similar stabilization for the two fragments and ruling out any attainment of aromaticity upon breaking of the rim C−C bond on the five-membered ring.

A third factor that favors the activation of C−C bonds is the anchoring of the metal in close proximity to the

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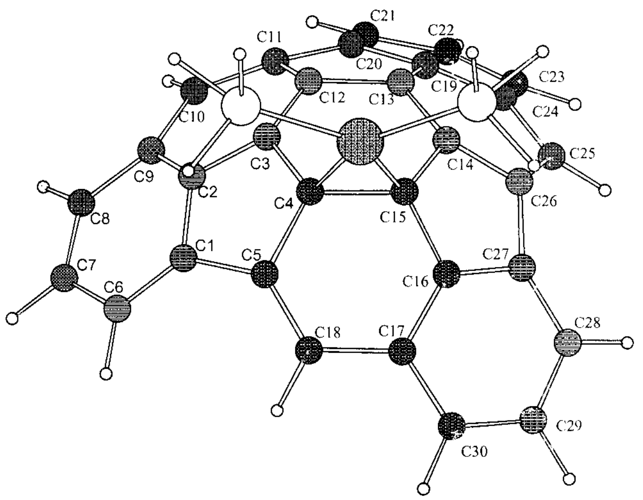

Figure 4. Optimized geometry for the Pt(η^2-π-$C_{30}H_{12}$)-(PH_3)$_2$ complex (**7**).

C−C bond. It has been suggested that the C−C bond cleavage in semibuckminsterfullene proceeds via π-coordination of the platinum diphosphine fragment to one of the C═C double bonds, adjacent to the five-membered-ring site, followed by C−C oxidative addition to the proximal metal center. The optimized structure of compound **1** shows that the C−C bonds at the fusion of two hexagonal rings (C3−C12, C4−C15, and C13−C14; see Figure 1) are the shortest among all the C−C bonds on the semibuckminsterfullerene (1.377 Å), thus suggesting a quite strong C−C double-bond character. The similarity of the reactivity of a series of PAHs to that of C_{60} on the [6,6] bond has been investigated by Mestres and Solà at a semiempirical level.[28] Several (PR_3)$_2$M-(η^2-C_{60}) complexes (M = Ni, Pd, Pt and R = Ph, Et), where the metal center is attached through a [6,6] bond, have been synthesized and structurally characterized.[29] A theoretical study at the DFT-NL level on these complexes provides a reliable estimate for the metal−fullerene bond dissociation energies and points out that the interaction is essentially based on π back-donation from the metal to the fullerene ligand.[30] Taking into account this ability of C_{60} to form stable π complexes with electron-rich metal fragments, we have checked the stability of a π complex also on the semibuckminsterfullerene, setting the Pt(PH_3)$_2$ fragment on one of the three equivalent [6,6] bonds, in a parallel configuration (see Figure 4). A geometry optimization has been performed, without imposing any symmetry constraints, and a stable η^2 configuration was found for the Pt(η^2-π-$C_{30}H_{12}$)(PH_3)$_2$ complex, **7**. Because C−C double bonds are present also on the perimeter of the semibuckminsterfullerene in close proximity to the rim C−C bond on the five-membered rings, geometry optimizations have been performed by also placing the metal fragment on the C1−C6 and C5−C18 bonds (which are equivalent to C20−C21, C10−C11 and C27−C28, C25−C26; see Figure 1), with respective distances of 1.385 and 1.393 Å. However, no stable energy minimum could be found, thus suggesting that the formation of the π complex is more favorable on the internal [6,6] bonds. The Pt−C bond distances in the optimized structure **7**, 2.104 Å (Pt−C4) and 2.126 Å (Pt−C15), are quite close to the values observed for the (PPh_3)$_2$Pt(η^2-C_{60}) complex, 2.115 and 2.145 Å.[29a] The metal attachment causes a lengthening of the C═C bond from 1.377 to 1.473 Å, as expected, because of the back-donation of electron density from the metal to the ligand. It is worth noting that the platinum center bound to the C4−C15 bond is closer to the rim C1−C5 bond on the five-membered ring and, therefore, it is suitably oriented to accomplish its cleavage. A comparison of the relative energies of the η^2:π complex **7** (21 kJ mol^{-1}) and the η^2-σ-oxidative product **6** (147 kJ mol^{-1}) reveals that the latter species is the final product of the metal attack to the rim five-membered ring of **1**.

Conclusions. Density functional calculations have been performed on the oxidative addition of a Pt(0) fragment, Pt(PH_3)$_2$, to one of the rim C−C bonds of semibuckminsterfullerene ($C_{30}H_{12}$) to give an η^2-σ-bonded Pt(II)−buckybowl complex. To evaluate the effect of the ring strain and of the hydrocarbon curvature on the C−C bond activation, analogous calculations have been performed on the oxidative addition of Pt(0) to the C−C bond in five-membered rings of less strained hydrocarbons, such as dihydro-3-fluorene ($C_{13}H_{10}$) and benzo[*ghi*]fluoranthene ($C_{18}H_{10}$). The optimized geometries of the η^2-σ-bonded Pt(II)−buckybowl and −dihydroanthracene complexes have been found to be in good agreement with the X-ray experimental data. Reliable values have been calculated for the energy of the Pt(0) oxidative addition to these hydrocarbons and compared with the corresponding energies of the C−C bond cleavage, allowing us to distinguish between strain energy within the five-membered ring and strain energy associated with the bowl-like curvature. The calculated bond dissociation energies show that the oxidative addition of the Pt(0) fragment to the C−C bond is strongly exothermic for the semibuckminsterfullerene (−147 kJ mol^{-1}), less exothermic for the benzo[*ghi*]-fluoranthracene (−39 kJ mol^{-1}), and even endothermic for the 9,10-dihydroplatinaanthracene (+17 kJ mol^{-1}). The C−C bond strength in compounds **1**, **3**, and **5** has been evaluated, and the rim C−C bond in the less strained $C_{13}H_{10}$ compound is the strongest among the three fragments, thus accounting for the endothermicity of the Pt(0) oxidative addition. The bowl-like curvature of semibuckminsterfullerene plays an essential role in the C−C bond-breaking reaction, while no attainment of aromaticity is involved in the process.

A stable η^2 configuration was found for the Pt(η^2-π-$C_{30}H_{12}$)(PH_3)$_2$ complex, **7**, placing the metal fragment on one of the C═C bonds at the fusion of two hexagonal rings. A comparison of the relative energies of the η^2-π-complex **7** (21 kJ mol^{-1}) and the η^2-σ-oxidative product **6** (147 kJ mol^{-1}) reveals that the latter species is the final product of the metal attack to the rim five-membered ring of **1**.

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