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Theoretical Study of $M(PH_3)_2$ Complexes of C_{60}, Corannulene ($C_{20}H_{10}$), and Sumanene ($C_{21}H_{12}$) (M = Pd or Pt). Unexpectedly Large Binding Energy of $M(PH_3)_2(C_{60})$

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DFT and MP2 to MP4(SDQ) methods were applied to $M(PH_3)_2(C_{60})$, $Pt(PH_3)_2(C_{20}H_{10})$, and $Pt(PH_3)_2(C_{21}H_{12})$ (M = Pd or Pt, $C_{20}H_{10}$ = corannulene, and $C_{21}H_{12}$ = sumanene). The binding energy considerably fluctuates around MP2 and MP3 levels but much less upon going from MP3 to MP4(SDQ) in $Pt(PH_3)_2(C_2H_4)$, $Pt(PH_3)_2(C_{20}H_{10})$, and $Pt(PH_3)_2(C_{21}H_{12})$. Also, the MP4(SDQ) method presents a binding energy similar to that of the CCSD(T) method in $Pt(PH_3)_2(C_2H_4)$. Thus, it is likely that the MP4(SDQ) method is useful to evaluate binding energies of these complexes. The binding energies of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$ are evaluated to be 24.9 and 26.1 kcal/mol, respectively, by the MP4(SDQ) method and only +5.8 and −2.6 kcal/mol, respectively, by the DFT(B3LYP) method. These MP4(SDQ)-calculated binding energies of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$ are similar to that of $Pt(PH_3)_2(C_2H_4)$, which strongly suggests that these complexes can be successfully synthesized. The binding energy of $Pt(PH_3)_2(C_{60})$ is evaluated to be 44.8 and 45.5 kcal/mol with the ONIOM(MP4(SDQ):UFF) and ONIOM(MP4(SDQ):B3LYP) methods, respectively, and that of the Pd analogue is evaluated to be 39.9 kcal/mol with the ONIOM(MP4(SDQ):UFF) method, whereas the DFT(B3LYP), DFT(BVP86), and DFT(BPW91) methods provide much smaller binding energies. It is noted that these binding energies are much larger than those of the ethylene, corannulene, and sumanene analogues. This difference is reasonably interpreted in terms that the LUMO of C_{60} is at much lower energy than those of ethylene, corannulene, and sumanene. We investigated also how to separate the high level and the low level regions in the ONIOM calculation of $M(PH_3)_2(C_{60})$ and proposed here the reasonable way to evaluate the binding energy of transition-metal complexes of C_{60}.

Introduction

Transition-metal complexes of fullerene have attracted a lot of researchers' interests[1] since 1991, when the first syntheses of $OsO_4(NC_5H_4CMe_3)(C_{60})$ and $Pt(PPh_3)_2(C_{60})$ were reported.[2,3] This is because transition-metal complexes of fullerene are expected to be new materials with interesting properties. Actually, various transition-metal η^2-fullerene[1,4−7] and η^5-fullerene complexes[8] have been reported so far.

To synthesize variety of transition-metal complexes of fullerene, we need detailed knowledge of geometry, bond strength, and bonding nature of the transition-metal complexes of fullerene. In this regard, several theoretical studies have been carried out; for instance, $Pt(PH_3)_2(C_{60})$ was investigated with Fenske−Hall,[9] Hartree−Fock,[10−12] and extended Hückel MO methods[13] previously, and with the DFT method[14] very recently. Also, the possibility of the existence of η^6-coordination complexes was theoretically investigated with the semiempirical and Hartree−Fock MO methods.[15,16] However, a theoretical attempt has not been sufficiently made to estimate the binding energy of transition-metal complexes of fullerene, despite the binding energy being one of fundamental data of the compound. In those studies, it is noted that only the DFT method has been applied to transition-metal complexes of C_{60} except for the Hartree−Fock and semiempirical MO methods, which were employed very previously. It is worthwhile to investigate the transition-metal complexes of C_{60} with the post Hartree−Fock method to evaluate the binding energy.

Besides C_{60}, transition-metal complexes of corannulene ($C_{20}H_{10}$) have drawn a lot of attention, too, because corannulene is considered a part of C_{60} and it is also expected to be a functional material. Actually, η^5-$C_{20}H_{10}$ complexes of RuCp* (Cp* = C_5Me_5),[17] $ZrCl_2$,[18] $Rh_2(CF_3COO)_4$,[19] and IrCp[20] have been experimentally reported. Interestingly, all these complexes take the η^5-coordination structure, but the η^2-coordination structure has not been reported, unlike transition-metal complexes of C_{60}, to our knowledge. Although corannulene complexes of bare metal ion were theoretically investigated with the DFT method,[21,22] no theoretical work has been reported on usual transition-metal complexes of corannulene. Sumanene ($C_{21}H_{12}$) is also considered to be a part of C_{60} like corannulene. However, a transition-metal complex of sumanene has not been reported yet, to our knowledge. In this regard, it is interesting to investigate the stabilities of transition-metal complexes of corannulene and sumanene.

In this work, we theoretically investigated $M(PH_3)_2(C_{60})$ (M = Pd or Pt), $Pt(PH_3)_2(C_{20}H_{10})$, and $Pt(PH_3)_2(C_{21}H_{12})$ with DFT and MP2 to MP4(SDQ) methods, where $C_{20}H_{10}$ and $C_{21}H_{12}$ represent corannulene and sumanene, respectively. One of our important purposes here is to evaluate binding energies of transition-metal complexes with such large π-conjugate systems as C_{60}, $C_{20}H_{10}$, and $C_{21}H_{12}$. We also wish to make comparisons

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TABLE 1: Basis Set Systems Used for the Calculations

	Pt	C	H	P	H in PH_3
BS-1	LANL2DZ	6-31G	6-31G	6-31G	6-31G
BS-2	(541/541/111/1) with ECP	6-31G	6-31G	6-31G	6-31G
BS-3	(541/541/111/1) with ECP	6-31G	6-31G	(21/21/1) with ECP	6-31G
BS-4	(541/541/111/1) with ECP	6-31G(d)	6-31G	(21/21/1) with ECP	6-31G
BS-5	(541/541/111/1) with ECP	6-31G(d)	6-31G	6-31G(d)	6-31G

of the binding energy of $Pt(PH_3)_2(C_{60})$ with those of $Pt(PH_3)_2(C_2H_4)$, $Pt(PH_3)_2(C_{20}H_{10})$, and $Pt(PH_3)_2(C_{21}H_{12})$, to indicate which coordination site of corannulene and sumanene is favorable to form transition-metal complexes, and to present a theoretical prediction whether transition-metal complexes of corannulene and sumanene are isolable or not.

Computational Details

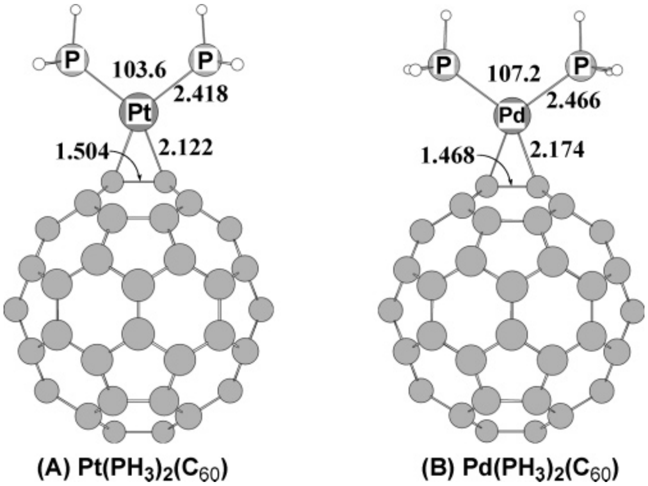
Geometries were optimized by the DFT method with the B3LYP functional.[23,24] In the geometry optimization, LANL2DZ basis sets[25] were used for Pd and Pt, where 6-31G basis sets[26,27] were employed for P, C, and H atoms. The binding energy of $Pt(PH_3)_2(C_2H_4)$ was evaluated with the DFT, MP2 to MP4(SDTQ), and CCSD(T) methods,[28] whereas those of $M(PH_3)_2(C_{60})$ (M = Pd or Pt), $Pt(PH_3)_2(C_{20}H_{10})$, and $Pt(PH_3)_2(C_{21}H_{12})$ were evaluated with the DFT and MP2 to MP4(SDQ) methods because the CCSD(T) method could not be applied to these complexes due to their very large sizes. Besides the B3LYP functional, BPW91[23,29] and BVP86[23,30,31] functionals were also used to evaluate the binding energy. In the evaluation of the binding energy, better basis sets were used. For Pd and Pt, (541/541/211/1) and (541/541/111/1) basis sets were used to represent valence electrons, respectively, where their core electrons were replaced with the effective core potentials (ECPs).[25,32,33] For C, the 6-31G(d) basis set was used.[26] In some calculations, either LANL2DZ basis set[34] or 6-31G(d) basis set[27] was used for P, where one d polarization function[35] was added to the LANL2DZ basis set. Combinations of these basis sets are summarized in Table 1. The reliability of the computational method and the basis sets used here are checked by the calculation of the binding energy of $Pt(PH_3)_2(C_2H_4)$ (see Supporting Information Table S1).

Part of the calculations for $M(PH_3)_2(C_{60})$ were performed with the ONIOM technique,[36] where the MP2 to MP4(SDQ) methods were used for the high level region and the MM method with the UFF force field[37] was employed for the low level region. We also carried out the ONIOM calculation with the DFT(B3LYP) method for the low level region.

Gaussian 98 program package was used for all calculations.[38] Orbital plots were drawn with MOLEKEL program package.[39]

Results and Discussion

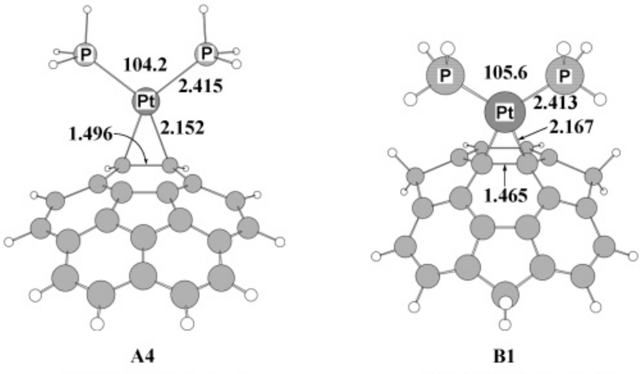
Optimized Geometries of $M(PH_3)_2(C_{60})$ (M = Pd or Pt), $Pt(PH_3)_2(C_{20}H_{10})$, and $Pt(PH_3)_2(C_{21}H_{12})$. As shown in Figure 1, Pt and Pd centers coordinate with the C−C bond between two C6 rings of C_{60}, as reported,[3] where C6 and C5 represent six-member ring and five-member one, respectively. The Pt−C and C−C bond distances (2.122 and 1.504 Å, respectively) of $Pt(PH_3)_2(C_{60})$ agree well with the corresponding experimental values (2.130 and 1.502 Å, respectively) reported for $Pt(PPh_3)_2(C_{60})$,[3b] whereas the Pt−P distance is somewhat longer than the experimental value,[40] as compared in Table 2. We optimized the other geometry in which the Pt center coordinates with the C−C bond between C6 and C5 rings, but it was considerably less stable than the above-mentioned most stable structure by 17 kcal/mol (DFT/BS-I) and 9.8 kcal/mol (MP2/BS-V), where the optimized geometry is given in Supporting Information Figure S1. This result agrees well with the experimental fact that the transition-metal atom interacts with the C−C bond between two C6 rings in all transition-metal complexes of η^2-C_{60} reported experimentally. We do not discuss further details about this coordination structure, because the comparison of two coordination structures has been previously discussed in theoretical work.[13] In $Pd(PH_3)_2(C_{60})$, the Pd−C and C−C bond distances agree well with the experimental values of $Pd(PPh_3)_2(C_{60})$,[4,5] too, but the Pd−P distance is somewhat longer than the experimental one. It is noted that the Pd−C distance is longer than the Pt−C distance by 0.052 Å and the C−C distance which coordinates with the Pd center is shorter than that of the Pt analogue by 0.036 Å. These results are consistent with the fact that the binding energy of $Pd(PH_3)_2(C_{60})$ is smaller than that of the Pt analogue, as will be discussed below.



(A) $Pt(PH_3)_2(C_{60})$ (B) $Pd(PH_3)_2(C_{60})$

Figure 1. Optimized geometries of $Pt(PH_3)_2(C_{60})$ and the Pd analogue. Bond distances in angstroms and bond angle in degrees.

In corannulene, four possible coordination sites (A1 to A4 in Chart 1) are expected to be utilized for the complexation with $Pt(PH_3)_2$. Among those coordination sites, A1 and A4 sites provide stable Pt(0) complexes, whereas the complexation with $Pt(PH_3)_2$ does not occur at the other coordination sites; in other words, the geometry optimization leads to a very long Pt−$C_{20}H_{10}$ distance and wrong orientation of $Pt(PH_3)_2$. In the most stable structure, $Pt(PH_3)_2$ coordinates with $C_{20}H_{10}$ at the A4 site, as shown in Figure 2; the other structure is given in Supporting Information Figure S2. In sumanene, we examined five possible coordination sites (B1 to B5 in Chart 1) and found that the



A4 B1

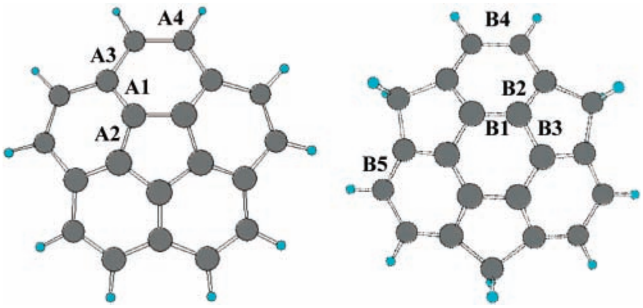
(A) $Pt(PH_3)_2(C_{20}H_{10})$ (B) $Pt(PH_3)_2(C_{21}H_{12})$

Figure 2. Optimized geometries of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$. Bond distances in angstroms and bond angle in degrees.

TABLE 2: Several Important Geometrical Parameters Optimized in This Work

	C−C (Å)	M−C (Å)	M−P (Å)	P−M−P (deg)	
$Pt(PH_3)_2(C_2H_4)$	1.439	2.137	2.412	103.5	this work
	1.427	2.152	2.317	107.2	ref 41
expt	1.434	2.112	2.268	111.67	ref 42
$Pt(PH_3)_2(C_{60})$	1.504	2.122	2.418	103.6	this work (B3LYP)
	1.495	2.082	2.466	101.1	ref 8 (HF)
	1.493	2.110	2.368	106.5	ref 11 (HF)
	1.505	2.103	2.289	107.4	ref 12 (LDA)
exp	1.502	2.130	2.278	102.4	ref 3
$Pd(PH_3)_2(C_{60})$	1.468	2.174	2.466	107.2	this work (B3LYP)
	1.464	2.180	2.378	111.0	ref 8 (LDA)
expt	1.447	2.104	2.322	109.7	ref 4
$Pt(PH_3)_2(C_{20}H_{10})$	1.496	2.152	2.415	104.2	this work (B3LYP)
$Pt(PH_3)_2(C_{21}H_{12})$	1.465	2.167	2.413	105.6	this work (B3LYP)

CHART 1



coordination with $Pt(PH_3)_2$ occurs at four sites, B1, B2, B4, and B5 but does not at the B3 site. In the most stable structure, $Pt(PH_3)_2$ interacts with $C_{21}H_{12}$ at the B1 site, as shown in Figure 2 (See Supporting Information Figure S3 for the other structures). The Pt−C distance increases in the order $Pt(PH_3)_2(C_{60})$ < $Pt(PH_3)_2(C_{20}H_{10})$ < $Pt(PH_3)_2(C_{21}H_{12})$, suggesting that the coordinate bonds of corannulene and sumanene are weaker than that of C_{60}, which will be discussed below in detail.

Binding Energies and Coordinate Bond Nature of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$. First, we calculated the binding energy of $Pt(PH_3)_2(C_2H_4)$ with the DFT-optimized geometry, to ascertain that the binding energy is reliably evaluated by the MP4(SDQ)/BS-5 and CCSD(T)/BS-5 methods with the DFT optimized geometry. This is because we are afraid that the overestimated M−P bond distance gives rise to some deviation of the binding energy; remember that the DFT(B3LYP)/BS-1 method overestimates the M−P distance (Table 2).

In $Pt(PH_3)_2(C_2H_4)$, the optimized bond distances and bond angles of the $Pt(C_2H_4)$ moiety agree well with the corresponding experimental values of $Pt(PPh_3)_2(C_2H_4)$,[42] whereas the Pt−P distance is somewhat overestimated like those of $Pt(PH_3)_2(C_{60})$ and the Pd analogue.[40] Despite the longer Pt−P distance here, the CCSD(T)-calculated binding energy (24.3 kcal/mol) is similar to the binding energy (23.7 kcal/mol) previously calculated for the better optimized geometry where the CCSD(T) method was employed with basis sets similar to those used in this work;[41,43] the optimized Pt−P distance was 2.317 Å[41] (see Supporting Information Table S1). From these results, it is likely that the DFT/BS-1 optimized geometry is useful to evaluate the binding energy even though the M−P distance is somewhat overestimated. It is also noted in Table 3 that the binding energy considerably fluctuates around the MP2 and MP3 levels but much less upon going to CCSD(T) from MP3. Although the binding energy does not completely converge at the MP4(SDQ) level, the MP4(SDQ)/BS-5 method presents a binding energy similar to that of the CCSD(T)/BS-5 method.[44] Thus, the MP4(SDQ)/BS-5 method is useful to evaluate the binding energy from a practical point of view.

The binding energies of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$ were evaluated with the DFT and MP2 to MP4(SDQ) methods, as shown in Table 3. Obviously, the DFT method extremely underestimates the binding energies of both $Pt(PH_3)_2$ complexes of corannulene and sumanene; also, the DFT-calculated binding energy of $Pt(PH_3)_2(C_{20}H_{10})$ with the A1 coordination site little changes by improving basis sets (see Table 3A). The binding energy by Mϕller−Plesset perturbation theory considerably fluctuates around MP2 and MP3 but much less upon going from MP3 to MP4(SDQ). Although we could not apply the CCSD(T) method to $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$ because of their large sizes, these results of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$ are similar to those of $Pt(PH_3)_2(C_2H_4)$, suggesting that the MP4(SDQ) method is useful to evaluate the binding energy and the DFT method tends to underestimate the binding energy of the Pt(0) complexes with these large π-conjugate systems. Here, we wish to discuss the relative stabilities on the basis of the MP4(SDQ)-calculated binding energy.

In $Pt(PH_3)_2(C_{20}H_{10})$, the A4 coordination structure is the most stable and its binding energy is 24.9 kcal/mol. The next is the A1 coordination structure, of which binding energy (22.3 kcal/mol) is moderately smaller than that of the A1 coordination structure. In $Pt(PH_3)_2(C_{21}H_{12})$, the B1 coordination structure is the most stable, of which the binding energy is 26.1 kcal/mol. The binding energies of the B2 and B4 coordination structures are somewhat smaller than that of the B1 coordination structure, and the B3 coordination structure is much less stable than the most stable B1 coordination structure. It is noted that the binding energies of these complexes are similar to that of $Pt(PH_3)_2(C_2H_4)$. From these results, we wish to predict that the platinum(0) complexes of corannulene and sumanene can be synthesized as stable species such as the platinum(0) ethylene complex.

It is of considerable interest to clarify the reason that A4 and B1 are the most stable coordination site in corannulene and sumanene, respectively. As shown in Table 4, Mulliken charges of corannulene and sumanene are negative in their Pt complexes. Moreover, their Mulliken charges become more negative with an increase in the binding energy. These results clearly indicate that the π-back-donation plays important roles in the coordinate bond and that the charge transfer from $Pt(PH_3)_2$ to corannulene and sumanene occurs the greatest in the most stable isomer. Because these population changes clearly show that the $d_\pi-\pi^*$ back-donation interaction contributes to the complexation with the Pt center, we examined the LUMO of corannulene and sumanene. The LUMO is degenerate, as shown in Figure 3. It is noted that one of the LUMO ($\phi_\pi{}^*{}_1$) of corannulene overlaps well with the HOMO of $Pt(PH_3)_2$ at the A1 and A4 sites, but it

TABLE 3: Binding Energies[a] (kcal/mol) of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$

coordination site	DFT	MP2	MP3	MP4(DQ)	MP4(SDQ)		
			(A) $Pt(PH_3)_2(C_{20}H_{10})$				
A1	−4.9 (−4.7)[b]	33.5	8.2	19.0	22.3		
A4	5.8	36.6	16.0	22.9	24.9		
			(B) $Pt(PH_3)_2(C_{21}H_{12})$				
B1	−2.6	36.5	12.0	23.0	26.1		
B2	−5.1	33.7	8.0	18.6	23.2		
B3	−5.0	24.9	3.8	10.7	13.3		
B4	−0.2	31.7	10.5	17.9	20.6		
			(C) $Pt(PH_3)_2(C_2H_4)$				
MP2	MP3	MP4(DQ)	MP4(SDQ)	MP4(SDTQ)	CCSD	CCSD(T)	
33.5	19.7	23.2	24.2	29.8	21.4	24.3	
						23.7[c]	ref 41

[a] The BS-5 system was used. [b] Pt; (3311/3111/111/1)[41] with the same effective core potentials as LANL2DZ. Ligand atoms; 6-311G(d,p). [c] See also ref 43.

TABLE 4: Mulliken Charge and d Orbital Population of Pt in $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$

		Pt d	$C_{20}H_{10}$ or $C_{21}H_{12}$
corannulene	A1	9.165	−0.150
	A4	9.166	−0.140
sumanene	B1	9.144	−0.176
	B2	9.162	−0.137
	B4	9.161	−0.085
	B5	9.158	−0.103

TABLE 5: Comparison of Binding Energy of $Pt(PH_3)_2(C_{60})$ between ONIOM and Full Calculations (kcal/mol)

(A) Basis Set Effects on the Binding Energy

	BS-1	BS-2	BS-3	BS-4	BS-5
B3LYP	17.1	18.8	14.2	14.8	14.9
MP2	51.2	54.7	50.0	55.2	55.0

(B) Effects of the Separation of High Level and Low Level Regions in the ONIOM(DFT or MP2:UFF) Calculation

highe level	cut 1	cut 2	cut 3	cut 4	full
DFT/BS-5	9.39	16.87	14.10	18.15	14.9
MP2/BS-5	43.54	53.22	50.24	57.76	55.0

does not overlap well with the HOMO of $Pt(PH_3)_2$ at the A2 and A3 sites because of the difference in the phase. The other LUMO ($\phi_\pi{}^*{}_2$) does not overlap well with the HOMO of Pt-$(PH_3)_2$ at the A2 and A3 sites because of the difference in the phase, too. Thus, the Pt(0) complex cannot coordinate with corannulene at the A2 and A3 sites. The largest stability of the Pt(0) complex at the A4 site is easily interpreted in terms that $\phi_\pi{}^*{}_1$ possesses the larger p orbital at the A4 site than that at the A1 site. The LUMO of sumanene is also degenerate, as shown in Figure 3. In sumanene, the B1 site is the best because one of the LUMO ($\psi_\pi{}^*{}_1$) overlaps well with the HOMO of Pt-$(PH_3)_2$ and the p orbital of C is the largest at this site. The worst is the B3 site, because the phase of $\psi_\pi{}^*{}_1$ does not fit at all with the HOMO of $Pt(PH_3)_2$ and the p orbitals of C in the other $\psi_\pi{}^*{}_2$ are small at this B3 site. The remaining B2, B4, and B5 sites are better than the B3 site for the coordination but worse than the B1 site. It is concluded that the good coordination sites of corannulene and sumanene are determined by their LUMO like that of C_{60}, as discussed previously.[13]

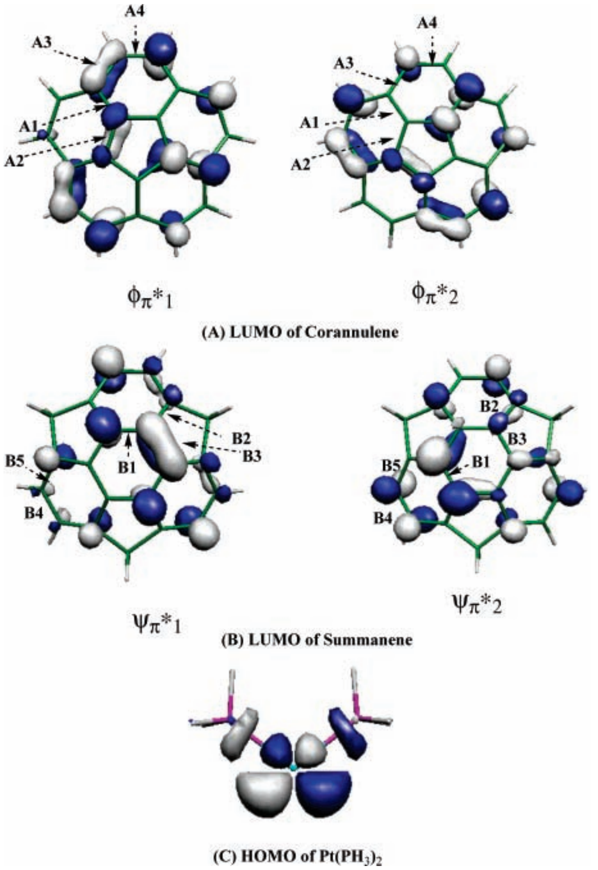


Figure 3. LUMO of corannulene and sumanene and HOMO of Pt-$(PH_3)_2$.

Binding Energy of $M(PH_3)_2(C_{60})$ (M = Pd or Pt). In Pt-$(PH_3)_2(C_{60})$, we carried out the DFT and MP2 calculations of $Pt(PH_3)_2(C_{60})$ using BS-1 to BS-5, as preliminary estimation of the binding energy. As shown in Table 5A, the binding energy converges upon going to BS-5 from BS-1 in both DFT and MP2 calculations. It should be noted that the DFT-calculated binding energy is much smaller than the MP2-calcualted one like those of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$. From this result as well as the results of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$ discussed above, it is concluded that not the DFT method but the MP4(SDQ) method should be applied to $Pt(PH_3)_2(C_{60})$ with the BS-5 basis set system. However, the MP4(SDQ)/BS-5 calculation could not be carried out with our computer system because of the very large size of the molecule.

Thus, we employed the ONIOM method to evaluate the binding energy, in which we examined several separations between high level (MP4(SDQ)) and low level (MM(UFF) or DFT) regions, as shown in Chart 2. Cut 1 contains the smallest high level region and cut 4 contains the largest high level region. First, we examined which separation presents the binding energy similar to that of full (noncut) calculation, where the DFT/BS-5 and MP2/BS-5 methods were employed because these methods

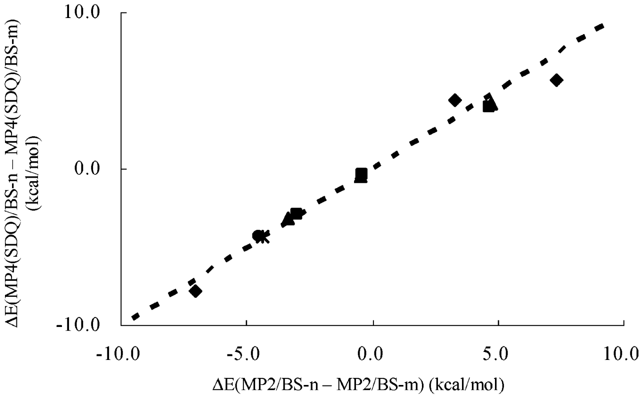


Figure 4. The binding energy changes ΔE by improving the basis set from BS-n to BS-m at the MP2 and MP4(SDQ) levels. The dotted line shows that the ΔE(MP2/BS-n − MP2/BS-m) is the same as ΔE(MP4(SDQ)/BS-n -MP4(SDQ)/BS-m).

CHART 2

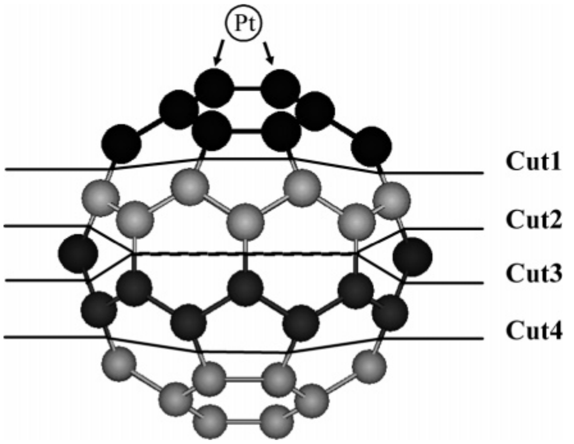


TABLE 6: Binding Energies[a] (kcal/mol) of M(PH$_3$)$_2$(C$_{60}$) (M = Pt or Pd)

	method	BE
Pt(PH$_3$)$_2$(C$_{60}$)	ONIOM(cut 2: MP4(SDQ)/BS-3→BS-5:UFF)[a]	47.5 (36.5)[b]
	ONIOM(cut 2: MP4(SDQ)/BS-3→BS-5:B3LYP)	45.5 (34.5)
	DFT(B3LYP)/BS-5	14.9 (12.6)[c]
	DFT(BPW91)/BS-5	19.7
	DFT(BVP86)/BS-5	20.1
Pd(PH$_3$)$_2$(C$_{60}$)	ONIOM(cut 2: MP4(SDQ)/BS-3→BS-5:UFF)	38.7
	DFT(B3LYP)/BS-5	14.8
Pt(PH$_3$)$_2$(C$_{60}$)	DFT(BP86)[14]	33.0 (25.8)[c]
Pd(PH$_3$)$_2$(C$_{60}$)	DFT(BP86)[14]	23.2 (15.1)[c]

[a] The "BS-3→BS-5" represents that the basis set effects by improving BS-3 to BS-5 are incorporated (see text). [b] The BSSE correction was made with factor 0.5. [c] The BSSE correction was made without any factor.

could be applied to Pt(PH$_3$)$_2$(C$_{60}$). As shown in Table 5B, only cut 1 presents very different binding energy from that of the full calculation. On the other hand, cut 4 presents a slightly larger binding energy than the full calculation, whereas cut 2 presents slightly smaller binding energy. Although cut 3 contains a larger high level region than cut 2, cut 3 presents considerably smaller binding energy than the full calculation, surprisingly. The reason will be discussed below. These results clearly indicate that both cut 2 and cut 4 are good separations to estimate the binding energy.

Even in cut 2, we could not apply the ONIOM(MP4(SDQ)/BS-5:UFF) method to Pt(PH$_3$)$_2$(C$_{60}$). Also, cut 4 is too large to perform the ONIOM(MP4(SDQ)/BS-3:UFF) calculation. Thus, we carried out the ONIOM(MP4(SDQ)/BS-3:UFF) calculation with cut 2. Because the BS-3 system is not considered sufficiently good, as shown in Table 5A, the effects of the basis set improvement from BS-3 to BS-5 should be taken into consideration. We evaluated the binding energies of Pt(PH$_3$)$_2$(C$_{20}$H$_{10}$), Pt(PH$_3$)$_2$(C$_{21}$H$_{12}$), and Pt(PH$_3$)$_2$(C$_{60}$) with cut 1, cut 2, and cut 3, to examine if the basis set effects at the MP2 level are similar to those of the MP4(SDQ) level. The changes in binding energy by the basis set improvement at the MP4(SDQ) level are almost parallel to the changes at the MP2 level, as shown in Figure 4. This result strongly supports the idea that the binding energy at the MP4(SDQ)/BS-5 level can be estimated from the binding energy at the MP4(SDQ)/BS-3 level by incorporating the basis set effects at the MP2 level, as follows: BE(MP4(SDQ)/BS-5) = BE(MP4(SDQ)/BS-3) + [BE(MP2/BS-5) − BE(MP2/BS-3)]. This idea is essentially the same as those of G2 and G3 methods.[45] Thus, we performed the estimation in two steps; in the first step, we estimated the binding energy at the MP4(SDQ)/BS-3 level with cut 2, and in the second step, we estimated the basis set effects by improving basis sets from BS-3 to BS-5 at the MP2 level.

The estimated binding energy at the MP4(SDQ)/BS-5 level is 47.5 kcal/mol.[46] We also applied the ONIOM(MP4(SDQ)/BS-3:B3LYP/BS-3) method to this complex. The similar binding energy of 45.5 kcal/mol is presented after correction for basis set effects. The binding energy of the Pd analogue is also evaluated to be 39.9 kcal/mol with the ONIOM(MP4(SDQ)/BS-3:UFF) method. This value is smaller than the binding energy of the Pt analogue, as expected.

Several kinds of binding energy of Pt(PH$_3$)$_2$(C$_{60}$) are summarized in Table 6, in comparison with the previously calculated binding energies. Obviously, the binding energy of Pt(PH$_3$)$_2$(C$_{60}$) estimated here is much larger than those calculated with the DFT method. The B3LYP functional extremely underestimates the binding energy. Although the BPW91 and BVP86 functionals provide somewhat larger binding energies than the B3LYP functional, their binding energies are still considerably smaller than those evaluated by the ONIOM(MP4(SDQ):UFF) and ONIOM(MP4(SDQ):B3LYP) methods. It is also noted that the binding energy of Pt(PH$_3$)$_2$(C$_{60}$) is much larger than that of Pt(PH$_3$)$_2$(C$_2$H$_4$); actually, the difference in the binding energy between Pt(PH$_3$)$_2$(C$_2$H$_4$) and Pt(PH$_3$)$_2$(C$_{60}$) is evaluated to be over 20 kcal/mol in this work, being much larger than that (about 10 kcal/mol) by the recent DFT(BP86) calculation,[14] whereas the present DFT(B3LYP) calculations present similar binding energies in Pt(PH$_3$)$_2$(C$_{60}$) and the Pd analogue. In the previous HF calculation,[10] the energy difference was evaluated to be 15 kcal/mol, which is not different very much from that of the present ONIOM calculation. The ONIOM-calculated binding energy of the Pd analogue is also larger than the DFT-calculated value in this work, whereas the difference in binding energy between Pt and Pd complexes here is similar to that of the DFT(BP86)-calculated ones.[14]

This larger binding energy of Pt(PH$_3$)$_2$(C$_{60}$) than that of Pt(PH$_3$)$_2$(C$_2$H$_4$) is not surprising, as follows: The π-back-donation plays important roles in these complexes, as was discussed previously.[10−14] The LUMO of C$_{60}$ is at much lower energy than those of ethylene, corannulene, and sumanene, and the HOMO is at much higher energy than those of ethylene, corannulene, and sumanene; the π and π* orbitals are at −10.1 and +4.87 eV, respectively, in ethylene, −7.90 and +1.72 eV, respectively, in corannulene, −7.24 and +2.74 eV, respectively,

TABLE 7: Mulliken Charges of $Pt(PH_3)_2(C_{60})$

	cut 1	cut 2	cut 3	cut 4	full	$Pt(PH_3)_2$
			(A) ONIOM(DFT(B3LYP)/BS-5:UFF)			
Pt	−0.226	−0.213	−0.210	−0.207	−0.208	−0.378
d[a]	9.191	9.206	9.204	9.204	9.206	9.157
PH3	0.206	0.238	0.226	0.248	0.251	0.189
C60	−0.185	−0.263	−0.262	-0.286	−0.293	
C_{Coord}	−0.138	−0.146	−0.148	−0.153	−0.153	
			(B) ONIOM(MP2/BS-3:UFF)			
Pt	−0.311	−0.300	−0.298	-0.294	−0.297	−0.543
d[a]	9.130	9.155	9.151	9.151	9.154	9.074
PH_3	0.248	0.281	0.279	0.292	0.298	0.272
C_{60}		−0.185	−0.261	−0.259	−0.290	−0.298
C_{Coord}		−0.175	−0.170	−0.170	−0.176	−0.175

[a] Mulliken orbital population.

in sumanene, and −7.60 and −0.42 eV, respectively, in C_{60}, where these are orbital energies calculated with the HF/BS-5 method (see ref 47 for the Kohn−Sham orbital). Thus, it is concluded that C_{60} can form a much stronger π-back-donation interaction with the transition-metal complex than the others.

At the end of this section, we wish to mention the basis set super position error (BSSE) in binding energy. Although the BSSE value is overestimated by Boy's method, as is well-known, we examined the BSSE correction of $Pt(PH_3)_2(C_2H_4)$ with Boy's method and found that the binding energy without BSSE correction little changes but the binding energy with BSSE correction somewhat decreases by improving the basis sets even when such good basis sets as triple-ζ + two polarization functions were used; see Supporting Information Table S3. This seems strange because the binding energy with BSSE correction is considered to change much less by improving the basis sets than that without BSSE correction; in other words, it is likely that the BSSE value is overestimated in this case (Supporting Information Table S3). To avoid the overcorrection of BSSE, we factored the BSSE value so that the binding energy with BSSE correction has fewer changes than that without BSSE correction when the good basis sets are further improved. When we employed a factor of 0.4−0.5, the binding energy with BSSE correction changes little by improving the basis sets (Supporting Information Table S3). The thus-corrected binding energy of $Pt(PH_3)_2(C_{60})$ is about 35−37 kcal/mol, as shown in Table 3.[48] This value is considerably larger than the B3LYP- and BP86-calculated binding energies with BSSE correction (12.6 and 25.8 kcal/mol,[14] respectively). Thus, inclusion of BSSE correction does not change the conclusion that the binding energy calculated by the MP4(SDQ) method is considerably larger than that by the DFT method.

Comparison of Electron Populations Between Full and ONIOM Calculations of $Pt(PH_3)_2(C_{60})$. Mulliken population changes by coordination of C_{60} are shown in Table 7. In the full calculation, the electron population of C_{60} increases and the C_{coord} atoms are negatively charged, where C_{coord} represents the C atom that coordinates with the Pt center. Consistent with these populations, the Pt atomic population and the d orbital population of Pt considerably decrease by the coordination with C_{60}. These population changes clearly show that the π-back-donation plays important roles in $Pt(PH_3)_2(C_{60})$, as discussed above and previously.[10−14] We stopped further discussion about the bonding nature of this complex, because detailed discussion has been presented previously.[10−14]

Here, we mentioned how much correctly the ONIOM calculation presents electron population. Fortunately, the cut 4 calculation presents almost the same population changes as those of full calculation in both the DFT and MP2 levels. Although the cut 3 calculation gives considerably different binding energy from the full calculation, the population changes by the cut 3 calculation are similar to those of the full calculation. The cut 2 calculation yields population changes similar to those of the full calculation, too. On the other hand, the cut 1 calculation presents somewhat different population changes, as expected, because of the very small high level region. From these results, the population changes are much less sensitive to the separation between high level and low level regions than the binding energy and the cut 2 to cut 4 calculations present reliable electron distribution.

It is interesting to compare electron populations between the DFT and MP2 calculations. In both calculations, the C_{60} moiety has −0.29*e* to −0.30*e* Mulliken charges. This result indicates that the π-back-donation from $Pt(PH_3)_2$ to C_{60} is evaluated to occur to a similar extent by both DFT and MP2 methods; in other words, the other factor is responsible for the underestimation of the binding energy by the DFT method. Although the strength of π-back-donation interaction is similarly evaluated by both DFT and MP2 methods, the C_{coord} atom is calculated to be less negatively charged by the DFT method than by the MP2 method. Also, the Pt atomic population and its d orbital population decrease in the MP2 calculation to a greater extent than in the DFT calculation, as shown in Table 7. These are probably because the DFT method tends to overestimate electron delocalization in C_{60} and $Pt(PH_3)_2$ moieties, compared to the MP2 method. As a result, the strength of the electrostatic interaction between these moieties is evaluated to be different between the DFT and MP2 methods. The $Pt(PH_3)_2$ moiety in $Pt(PH_3)_2(C_{60})$ is positively charged, because the π-back-donation interaction is formed between $Pt(PH_3)_2$ and C_{60}. This means that the $Pt(PH_3)_2$ moiety in $Pt(PH_3)_2(C_{60})$ exhibits the positive electrostatic potential, which stabilizes the negatively charged species; actually, the electrostatic potential at the C_{coord} atom is evaluated to be +0.193 with the MP2 method and +0.184 with the DFT method when $Pt(PH_3)_2$ possesses +1 charge.[49] The electrostatic stabilization energy between $Pt(PH_3)_2$ and one C_{coord} atom is evaluated to be 17.7 kcal/mol when the DFT-charge and DFT-potential are employed, and to be 21.2 kcal/mol when the MP2-charge and MP2-potential are employed. The difference is about 3.5 kcal/mol. Considering that two C_{coord} atoms interact with $Pt(PH_3)_2$, the difference amounts to 7 kcal/mol. This difference is overestimated, because the positive charge of the $Pt(PH_3)_2$ moiety is evaluated to be about +0.4*e* in $Pt(PH_3)_2(C_{60})$, being much smaller than +1.0*e*. Considering that the $Pt(PH_3)_2$ moiety has +0.4*e* charge, this difference is reduced to about 3 kcal/mol (=7.0 × 0.4), which is much smaller than the DFT- and MP2-calculated binding energies. Thus, the other factor should participate in the underestimation by the DFT method. One of such factors is the electrostatic stabilization energy between the electrostatic potential of C_{60} and the positively charged $Pt(PH_3)_2$ moiety. However, it is very difficult to estimate the electrostatic potential of the C_{60} moiety in $Pt(PH_3)_2(C_{60})$. The other factor is the electrostatic interaction between the dipole moment of the C_{60} and $Pt(PH_3)_2$ moieties; the MP2 calculation presents a larger dipole moment of the C_{60} moiety than does the DFT calculation, which induces larger stabilization energy between the dipole moment and the positively charged Pt atom. Unfortunately, the dipole moment of the C_{60} moiety in $Pt(PH_3)_2(C_{60})$ is not easily estimated. Also, the dispersion interaction is one of the reasons of the underestimation by the DFT method. In the case of benzene dimer, the difference in binding energy between CCSD(T) and DFT-(B3LYP) methods amounts to about 3 kcal/mol, which is

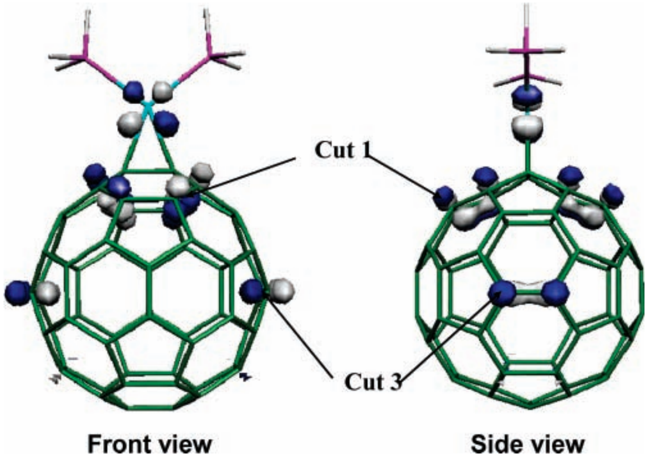


Figure 5. HOMO of Pt(PH$_3$)$_2$(C$_{60}$).

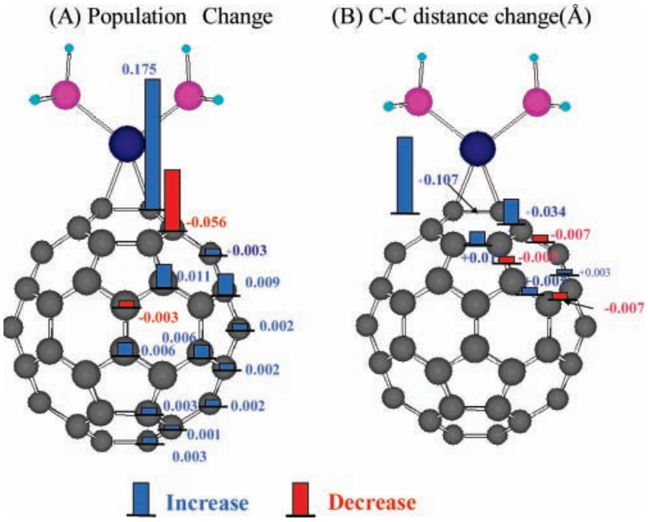


Figure 6. Changes in C atomic population (a) and C−C distance (b) by complexation of C$_{60}$ with Pt(PH$_3$)$_2$: (a) MP2-calculated Mulliken population; (b) DFT-optimzied value. Bond distance in angstroms and atomic population in atomic units.

considered to be mainly due to the dispersion interaction.[50] In Pt(PH$_3$)$_2$(C$_{60}$), the interfragment distance beween Pt(PH$_3$)$_2$ and C$_{60}$ is shorter than that of benzene dimer. This suggests that the dispersion interaction more contributes to the binding energy of Pt(PH$_3$)$_2$(C$_{60}$) than that of benzene dimer. All these factors are responsible to the underestimation of the binding energy by the DFT method. However, the above discussion is not quantitative. We did not reach the final conclusion, and we need further analysis to clarify the reason.

How to Separate High Level and Low Level Regions in ONIOM Calculation. Interestingly, cut 3 is worse than cut 2 despite cut 3 containing the larger high level region as compared with cut 2. Of course, cut 4, which contains the largest high level region, here is better than cut 2 and cut 3. It is of considerable importance to clarify the reason cut 3 is worse than cut 2. Such a reason would provide us some idea how to select the high level region in the ONIOM calculation. We can easily find the reason by considering the orbital plot of the HOMO of the complex. The HOMO mainly consists of the d$_\pi$ orbital of Pt and the π* orbital of C$_{60}$, as shown in Figure 5. It is noted that the C atoms that considerably contribute to this HOMO are on the borders between the high level and low level regions in cut 1 and cut 3. This situation is not good, obviously. On the other hand, these C atoms are not on the border in cut 2 and cut 4. Thus, cut 2 is better than cut 3 despite its high level region being smaller than that of cut 3.

Coordination of C$_{60}$ with Pt(PH$_3$)$_2$ induces changes of the C−C bond distance and the C atomic populations, as shown in Figure 6. Ten C−C bond distances and ten C atomic populations around the C$_{\text{coord}}$ atoms considerably change by the coordination with Pt(PH$_3$)$_2$, whereas little change is observed in the other C−C bonds and the other C atomic populations. These results suggest that the coordination with Pt(PH$_3$)$_2$ considerably influences these C atoms and C−C bonds. Thus, the high level region should contain these C atoms and C−C bonds, at least. Certainly, the high level region of cut 2 contains these important C atoms and C−C bonds. This is the other reason that cut 2 presents reliable results.

Conclusions

The MP2 to MP4(SDQ) methods and the DFT method with B3LYP, BPW91, and BVP86 functionals were applied to M(PH$_3$)$_2$(C$_{60}$) (M = Pd or Pt), Pt(PH$_3$)$_2$(C$_{20}$H$_{10}$), and Pt(PH$_3$)$_2$(C$_{21}$H$_{12}$), to estimate their binding energies. The DFT method with these functionals presents much smaller binding energies than the MP2 to MP4(SDQ) methods. For instance, the binding energy of Pt(PH$_3$)$_2$(C$_{20}$H$_{10}$) was evaluated to be 24.9 kcal/mol by the MP4(SDQ) method but only 5.8 kcal/mol by the DFT(B3LYP) method. Also, the binding energy of Pt(PH$_3$)$_2$(C$_{21}$H$_{12}$) was evaluated to be 26.1 kcal/mol by the MP4(SDQ) method but −2.6 kcal/mol by the DFT(B3LYP) method.

The binding energies of Pt(PH$_3$)$_2$(C$_2$H$_4$), Pt(PH$_3$)$_2$(C$_{20}$H$_{10}$), and Pt(PH$_3$)$_2$(C$_{21}$H$_{12}$) considerably fluctuate around the MP2 and MP3 levels but much less upon going to MP4(SDQ) from MP3, and the MP4(SDQ) method presents a binding energy similar to that of the CCSD(T) method in Pt(PH$_3$)$_2$(C$_2$H$_4$). From these results, it is likely that the MP4(SDQ) method is useful to evaluate binding energies of these complexes. It is noted that the MP4(SDQ)-calculated binding energies of Pt(PH$_3$)$_2$(C$_{20}$H$_{10}$) and Pt(PH$_3$)$_2$(C$_{21}$H$_{12}$) are similar to that of Pt(PH$_3$)$_2$(C$_2$H$_4$). These binding energies strongly suggest that the Pt(0) complexes of η^2-corannulene and η^2-sumanene can be synthesized, whereas the Pt(0) complexes of η^2-corannulene and η^2-sumanene have not been reported yet to our knowledge.

However, the MP4(SDQ)/BS-5 method could not be applied to M(PH$_3$)$_2$(C$_{60}$) due to the limit of our computation facility. We employed the ONIOM method, in which the high level region was calculated with the MP4(SDQ) method and the low level region was calculated with the MM(UFF) method. The evaluated binding energy of M(PH$_3$)$_2$(C$_{60}$) is 47.5 kcal/mol for M = Pt and 38.7 kcal/mol for M = Pd. Almost the same binding energy (45.5 kcal/mol) of Pt(PH$_3$)$_2$(C$_{60}$) is presented by the ONIOM calculation in which the DFT(B3LYP) method was employed for the low level region. These values are much larger than those of the ethylene, corannulene, and sumanene complexes with Pt(PH$_3$)$_2$. This is not surprising because C$_{60}$ possesses its π* orbital at much lower energy than those of ethylene, corannulene, and sumanene.

The DFT method presents delocalized electron distribution in the C$_{60}$ and Pt(PH$_3$)$_2$ moieties than does the MP2 method. The reason that the DFT method underestimates the binding energy was examined from the electrostatic interaction. However, the difference in electrostatic interaction between DFT and MP2 methods is smaller than the difference in the binding energy between these two methods. The reason is still ambiguous.

In the ONIOM calculation, the appropriate separation between the high level and low level regions should be employed to present reliable results. We examined several ways to separate two regions. The important result is that the C atom, whose p orbital considerably participates in the π-back-donation with the metal moiety, should not be on the border of two regions.

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Supporting Information Available: Complete form of ref 35. Table of basis set effects on the binding energy of $Pt(PH_3)_2(C_2H_4)$. Table of Cartesian coordinates of optimized structures. Figure of the optimized geometry of $Pt(PH_3)_2(C_{60})$ in which the C−C bond between C6 and C5 rings coordinates with the Pt center. Figures of optimized geometries of less stable structures of $Pt(PH_3)_2(C_{20}H_{10})$ and $Pt(PH_3)_2(C_{21}H_{12})$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) The binding energy considerably depends on the basis sets used. The best value reported in ref 41 is 22.9 kcal/mol, which was evaluated by the CCSD(T) method using very good basis sets, where the basis set effects were incorporated at the MP2 level. When the similar basis sets were used in ref 41 and this work, the similar binding energy was calculated; the binding energy of 23.7 kcal/mol was calculated with the CCSD(T) method, where (441/2111/21) set with effective core potentials[25] was used for Pt and 6-31G(d) sets was used for the other atoms.[41]

(44) The MP4(SDQ) method presents larger binding energy than the CCSD method. Also, incorporation of triple excitations increases the binding energy by 3−5 kcal/mol in both MP4 and CCSD methods (see Table 3). As a result, the MP4(SDQ) method presents the binding energy similar to that of the CCSD(T) method. Thus, the MP4(SDQ) method is useful to evaluate the binding energy from practical point of view.

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(46) In cut 3, almost the same binding energy is calculated to be 44.3 kcal/mol with the ONIOM(MP4(SDQ)/BS-5:UFF) method, whereas the binding energy is somewhat smaller than that of the cut 2 calculation when the MP2 method was employed. The reason is not clear, but some

cancellation occurs in the ONIOM and/or in the correction of basis set effects.

(47) The π and π* Kohn−Sham orbital energies are −7.23 and +0.48 eV, respectively, in ethylene, −5.94 and −1.58 eV, respectively, in corannulene, −5.48 and −0.74 eV, respectively, in sumanene, and −6.00 and −3.23 eV, respectively, in benzene, where the BS-5 basis set system was employed.

(48) The factor of 0.5 was applied to the BSSE value evaluated with Boy's method; see also Supporting Information Table S3.

(49) When $Pt(PH_3)_2$ is neutral, it exhibits very small electrostatic potentials that can be neglected. The geometry of $[Pt(PH_3)_2]^+$ was taken to be the same as that involved in $Pt(PH_3)_2(C_{60})$.

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