Thermochemistry of Pt−Fullerene Complexes: Semiempirical Study[†]

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Modified Neglect of Differential Overlap (MNDO) and MNDO/d based semiempirical methods are widely employed to explore structure and thermochemistry of molecular systems. In this work, the AM1/d method has been parametrized for systems containing platinum. The proposed scheme delivers excellent performance for binding energies of Pt complexes with ethylene and large π conjugated hydrocarbons. The estimated bond energies accurately reproduce the results of MP4(SDQ) calculations and show significant improvement over DFT (B3LYP and M05) data. We apply the AM1/d scheme to explore the structure and thermochemistry of several Pt compounds with C_{60} and C_{70}. The calculated binding energies of bare Pt atoms and $[Pt(PH_3)_2]$ units to the fullerenes are 75 and 45 kcal/mol, respectively. We find that coordination of a single metal center to C_{60} activates the fullerene cage making subsequent coordination of Pt more favorable. The bond energy $[C_{60}-PtC_{60}]$ is calculated to be 65 kcal/mol. The estimated reaction enthalpies are useful for exploring the stability of Pt_xC_{60} polymer systems and their interaction with phosphines. AM1/d predicts a very low barrier to rotation of the coordinated fullerenes in $[Pt(C_{60})_2]$. The AM1/d scheme is computationally very efficient and can be employed to obtain fast quantitative estimates for binding energies and structural parameters of Pt complexes with large π conjugated systems like fullerenes and carbon nanotubes.

Introduction

In 1978, Dewar and Thiel published a seminal paper that describes a new semiempirical approach called MNDO (modified neglect of differential overlap).[1] This method employs an elegant and efficient scheme to calculate two-center two-electron integrals using point charges.[2] Nowadays, several methods based on the MNDO Hamiltonian like AM1[3] and PM3[4] are widely used for computational modeling of molecular systems,[5] in particular, to estimate the structure and thermochemistry of extended species.[6] As many chemical and biological models lie often beyond high-level ab initio and DFT calculations, the much less demanding semiempirical schemes allow such systems to be addressed at the quantum chemical level.[7] Accurate solvation models developed by Cramer and Truhlar for the semiempirical methods provide reliable treatment of chemical reactions in solution.[8] Further development of MNDO related computational techniques has been performed. In particular, including pairwise distance directed gaussians (PDDG) in the core−core repulsion improves considerably the accuracy of the standard schemes.[9,10] The OMx methods[11,12] in which one-electron orthogonalization corrections are accounted for in the Hamiltonian describe organic and bioorganic systems more accurately than commonly used semiempirical approaches. It has been shown that augmenting the AM1, PM3, and OMx methods with an empirical dispersion term can significantly improve the description of hydrogen bonding and van der Waals interactions.[13,14]

The MNDO-related schemes and OMx methods are based on the sp-AO basis formulation and, therefore, cannot be applied to transition metal compounds because of the omission of d orbitals. An extension of the MNDO scheme to spd basis, MNDO/d, has been suggested by Thiel and Voityuk.[15,16] MNDO/d has been extensively tested for main group elements;[16,17]

in particular, it has been shown that hypervalent compounds of P, S, and halogens are described much more accurately upon including d orbitals. Several schemes based on the MNDO/d scheme have been reported. Reaction-specific parametrization of AM1/d for phosphoryl transfer processes was described by York et al.[18] In this work, DFT results for selected reactions were used as reference data. Only a few parametrizations of transition metal atoms have still been developed.[19−23] The main problem here is that experimental heats of formation and metal−ligand bond enthalpies are sparse and prone to errors. High-level calculations of transition metal compounds are very time-consuming. Moreover, systems containing transition metals are often prone to convergence problems prohibiting smooth optimization of semiempirical parameters.

In the present work, we assess the AM1/d performance for bond energies of platinum with π systems and apply this method to explore the energetic and structural parameters of Pt compounds with fullerene.

Platinum was the first metal found to form π complexes with fullerenes.[24] Currently, Pt compounds with fullerenes are of increasing interest.[25] Several quantum chemical studies of such systems have been reported.[26−28] Because C_{60} is an important element of molecular electronics,[29] its ability to coordinate several Pt centers opens the door for new types of nanoelectronic devices. Synthesis of stable polymers Pt_xC_{60} suggests that Pt can coordinate two or three fullerenes.[30] Distinct structures can be imagined for Pt−fullerene systems. Quantitative description of these systems is hardly possible without reliable thermochemical data. Unfortunately, experimental estimates are very scarce. High-level quantum chemical calculations may be performed only for relatively small models. While the DFT method with the commonly used exchange-correlation potentials (e.g., B3LYP) provides rather accurate energetics for small-size molecules, its performance for large systems is less satisfactory.[31−33] Remarkable problems have been found for

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TABLE 1: AM1/d Hamiltonian Parameters of Pt

U_s (eV)	-81.278
U_p (eV)	-59.250
U_d (eV)	-114.023
ζ_s (au)	2.721
ζ_p (au)	2.000
ζ_d (au)	2.400
β_s (eV)	-3.742
β_p (eV)	-2.009
β_d (eV)	-9.564
$\zeta_s{}'$ (au)	1.770
$\zeta_p{}'$ (au)	1.540
$\zeta_d{}'$ (au)	2.593
$F^0{}_{sd}$ (eV)	7.835
$G^2{}_{sd}$ (eV)	1.000
ρ_{core} (au)	0.831

TABLE 2: Pt−X Core−Core Repulsion Parameters

Pt−X	α_{Pt-X} (Å^{-1})	δ_{Pt-X}
Pt−H	2.740	1.00
Pt−C	2.740	2.00
Pt−P	1.400	0.10
Pt−Cl	1.975	0.50
Pt−Pt	1.000	0.04

TABLE 3: CCSD(T), MP4(SDQ), and AM1/d Binding Energies (kcal/mol)

complex[a]	CCSD(T)[34]	MP4(SDQ)[34]	AM1/d	B3LYP	M05
Pt−C_2H_4	72.4	70.7	68.1	49.3	57.8
$(PH_3)_2$Pt−C_2H_4	22.2	22.2	22.1	13.9	15.8
$(PH_3)_2$Pt−C_2H_3R	22.6	22.3	23.2	11.0	13.8
$(PH_3)_2$Pt−$C_2H_2R_2$	21.9	21.5	22.8	8.8	11.9

[a] R = vinyl

TABLE 4: Comparison of Binding Energies Pt−Ethylene and Pt−Tetravinylethylene ($C_{10}H_{12}$) in Different Complexes (kcal/mol)

	complex	MP4(SDQ)[a]	AM1/d	B3LYP	M05
1	Pt−C_2H_4	70.7	68.1	49.3	57.8
2	Pt−$C_{10}H_{12}$	70.0	69.1	38.3	41.9
3	$(PH_3)_2$Pt−C_2H_4	22.2	22.1	13.9	15.8
4	$(PH_3)_2$Pt−$C_{10}H_{12}$	21.1	18.3	0.32	8.7
5	$[Cl_3$Pt−$C_2H_4]^-$	54.0	46.2	36.5	37.2
6	$[Cl_3$Pt−$C_{10}H_{12}]^-$	40.0	39.1	16.3	17.6
7	$[Cl_5$Pt−$C_2H_4]^-$	38.0	40.8	20.8	22.3
8	$[Cl_5$Pt−$C_{10}H_{12}]^-$	30.0	33.3	6.6	10.5

[a] Reference 34.

TABLE 5: Binding Energy, in kcal/mol, in Complexes $[Pt(PH_3)_2C_{20}H_{10}]$ and $[Pt(PH_3)_2C_{21}H_{12}]$

coordination		AM1/d	MP4(SDQ)[a]
$C_{20}H_{10}$	A1	20.8	22.3
	A2	17.4	
	A3	3.7	
	A4	21.1	24.9
$C_{21}H_{12}$	B1	28.3	26.1
	B2	21.0	23.2
	B3	6.5	
	B4	9.1	13.3
	B5	17.9	20.6

[a] Reference 44.

platinum organometallics; in particular, the DFT calculations considerably underestimate the binding energy of Pt to extended π-conjugated systems.[34] Moreover, the errors depend on the coordination number and oxidation state of the metal and, therefore, are difficult to correct. Unlike DFT, the performance of MNDO-based methods does not change much when the size of a molecular system increases.[9] Therefore, one may expect that the accuracy of AM1/d documented for relatively small models will be held also for extended systems.

Method

AM1/d Parameters of Pt. The extension of the AM1 method to AM1/d has already been described in detail.[19] We note that the established AM1 formalism and parameters[3] remain unchanged for all main group elements, and therefore, AM1 and AM1/d results are identical for all molecule containing only atoms of the main-group elements.

The AM1/d parameters of Pt that determine the Hamiltonian matrix are presented in Table 1. The one-center one-electron energies U_s, U_p, and U_d are required to calculate the corresponding diagonal elements; the exponents ζ_s, ζ_p, and ζ_s and the parameters β_s, β_p, and β_d are used to calculate the resonance integrals. Using Slater-type function with orbital exponents $\zeta_s{}'$, $\zeta_p{}'$, and $\zeta_d{}'$, one calculates the Slater−Condon parameters (with the exception of $F^0{}_{sd}$ and $G^2{}_{sd}$) needed to determine one-center two-electron integrals. These exponents, as well as parameters $F^0{}_{sd}$ and $G^2{}_{sd}$, were derived from experimental valence state energies of the atomic configurations for Pt, Pt$^+$, and Pt^{2+}.[35,36] The parameter ρ_{core} is used to compute the electron−core attraction and core−core repulsion terms. Two-center two-electron integrals are found using an extended multipole-multipole interaction scheme.[15]

The core−core repulsion interaction for atom pairs Pt−X is calculated using two bond specific parameters α_{Pt-X} and δ_{Pt-X}:

$$E^{core}(Pt-X) = Z_{Pt}Z_X\gamma_{ss}[1 + 2\delta_{Pt-X}\exp(-\alpha_{Pt-X}r_{Pt-X})]$$

For the core−core term for Pt−H, a slightly modified expression is used:

$$E^{core}(Pt-H) = Z_{Pt}Z_H\gamma_{ss}[1 + 2\delta_{Pt-H}r_{Pt-H}\exp(-\alpha_{Pt-H}r_{Pt-H})]$$

In these equations, Z_{Pt} and Z_X are the core charges, γ_{ss} is a Coulomb repulsion integral between two s orbitals centered on atoms Pt and X; the interatomic distance r_{Pt-X} is in Å. The parameters α_{Pt-X} and δ_{Pt-X} are listed in Table 2.

The adjustable parameters were fitted using reference energetics and geometries for selected molecules. We note that reliable experimental data on the structure and energetics of Pt compounds in the gas phase are rather sparse.[37,38] Because of that, we also use the results of reliable quantum chemical calculations as reference data. A nonlinear least-squares method was used to optimize the semiempiricalparameters. (In a separate paper, we will describe in detail the parametrization procedure as well as an assessment of the AM1/d method for Pt compounds containing the following elements H, C, N, O, Si, P, S, and halogens). In the present work, we focus on molecules of Pt with π-conjugated systems.

DFT Calculations. For comparison, we carried out DFT calculations of several key Pt molecules. Two exchange-correlation potential, B3LYP[39] and M05,[40] were employed. The B3LYP scheme is commonly applied to calculate the transition metal compound. In line with an evaluation of Zhao and Truhlar,[41] the M05 potential is one of the most accurate schemes to calculate metal−ligand binding energies. The DFT calculations were carried out with full geometry optimization using the program Gaussian03.[42] We employed the LanL2DZ basis

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TABLE 6: Bond Energies in kcal/mol, and Pt–C and C–C Bond Lengths, in Å in [Pt–C$_{70}$] Isomers; C–C Bond Lengths in Non-Coordinated C$_{70}$

system	[Pt–C$_{70}$] AM1/d			C$_{70}$ AM1/d	ND^a
C–C bond/isomer^b	BE	Pt–C	C–C	C–C	C–C
aa	63.4	2.218	1.535	1.464	1.460
ab	74.8	2.196	1.484	1.387	1.382
bc	63.3	2.226	1.521	1.460	1.449
cc	75.0	2.194	1.469	1.375	1.396
cd	58.2	2.261	1.528	1.467	1.464
dd	70.9	2.205	1.424	1.434	1.420
de	65.8	2.188	1.489	1.414	1.415
ee	54.0	2.257	1.539	1.465	1.477

^{a} Nuclear diffraction in solid state.[46,47] ^{b} Symbols aa, bc, cd, and dd are 5:6 ring junctions; ab, cc, de, and ee are 6:6 ring junctions.

CHART 2
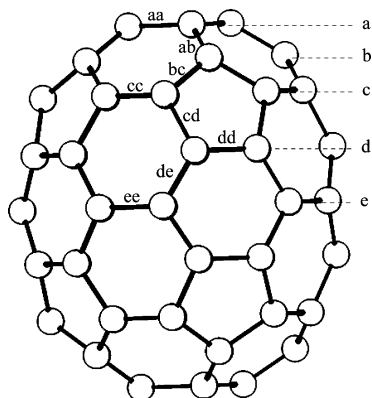
set with inner electrons substituted by effective core potentials and double-ζ quality valence functions.[43]

Results and Discussion

Assessment of the AM1/d Scheme. Coordination of ethylene to a Pt atom provides the simplest example of a π complex. The bonding situation is more complicated in compounds with π-conjugated oligoolefins, where several delocalized π MOs of the ligand are involved in the interaction with the transition metal and distinct coordination modes are accessible. Recently, Sakaki et al. reported the results of systematic high-level ab initio calculations for a number of Pt complexes with ethylene and π conjugated ligands.[34,44] In particular, it has been shown that the results obtained using the MPn series converge to the corresponding CCSD(T) values.[34] Table 3 compares binding energies (BE) derived from CCSD(T), MP4(SDQ), AM1/d, and DFT calculations. As seen, the MP4(SDQ) values for all systems are in very good agreement with CCSD(T) results suggesting that MP4(SDQ) provides quite reliable values of the bond energy of Pt with π ligands. In this study, we use MP4(SDQ) data[34,44] as benchmarks to assess the AM1/d performance for the metal–ligand bond energetics. The preliminary comparison presented in Table 3 also shows that AM1/d provides quite accurate estimates while B3LYP considerably underestimates the BEs. Moreover, the B3LYP binding energy decreases with the size of the π system, as opposed to the CCSD(T) and MP4(SDQ) data (Table 3). The M05 method shows a better performance than B3LYP; however, the M05 energies are still too low. Below, we consider the metal–ligand BEs in complexes with different oxidation states and coordination numbers of Pt.
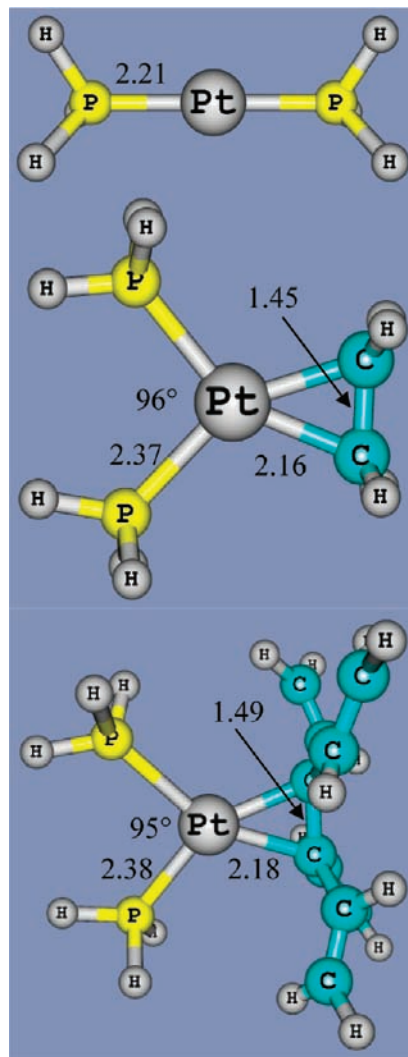

Figure 1. Geometries of [Pt(PH$_3$)$_2$] and its adducts with ethylene and tetravinylethylene; bond lengths are in Å.

Complexes with Ethylene and Tetravinylethylene. First, we compare BE of a bare Pt atom to ethylene and tetravinylethylene (C$_{10}$H$_{12}$). The last molecule has an extended π system with five conjugated C=C bonds. The binding energies in these complexes calculated using AM1/d, 68.1 and 69.1 kcal/mol, are in very good agreement with the MP4(SDQ) results (Table 4). Less accurate estimates (especially for the extended π ligand) are provided by the DFT calculations; the B3LYP and M05 schemes underestimate the BEs by approximately 30 kcal/mol.

Pt(0) compounds with olefins are of special interest. [(PPh$_3$)$_2$Pt(η^2-C$_2$H$_4$)] is a prototype complex of this class of organometallics. The binding energies Pt–ethylene and Pt–C$_{10}$H$_{12}$ in the phosphine complexes are compared in Table 4 (entries 3 and 4). The AM1/d values of 22.1 and 18.3 kcal/mol for ethylene and tetravinylethylene are in good agreement with the MP4(SDQ) estimates to be approximately 22 kcal/mol.[34] As seen, the Pt–ligand bond energies in the phosphine complexes are much smaller than those in the related species of bare Pt while the metal has the same formal oxidation state in both types of compounds. B3LYP considerably underestimates the binding energies of [(PH$_3$)$_2$Pt] to tetravinylethylene giving 0.3 kcal/mol (the complex is predicted thermodynamically unstable with respect to the metal–ligand bond breaking). M05 provides more satisfactory results.

In the Pt(II) species (entries 5 and 6 in Table 4), the Pt–olefin bond is essentially stronger than that in the phosphine com-
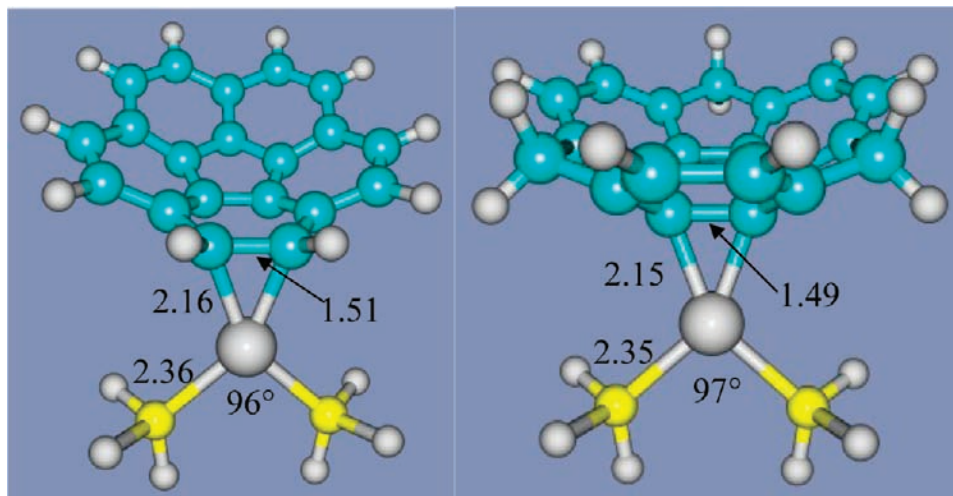
Figure 2. AM1/d geometries of the most stable isomers of [Pt(PH$_3$)$_2$(C$_{20}$H$_{10}$)] and [Pt(PH$_3$)$_2$(C$_{21}$H$_{12}$)]; bond lengths are in Å.
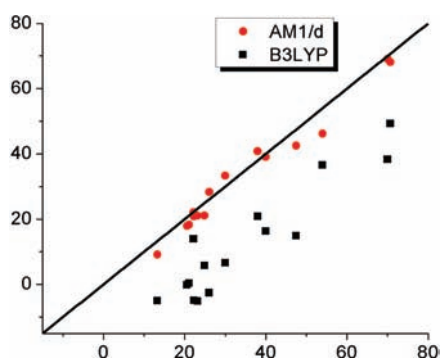

Figure 3. AM1/d and B3LYP binding energies of Pt to ethylene and oligoolefins in different complexes. The solid line indicates an ideal correlation with the MP4(SDQ) data. The values are in kcal/mol.

pounds. For ethylene and tetravinylethylene, the AM1/d binding energies are 46.2 and 39.1 kcal/mol, in good agreement with the corresponding MP4(SDQ) results (54 and 40 kcal/mol). Also, in the Pt(IV) complexes (entries 7 and 8, Table 1), the AM1/d estimates (40.8 and 33.3 kcal/mol) are very close to the reference data. The B3LYP and M05 calculations strongly underestimate the BEs and, therefore, are of limited usefulness for this type of compound.

The results listed in Table 4 demonstrate that the binding energy Pt−olefin ranges from 20 kcal/mol in Pt(0) phosphines to ∼30−50 kcal/mol in Pt(IV) and Pt(II) compounds and to 70 kcal/mol for bare Pt atoms; thus, depending on the structure of the Pt coordination center, the strength of the Pt−olefin interaction can be quite different. In all instances, the AM1/d method reproduces the MP4(SDQ) energies accurately.

The calculated structural parameters of the phosphine complexes are shown in Figure 1. The AM1/d bond lengths and bond angles agree well with the reference data. AM1/d correctly describes the arrangement of coordinated ligands. In [Pt(PH$_3$)$_2$], the P−Pt−P fragment is linear, while the angle Cl−Pt−Cl in [PtCl$_2$] is approximately 90° in agreement with DFT and ab initio calculations.[34] Then in [Pt(PH$_3$)$_2$(C$_2$H$_4$)], the coordinated ethylene lies in the PPtP plane (Figure 1), whereas in [PtCl$_3$(C$_2$H$_4$)]$^-$, this ligand is oriented perpendicular to the PtCl$_3$ plane. Also, the AM1/d structure of [PtCl$_5$(C$_2$H$_4$)]$^-$ closely resembles the reference structure. The interaction of a C=C bond with Pt weakens the bond, and the C−C distance increases by 0.05−0.10 Å. However, no correlation is found between the Pt−ethylene binding energy and the C−C bond length: the longest C−C bond length (1.45 Å) is
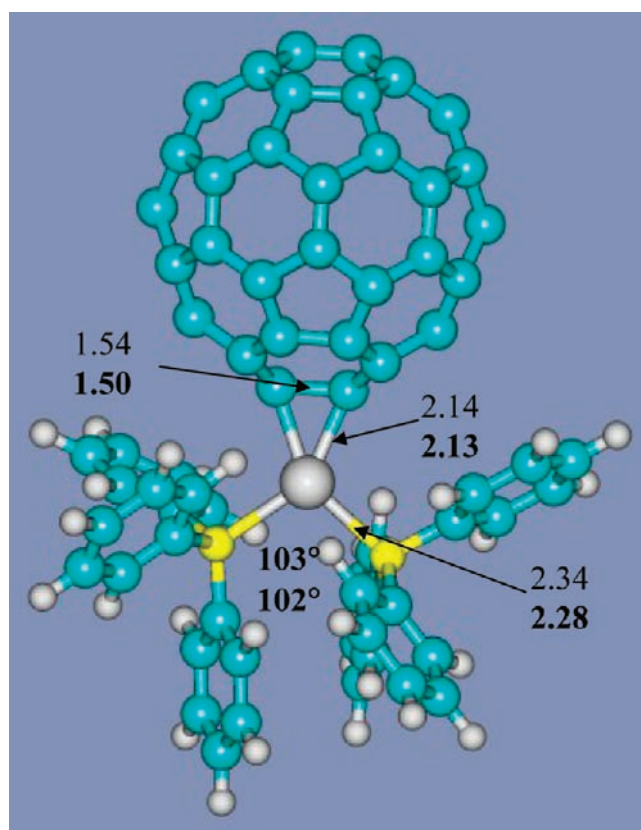
found in the phosphine complex with the smallest bond energy (ca. 20 kcal/mol), while the coordination of bare Pt to ethylene (BE is ca. 70 kcal/mol) leads only to a moderate elongation of C=C (the calculated C−C distance in [Pt(C$_2$H$_4$)] is ca. 1.42 Å). In the Pt(II) and Pt(IV) compounds, AM1/d predicts R_{C-C} to be 1.39 and 1.37 Å, respectively. The Pt−C bond lengths in complexes with C$_{10}$H$_{12}$ are found to be longer by 0.05−0.20 Å than in the related ethylene compounds.

Complexes with Corannulene and Sumanene. A number of polyaromatic nonplanar molecules can be considered as fullerene fragments. The simplest molecule is corannulene, C$_{20}$H$_{10}$, which consist of five hexagonal rings fused to a central five-membered ring; another related system is sumanene, C$_{21}$H$_{12}$, which has a central six-membered ring. Distinct η^2 coordination
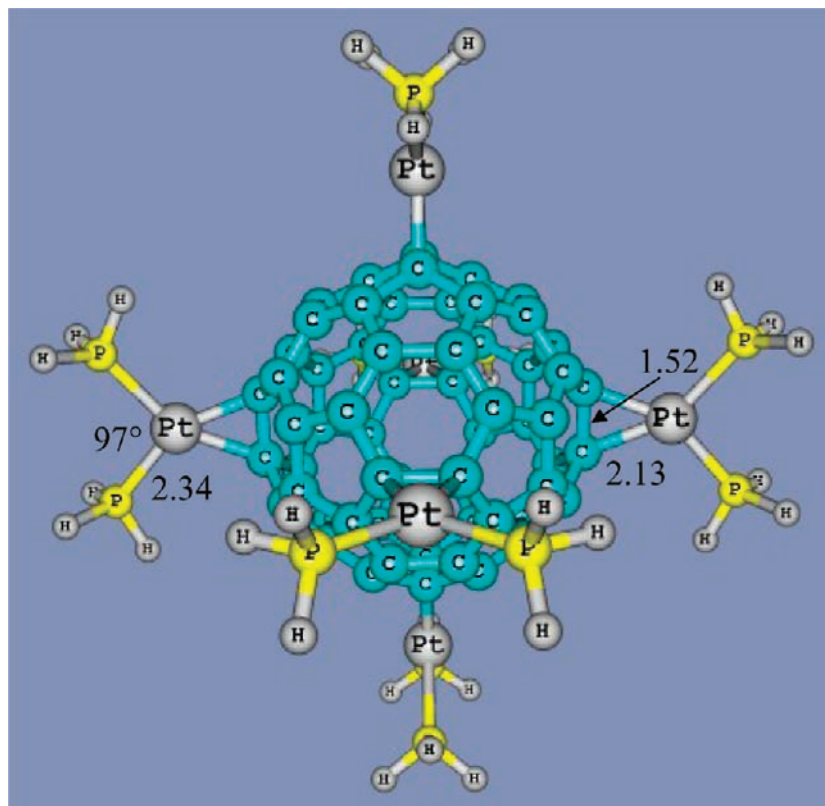

Figure 4. AM1/d and experimental (in bold) structural parameters of [(PPh$_3$)$_2$PtC$_{60}$].

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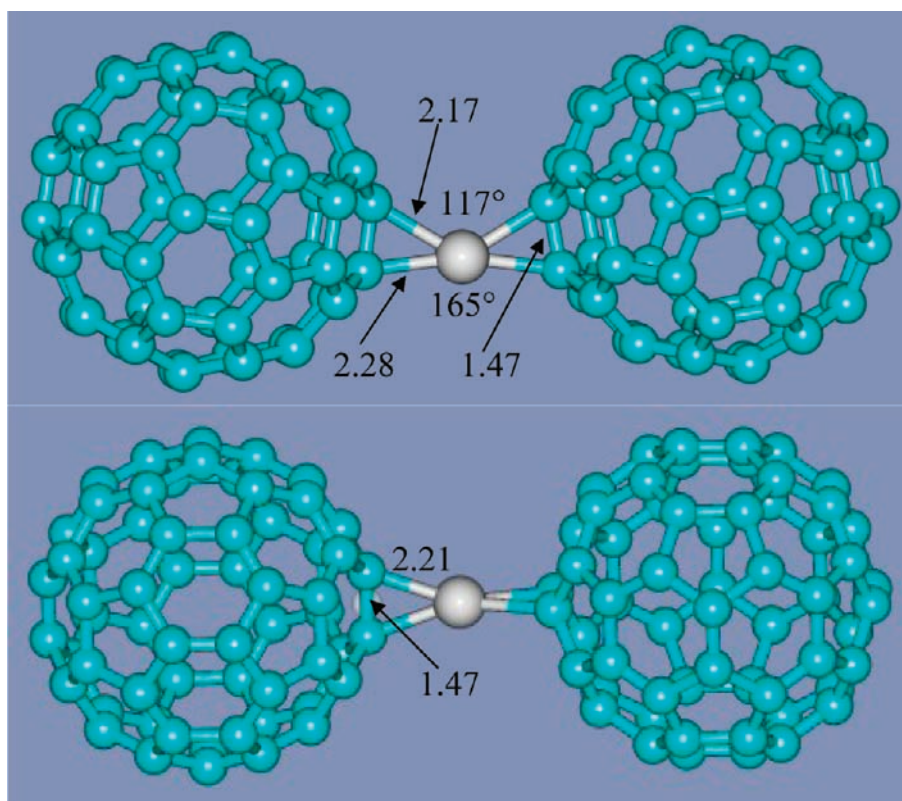**Figure 5.** Structure of [{(PH$_3$)$_2$Pt}$_6$Pt]. Bond lengths are in Å.

Figure 6. Planar and tetrahedral isomers of [C$_{60}$Pt.C$_{60}$]. Bond lengths are in Å.

modes in corannulene and sumanene are shown in Chart . The MP4(SDQ) data obtained for several Pt complexes with these ligands[44] allow for further assessment of the AM1/d method. Table 5 compares the binding energies calculated using AM1/d and MP4(SDQ).

1.

According to AM1/d, the most stable regioisomers of [Pt(PH$_3$)$_2$ (C$_{20}$H$_{10}$)] are formed by Pt coordination to the A4 and A1 bonds (see Chart); the corresponding binding energies are of 21.1 and 20.8 kcal/mol. These estimates agree very well

C₂₀H₁₀   **C₂₁H₁₂**
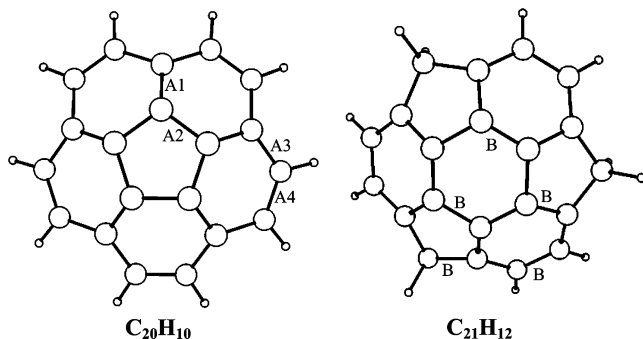
with the MP4(SDQ) values, 24.9 and 22.3 kcal/mol.[44] The A4 isomer is depicted in Figure 2. AM1/d predicts the A2 and A3 isomers to be approximately 4 and 17 kcal/mol higher than A4 (Table 2). No MP4(SDQ) data are provided for these structures.

The most stable structure of $[Pt(PH_3)_2 (C_{21}H_{12})]$ is shown in Figure 2. The stability of its regioisomers calculated by AM1/d decreases as B1 > B2 > B5 > B4 > B3. The AM1/d bond energies are in good agreement with the reference data (Table 6). The bond energies of $[Pt(PH_3)_2]$ to the A4 and A1 sites of corannulene and the B1, B2, and B5 sites of sumanene are in the range of 22−26 kcal/mol and close to that of ethylene.

For completeness, we also calculated the complexes of a bare Pt atom with corannulene and sumanene. As expected, the bond energies in these species are considerably larger than those in phosphine compounds. The BEs of approximately 70 kcal/mol are found for the most stable structures of $[Pt(C_{20}H_{10})]$ and $[Pt(C_{21}H_{12})]$. The $Pt-C_{20}H_{10}$ bond energy decreases as A1 (69.3) ∼ A4 (67.9) > A2 (66.0) > A3 (56.5); for $Pt-C_{21}H_{12}$, we found B1 (74.4) > B5 (69.3) ∼ B2 (68.5) > B4 (62.7; the structure B3 cannot be localized). The relative stability of these complexes is qualitatively similar to the trends found in the corresponding phosphine compounds.

Closing this section, we compare the binding energies derived for all considered species (Figure 3) using AM1/d and B3LYP with the MP4(SDQ) data.[34,44] The reference values range from 20 to 70 kcal/mol. The AM1/d scheme can accurately reproduce these data: the mean deviation is −1.75 kcal/mol, and the mean absolute deviation is 2.85 kcal/mol. In contrast to AM1/d, the B3LYP calculations strongly underestimate the binding energy (mean deviation is −22.59 kcal/mol). Especially large deviations are found for large molecules. While the M05 scheme provides more accurate BEs than B3LYP (mean deviation is −16.78 kcal/mol), it appears to also be of limited usefulness for estimating BEs in Pt complexes with large π conjugated systems.

Complexes of Pt with Fullerene. The π complexes formed by fullerenes with platinum and other transition metals have drawn considerable attention.[25,45] In C_{60}, there are two distinct types of C−C bonds: short bonds (bond length 1.38 Å) at the 6:6 ring junctions and long bonds (bond length 1.44 Å) at the 5:6 ring junctions; these bond types are referred to below as C_6-C_6 and C_5-C_6. Correspondingly, two types of η^2 coordination of Pt to C_{60} are possible. One may expect that a more stable structure should be formed by coordination of the transition metal to one of the C_6-C_6 bonds enriched with π-electron density.[46] Indeed, in all experimentally studied transition metal compounds with C_{60}, η^2 coordination occurs only to the C_6-C_6 bonds[24,25]

Phosphine Complexes. Figure 4 compares structural parameters of $[Pt(PPh_3)_2C_{60}]$ calculated by the AM1/d scheme with experimental data.[24] Overall, the AM1/d geometries agree well with experimental values. By coordination of C_{60} to Pt, the

C_6-C_6 bond length increases from 1.39 to 1.53 Å indicating strong electronic interactions of the transition metal with the ligand. The Pt−C distance, 2.13 Å, is similar to that found in the ethylene complex $[Pt(PH_3)_2C_2H_4]$ (Figure 1).

The $(PH_3)_2Pt-C_{60}$ bond energy calculated with AM1/d is 42.3 kcal/mol. This value is in good agreement with 47.5 kcal/mol computed using the MP4(SDQ) scheme within an ONIOM model.[44] This BE is considerably larger than the BEs obtained for the phosphine complexes with ethylene and the π-conjugated systems (Tables 4 and 5). B3LYP strongly underestimates the $Pt-C_{60}$ binding energy giving 14.9 kcal/mol.[44] According to the AM1/d calculation, a complex formed by η^2 coordination of 5:6 junction is by 17 kcal/mol less stable than the Pt < (C_6-C_6) structure. This remarkable difference in the thermodynamical stability should prevent the formation of Pt < (C_5-C_6) adducts.

[(PH₃)₂PtC₇₀]. Unlike C_{60}, higher fullerenes have several types of 6:6 and 5:6 junctions. Let us consider C_{70} as an example. This fullerene (Chart 2) has a layered structure with five types of carbon atoms (labeled with a, b, c, d, and e from the capping pentagon to the equator). The structure has D_{5h} symmetry and contains eight distinct types of C−C bonds (four C_6-C_6 and four C_5-C_6). The bond between atoms belonging to circles k and l is labeled by kl. Thus, there are four isomers where Pt is coordinated to the C_6-C_6 bonds (ab, cc, de, and ee) and four isomers with the Pt < (C_5-C_6) coordination (aa, bc, cd, and dd). The AM1/d bond energy of $[(PH_3)_2Pt]$ to C_{70} decreases from approximately 43 kcal/mol for the cc and ab isomers to 16 kcal/mol for the cd isomer. As expected, the strongest interaction Pt−fullerene occurs by coordination to 6:6 junctions. The strongest bond Pt < (C_5-C_6) is found in the isomer dd (37.8 kcal/mol). The Pt−C distances in the complexes are within 2.13 to 2.15 Å and, thus, cannot be used as a qualitative measure of the bond strength. By coordination to the $[(PH_3)_2Pt]$ fragment, the C−C bond becomes significantly longer; for example, in the isomer cc, the bond length increases by 0.14 Å.

Interaction of Single Pt Atom with Fullerenes. As already mentioned, distinct polymer structures $[C_{60}Pt_x]$ have been experimentally found.[25,30] Therefore, thermochemistry of model systems like $C_{60}Pt_n$ and $C_{60}PtC_{60}$ is of special interest. Below, we also consider the formation of $[PtC_{70}]$.

[PtC₆₀] and [PtC₇₀]. The bond energy Pt−fullerene depends on the type of a C−C bond interacting with the metal. In $Pt-C_{60}$, the binding energies Pt < (C_6-C_6) and Pt < (C_5-C_6) are calculated to be 74.4 and 62.1 kcal/mol, respectively. In the first structure, the BE is similar to BEs of bare Pt atoms with ethylene and π conjugated hydrocarbons. In Table 6, we compare BEs calculated for all possible isomers of $[PtC_{70}]$. The bond energy ranges from 75 to 54 kcal/mol depending on the coordination mode. The strongest metal−ligand bonds are found in the isomers cc and ab. Note that the most unstable structure, ee isomer, is also formed by coordination of Pt to C_6-C_6. On the other hand, the binding interaction of Pt to the 5:6 junction dd is quite strong and comparable to those in the most stable structures cc and ab.

Because the C−C bond lengths in C_{70} are found to be quite different,[47,48] we compare the Pt < (C−C) bond energies with the corresponding C−C distances in the fullerene (Table 6). As expected, the BE decreases when the corresponding C−C bond becomes longer. The most stable complexes (with binding energy ca. 75 kcal/mol) are formed by coordination of Pt to the shortest bonds cc and ab (bond lengths ∼1.38 Å), whereas the interaction with the longest bonds ee and cd (∼1.47 Å) is

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TABLE 7: Bond Energies in Isomers of [Pt$_2$C$_{60}$] and [{(PH$_3$)$_2$Pt}$_2$C$_{60}$] (kcal/mol)

regioisomer[a]	Pt−C$_{60}$Pt	[(PH$_3$)$_2$Pt−C$_{60}$Pt(PH$_3$)$_2$]
cis-1	94.2	55.7
cis-2	79.9	44.2
cis-3	77.6	45.4
e′	76.4	44.4
e″	76.1	44.2
trans-4	75.5	43.3
trans-3	75.2	42.9
trans-2	74.8	42.5
trans-1	74.7	42.4

[a] Only 6:6 ring junctions are considered.

TABLE 8: Average Pt−C$_{60}$ Bond Enthalpies in the Complexes [{Pt(PH$_3$)$_2$}$_n$C$_{60}$] and [Pt$_n$C$_{60}$] in kcal/mol

n		[{Pt(PH$_3$)$_2$}$_n$C$_{60}$]	[Pt$_n$C$_{60}$]
1		42.3	74.4
2	C_{2v}	43.3	75.4
	D_{2h}	42.3	75.1
3	C_{3v}	44.6	76.5
	C_{2v}	43.9	75.9
4	C_{2v}	45.3	77.1
	D_{2h}	44.7	76.6
5	5	46.2	77.9
6	6	47.4	78.8

remarkably weaker, 54−58 kcal/mol. The results obtained for [PtC$_{60}$] and [PtC$_{70}$] indicate that the C−C distance in fullerenes can be used for qualitative prediction of favorable sites to bind transition metal atoms.

We note that the structure of Pt < (C$_6$−C$_6$) units in [PtC$_{60}$] and [PtC$_{70}$] is similar to that found in [Pt−ethylene]. The C−C bond of the fullerene cage incorporated into the ring Pt < (C−C) is elongated by ∼0.08 Å while other bond lengths remain almost unchanged. In fullerene complexes with [Pt(PH$_3$)$_2$], the Pt−C distances are not sensitive to the C−C bond type. In contrast, the metal−carbon bond length in [PtC$_{70}$] varies from 2.19 Å in the cc isomer to 2.26 Å in the ee isomer.

Coordination of Two and More Pt Atoms to C$_{60}$. Usually, the formation of a metal−ligand bond decreases the ability of the ligand to bind additional metal atoms. In fullerene complexes, the binding situation appears to be different. Let us consider BEs in [Pt$_n$C$_{60}$] and [{(PH$_3$)$_2$Pt}$_n$C$_{60}$]. Only complexes with the Pt < (C$_6$−C$_6$) bonds will be discussed. There are nine regioisomers that can form when two Pt atoms are coordinated to the 6:6 ring junctions. The calculated reaction enthalpies for

$$PtC_{60}−Pt \rightarrow PtC_{60} + Pt$$
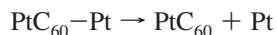
are listed in Table 4. The generally accepted nomenclature is used.[49] The largest bond energy, 94.2 kcal/mol, is found for the cis-1 isomer where both Pt atoms are connected to the same ring. This energy is considerably larger than the value of 74.4 kcal/mol in [Pt−C$_{60}$]. The BE Pt−C$_{60}$Pt decreases with increase of the Pt...Pt distance from 79.9 kcal/mol (cis-2) to 74.7 kcal/mol (trans-1). Note that the interaction Pt−C$_{60}$Pt in all isomers of Pt$_2$C$_{60}$ is found to be stronger than that in PtC$_{60}$.

We also estimated the reaction enthalpy for

$$[(PH_3)_2PtC_{60}−Pt(PH_3)_2] \rightarrow [(PH_3)_2PtC_{60}] + [Pt(PH_3)_2]$$
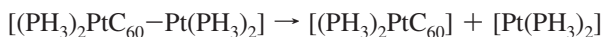
The dependence of binding energies [{PH$_3$)$_2$Pt−C$_{60}$Pt{PH$_3$)$_2$] on the arrangement of the Pt centers is qualitatively similar to that obtained for [Pt$_2$C$_{60}$] (Table 7). The most stable isomer is cis-1 ($R_{Pt−Pt}$ = 3.60 Å and BE = 55.7 kcal/mol). In other isomers, the BEs are somewhat larger than 42.5 kcal/mol calculated for [(PH$_3$)$_2$Pt−C$_{60}$] and rather insensitive to mutual position of the [(PH$_3$)$_2$ Pt] units. Obviously, replacing PH$_3$ by extended phosphines should considerably decrease the stability of cis-1 isomer because of the interligand steric repulsion.

[C$_{60}${Pt(PH$_3$)$_2$}$_n$] and [C$_{60}$Pt$_n$] Complexes. Multiple addition of Pt centers to C$_{60}$ may be exemplified by [C$_{60}${Pt(PEt$_3$)$_2$}$_6$] which has been isolated and crystallized.[24] The six platinum atoms are arranged in an octahedral array about the fullerene core with each platinum atom coordinated to a 6:6 ring junction

(Figure 5). This arrangement of the Pt centers minimizes steric repulsion between the phosphine groups. Table 8 presents the results of the AM1/d calculation of [C$_{60}${Pt(PH$_3$)$_2$}$_6$] and smaller complexes generated by stepwise elimination of the Pt(PH$_3$)$_2$ fragments. Also, BEs in related core complexes [Pt$_n$ C$_{60}$] are provided. Each of the compounds with n = 2, 3, and 4 has two isomers. The average bond enthalpy of Pt to the fullerene, $\bar{E}(n)$ = $\Delta H(n)/n$, is estimated from the reaction enthalpy $\Delta H(n)$ for [C$_{60}$Pt$_n$] → nPt + C$_{60}$. In a similar manner, we derive the average bond enthalpies for [C$_{60}${Pt(PH$_3$)$_2$}$_n$]. The enthalpy $\Delta H(n)$ can be easily obtained from the average energies, $\Delta H(n) = n \bar{E}(n) − (n − 1)\bar{E}(n − 1)$. The average energy increases with a number of Pt. In [C$_{60}$Pt$_n$], it ranges from 74.4 (n = 1) to 78.8 kcal/mol (n = 6), whereas in [C$_{60}${Pt(PH$_3$)$_2$}$_n$], it ranges from 42.3 to 47.4 kcal/mol. The values listed in Table 8 show that the ability of fullerenes to coordinate Pt centers increases with a number of coordinated metal centers. The reaction enthalpy slightly depends on the mutual position of the metal atoms. Because of the strong interaction of Pt bare atoms with C$_{60}$, a high coverage of the fullerene surface by metal centers is expected. Note that the average BE of a PH$_3$ group to Pt in [C$_{60}${Pt(PH$_3$)$_2$}$_6$] is calculated to be 25.9 kcal/mol which is remarkably smaller than 42.4 kcal/mol found in the complex Pt(PH$_3$)$_2$. Thus, the Pt−P bond [Pt(PR$_3$)$_2$] becomes significant weaker by coordination of this unit to a fullerene.

The results presented in Tables 7 and 8 suggest that fullerenes can perfectly function as a multiple ligand connecting several Pt centers. Coordination of Pt activates the fullerene cage leading to more favorable interaction with further Pt centers.

[C$_{60}$−Pt-C$_{60}$] Complex. The formation of polymer compounds [C$_{60}$Pt$_x$] implies two conditions: (1) the ability of C$_{60}$ to function as a bridge ligand and (2) the ability of Pt to connect at least two fullerene molecules. In the previous section, we showed that multiple coordination of Pt to fullerenes should be energetically very favorable. Now, we consider the formation of [C$_{60}$−Pt−C$_{60}$]. We calculated two isomers of this complex with the planar and tetrahedral structure of the fragment [(C−C)>Pt<(C−C)] (Figure 6) and found that the planar isomer is approximately 1 kcal/mol more stable than the tetrahedral structure. This small difference suggests a low energy barrier to rotation of the coordinated fullerenes around the main axis of the complex.

The reaction enthalpy for [C$_{60}$−Pt−C$_{60}$] → C$_{60}$ + [Pt−C$_{60}$] is predicted to be 62.5 kcal/mol. This value is in between those of 74.4 and 42.5 kcal/mol found for the bond energies of C$_{60}$−Pt and C$_{60}$−Pt(PH$_3$)$_2$. Thus, the formation of the C$_{60}$−Pt−C$_{60}$ structure should be quite favorable. Our calculation also shows that the reaction

$$[C_{60}−Pt−C_{60}] + 2PH_3 \rightarrow C_{60}+C_{60}−Pt(PH_3)_2$$

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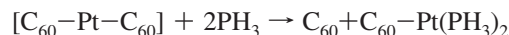
is exothermic and has $\Delta H = -5.8$ kcal/mol. This finding is in line with experiments which demonstrate a disruption of [C_{60} Pt$_x$] polymers by adding phosphines.[25]

Conclusions

The assessment of the AM1/d method parametrized for Pt shows that this scheme may be used for accurate estimation of bond energies and structural parameters in Pt complexes with conjugated π systems. The AM1/d binding energies are in very good agreement with the MP4(SDQ) results and show significant improvement over B3LYP and M05 estimates.

Using the AM1/d scheme, we have investigated several systems formed by interaction of bare Pt atoms and [Pt(PH$_3$)$_2$] complexes with C_{60} and C_{70}. These fullerenes are found to perfectly function in multiple coordination modes connecting several Pt centers. The average bond energy of bare Pt atoms and Pt(PH3)2 units to the fullerenes are approximately 78 and 45 kcal/mol. The most favorable η^2 coordination modes of C_{70} are the 6:6 ring junctions cc and ab. The predicted [C_{60}−PtC$_{60}$] bond energy is 63 kcal/mol. This estimation suggests that the formation of two- and three-dimensional Pt−fullerene frameworks should be energetically more favorable than the formation of one-dimensional polymers.

The parametrized scheme can be used as a computationally inexpensive tool for screening the stability of large complexes containing Pt centers coordinated to extended π systems like fullerenes or carbon nanotubes. The model is expected to have considerable impact on semiempirical QM/MD calculations of Pt organometallics.

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