Binding Energy of Transition-Metal Complexes with Large π-Conjugate Systems. Density Functional Theory vs Post-Hartree−Fock Methods

Atsushi Ikeda,[†] Yoshihide Nakao,[†] Hirofumi Sato,[†] and Shigeyoshi Sakaki*,[†,‡]

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, and Fukui Institute for Fundamental Chemistry, Nishihiraki-chou, Takano, Sakyo-ku, Kyoto 606-8103, Japan

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We systematically evaluated the binding energies of d^{10}, d^8, and d^6 transition-metal complexes with various π-conjugate systems such as $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$, $Pd(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$, $[PtCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$, $[PdCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$, and $[PtCl_5\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$ ($n = 0-4$) using the MP2 to MP4, CCSD(T), and density functional theory (DFT) methods. The MP4(SDQ) and CCSD(T) methods present a reliable binding energy, whereas the DFT method significantly underestimates the binding energy when the size of the π-conjugate system is large. The underestimation occurs independently of the coordinate bonding nature; the π-back-donation is stronger than the σ-donation in the Pt(0) complexes, as expected, they are comparable in the Pt(II) complexes, and only the σ-donation participates in the coordinate bond of the Pt(IV) complexes. The DFT method provides moderately stronger charge-transfer (CT) interaction than the MP4(SDQ) method, suggesting that the underestimation of the binding energy by the DFT method does not arise from the insufficient description of the CT interaction. From theoretical investigation of several model systems, it is concluded that the underestimation arises from the insufficient description of electron correlation effects.

Introduction

Density functional theory (DFT) is believed to be very useful, in particular for large systems, nowadays. However, several weak points have been pointed out. One of them is insufficient description of van der Waals interaction.[1−5] For instance, the conventional DFT method fails to evaluate the dispersion interaction, which plays important roles in van der Waals complexes, crystal packing of organic molecules, and three-dimensional structures of biological systems.[6−8] Another weak point is the incorrect evaluation of polarizabilities and hyperpolarizabilities of large π-conjugate molecules. This weak point has been discussed in terms of the exchange-correlation functionals, which shows the hybrid functionals present better results than the pure functionals.[9]

Recently, we theoretically investigated Pt(0) complexes of corannulene ($C_{20}H_{10}$), sumanene ($C_{21}H_{12}$), and C_{60},[10] because these transition-metal complexes have drawn considerable attention in wide areas of chemistry.[11] In the study, we observed that the DFT method underestimated the binding energy between $Pt(PH_3)_2$ and the π-conjugate system in comparison with the MP2 to MP4(SDQ) methods. This is another serious problem in the DFT method because many transition-metal complexes have been theoretically investigated with the DFT method.

Because $Pt(PH_3)_2(C_{20}H_{10})$, $Pt(PH_3)_2(C_{21}H_{12})$, and $Pt(PH_3)_2(C_{60})$ are Pt(0) complexes in which the Pt center takes a d^{10} electron configuration, the π-back-donation interaction mainly participates in the coordinate bond.[12,13] In Pt(II) and Pt(IV) complexes, on the other hand, not only the π-back-donation but also the σ-donation participates in the coordinate bond because Pt(II) and Pt(IV) atoms possess one and two unoccupied d orbitals, respectively. Actually, it was theoretically shown that the π-back-donation interaction mainly participates in the coordinate bond of a Pt(0) complex, $Pt(PH_3)_2(C_2H_4)$, and both the σ-donation and the π-back-donation interactions participate in the coordinate bond of a Pt(II) complex, $[PtCl_3(C_2H_4)]^-$.[12−14] Thus, it is of considerable importance to clarify whether the DFT method underestimates the binding energy of the transition-metal complex when only the π-back-donation participates in the coordinate bond or when both the π-back-donation and the σ-donation participate in the coordinate bond.

In the present study, we systematically investigated d^{10}, d^8, and d^6 transition-metal complexes of π-conjugate systems using various computational methods such as DFT, MP2 to MP4(SDTQ), and CCSD(T). Our purposes here are to evaluate correctly their binding energies, to examine the reliability of the DFT method, and to clarify the reasons why the DFT method underestimates the binding energies of such d^{10}, d^8, and d^6 metal complexes as $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$, $Pd(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$, $[PtCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$, $[PdCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$, and $[PtCl_5\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$ ($n = 0-4$). These complexes were selected here as typical examples of d^{10}, d^8, and d^6 transition-metal complexes.

Computational Details

The geometry of $Pt(PH_3)_2(C_2H_4)$ was optimized by the MP2 and DFT methods, where B3LYP[15,16] and B3PW91[15,17] functionals were used in the DFT calculation. Because the MP2- and DFT(B3PW91)-optimized geometries agree better with the experimental geometry than the DFT(B3LYP)-optimized one, as will be described below, the geometries of the other complexes were optimized by the DFT(B3PW91) method. In the geometry optimization, split-valence-type basis sets, (541/

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* To whom correspondence should be addressed. E-mail: sakaki@moleng.kyoto-u.ac.jp.

[†] Kyoto University.

[‡] Fukui Institute for Fundamental Chemistry.

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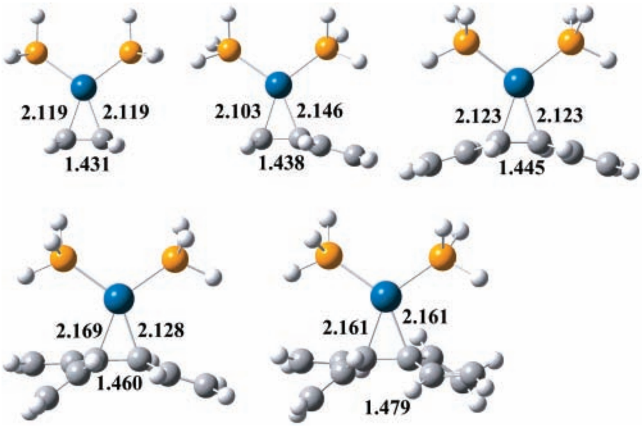


Figure 1. B3PW91-optimized structure of $Pt(PH_3)_2(C_2H_{4-n}(CH{=}CH_2)_n)$ (bond lengths in angstroms).

541/111/1) and (541/541/211/1), were used for the valence electrons of Pt and Pd,[18,19] respectively, and the effective core potentials (ECPs) of Hay and Wadt[18] were employed to replace their core electrons, where one f polarization function was added to each basis set.[20] For the other atoms, the 6-31G(d) basis sets were used.[21] This basis set system is named BS1.

The binding energies of these complexes were evaluated with the MP2 to MP4, CCSD(T),[22] and DFT methods using better basis set systems, BS2 and BS3. In the DFT calculation, various functionals such as SVWN,[23,24] BLYP,[15,16] BP86,[24,26] B3LYP,[15,16] B3PW91,[15,17] BHandHLYP,[16,23,24] MPW1PW91,[17,28] and PBE1PBE[29] were employed to investigate what functional presents good results. In BS2, the 6-311G(d) basis sets[30] were used for H, C, P, and Cl. For Pd and Pt, the core electrons were replaced with Stuttgard−Dresden−Bonn ECPs, and their valence electrons were represented by the (311111/22111/411/11) basis set.[31,32] We did not add the g polarization function here, because the MP4(SDQ)-calculated binding energy of $Pt(PH_3)_2(C_2H_4)$ changes little by addition of the g function.[33] In BS3, the core electrons of Pt were replaced with the ECPs of Hay and Wadt,[18] and the (33111/31111/ 1111/111/11) basis set was used for its valence electrons.[34] For the C, P, and H atoms, the (63111/3111/11/1), (6311111/421111/111/11), and (3111/11) basis sets were employed,[35] respectively. These basis sets were used in the G3MP2 calculation previously.[34]

The Gaussian 03 program package was used for all calculations.[36] Population analysis was carried out with the method of Weinhold et al.[37] Orbital pictures were drawn with the MOLEKEL program package.[38]

Results and Discussion

Binding Energies of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ ($n = 0-4$). Because the DFT method underestimated the binding energies of the Pt(0) complexes of the large π-conjugate systems in our previous work,[10] we evaluated the binding energy of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ in which vinyl groups were introduced into the C=C double bond one after another, as shown in Figure 1. Our purpose here is to investigate whether the underestimation of the binding energy depends on the size of the π-conjugate system. Their geometries were optimized with the DFT(B3PW91) method, because the DFT(B3PW91)-optimized geometry of $Pt(PH_3)_2(C_2H_4)$ agrees well with the experimental geometry of $Pt(PPh_3)_2(C_2H_4)$[39] and the MP2-optimized geometry of $Pt(PH_3)_2(C_2H_4)$, as compared in Table 1; note that the DFT(B3LYP) method presents considerably longer Pt−C and Pt−P bonds than their experimental values. Interestingly, the Pt−C bond and the C=C bond coordinating with Pt become longer as the number of vinyl groups increases.

TABLE 1: Selected Bond Lengths (Å) of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ ($n = 0, 2$) Optimized by the MP2 and DFT Methods

	$Pt(PH_3)_2(C_2H_4)$			$Pt(PH_3)_2(C_6H_8)$	
	Pt−P	Pt−C	C=C	Pt−C	C=C
B3LYP	2.306	2.140	1.431	2.163	1.442
B3PW91	2.280	2.119	1.431	2.123	1.445
MP2	2.245	2.120	1.431	2.121	1.439
expt[a]	2.268	2.112	1.434		

[a] Reference 39.

As shown in Table 2, the binding energy considerably fluctuates around the MP2 and MP3 levels but much less around the MP4(SDQ) and MP4(SDTQ) levels in all the complexes examined. The MP4(SDTQ) method tends to present a larger binding energy than the CCSD(T) method, and the inclusion of triple-excitation increases the binding energies in both the MP4 and CCSD calculations; see Table 2 for the MP4(SDQ)-, MP4(SDTQ)-, CCSD-, and CCSD(T)-calculated binding energies. As a result, the MP4(SDQ)-calculated binding energy is almost the same as the CCSD(T)-calculated value in these complexes. Thus, here we applied the MP4(SDQ) method to large systems which could not be calculated with the CCSD(T) method due to the large size.

Though the MP4(SDQ)-calculated binding energies change little as the size of the π-conjugate system increases, as shown in Table 2, the DFT-calculated binding energy considerably decreases;[40] for instance, the B3LYP-calculated binding energy is 14.4, 6.7, and −1.1 kcal/mol for $Pt(PH_3)_2(C_2H_4)$, $Pt(PH_3)_2\{C_2H_2(CH{=}CH_2)_2\}$, and $Pt(PH_3)_2\{C_2(CH{=}CH_2)_4\}$, respectively. It is noted that the DFT-calculated binding energy decreases in all the functionals used here. For convenience, we defined ΔBE(B3LYP) and ΔBE(B3PW91) as the difference between the MP4(SDQ)- and DFT(B3LYP)-calculated binding energies (eq 1) and that between the MP4(SDQ)- and DFT(B3PW91)-calculated binding energies (eq 2),

$$\Delta BE(\mathrm{B3LYP}) = \mathrm{MP4(SDQ)\ binding\ energy} - \mathrm{B3LYP\ binding\ energy} \quad (1)$$

$$\Delta BE(\mathrm{B3PW91}) = \mathrm{MP4(SDQ)\ binding\ energy} - \mathrm{B3PW91\ binding\ energy} \quad (2)$$

respectively. The ΔBE(B3LYP) and ΔBE(B3PW91) values increase as the size of the π-conjugate system increases; for instance, the ΔBE(B3LYP) and ΔBE(B3PW91) values become very large in $Pt(PH_3)_2\{C_2(CH{=}CH_2)_4\}$, that is, 22.2 and 13.3 kcal/mol, respectively.

It is noted that the binding energies calculated with the MP2-optimized geometries are almost the same as those calculated with the B3PW91-optimized geometry, suggesting that the MP4(SDQ)//DFT(B3PW91) calculation presents a reliable binding energy; see the values in parentheses of Table 2 for the binding energy calculated with the MP2-optimized geometry.

We investigated $Pd(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ too. In these complexes, the MP4(SDQ)-calculated binding energy changes little as the size of the π-conjugate system increases, but the DFT-calculated binding energy considerably decreases, similar to that of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$; see Figures S1 and S2 of the Supporting Information for the geometries and the binding energies of the Pd(0) complexes, respectively.

Basis Set Superposition Error (BSSE) Correction. It is necessary to examine how much BSSE influences the binding energy. Because $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ ($n = 2-4$) could

TABLE 2: Binding Energies (kcal/mol) of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ ($n = 0-4$)

(A) Binding Energies Evaluated by the Post-Hartree−Fock Method

n	MP2	MP3	MP4(DQ)	MP4(SDQ)	MP4(SDTQ)	CCSD	CCSD(T)
0	33.7 (32.7)[a]	16.7 (14.7)	22.3 (22.0)	22.2 (21.7)	28.0 (−)	19.1 (−)	22.2
1	34.0	15.8	22.3	22.5	29.7	19.6	22.6
2	34.0	13.9	21.5	22.1	30.1	18.5	21.9
3	35.2	12.5	21.6	22.6			
4	34.1	9.0	19.7	21.1			

(b) Binding Energies Evaluated by the DFT Method with Various Functionals

n	B3LYP	B3PW91	BLYP	SVWN	ΔBE(B3LYP)	ΔBE(B3PW91)
0	14.4 (13.9)[a]	21.5 (21.2)	12.1 (11.2)	40.8 (41.0)	7.9	0.8
1	11.3	18.4	8.3	38.2	11.3	3.9
2	6.7	13.8	3.2	34.1	15.4	7.7
3	4.0	11.3	0.4	32.7	18.7	10.4
4	−1.1	6.5	−4.8	30.0	22.2	13.3

n	BP86	BH and HLYP	MPW1PW91	PBE1PBE
0	21.8	14.5	23.5	25.3
2	13.4	7.6	16.2	18.2
4	6.3	−0.4	9.2	11.6

[a] In parentheses are given the binding energies calculated with the MP2-optimized geometry.

TABLE 3: BSSE-Corrected and BSSE-Non-Corrected Binding Energies (kcal/mol) of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ (n = 0 or 1) Calculated by the MP4(SDQ) and DFT(B3LYP) Methods with the BS2 and BS3 Basis Sets

	MP4(SDQ)		B3LYP	
	BSSE-non-corrected	BSSE-corrected	BSSE-non-corrected	BSSE-corrected
		$Pt(PH_3)_2(C_2H_4)$		
BS2	22.2	11.3	14.4	12.5
BS3	22.4	17.3	11.4	11.1
		$Pt(PH_3)_2(C_4H_8)$		
BS2	22.5	10.3	11.3	9.2
BS3	22.3	16.3	8.3	7.4

not be calculated with the CCSD(T)/BS3 and MP4(SDQ)/BS3 methods, due to the large size, we made a comparison between the MP4(SDQ)- and B3LYP-calculated binding energies of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ (n = 0 or 1), as shown in Table 3, where the counterpoise method was employed to evaluate BSSE.[41] In the MP4(SDQ)/BS2 calculation, the binding energies with BSSE correction are significantly smaller than the binding energies without BSSE correction. In the DFT-(B3LYP)/BS2 calculations, on the other hand, the binding energies with BSSE correction are little different from those without BSSE correction. As a result, the BSSE-corrected ΔBE value becomes very small; for instance, the BSSE-corrected ΔBE value is −1.2 kcal/mol for $Pt(PH_3)_2(C_2H_4)$. Seemingly, these results mean that the large binding energy by the MP4-(SDQ) method arises from the large BSSE and that the DFT method presents a reliable binding energy due to the small BSSE. However, we must remember that the counterpoise method overestimates the BSSE correction.

It is expected that if the BSSE is large, the binding energy without BSSE correction should decrease and the binding energy with BSSE correction should increase as the basis sets used become better. However, the MP4(SDQ)-calculated binding energy without BSSE correction changes little when BS3 is used instead of BS2, while the binding energy with BSSE correction considerably increases, as shown in Table 3; for instance, it increases to 17.3 from 11.3 kcal/mol in $Pt(PH_3)_2(C_2H_4)$ and to 16.3 from 10.3 kcal/mol in $Pt(PH_3)_2\{C_2H_3(CH{=}CH_2)\}$. These results are against the above-mentioned expectation. This discrepancy between the expectation and the computational results suggests that the BSSE is overcorrected by the counterpoise method and the binding energy calculated with the MP4(SDQ)/BS2 and MP4(SDQ)/BS3 methods are reliable. Similar results were reported recently; the BSSE evaluated with the counterpoise method is too large and should be decreased to 50%.[10] Because much better basis sets were used here than in the previous work,[10] the BSSE is much smaller here than in the previous work. From these results, it is likely that the BSSE is not significantly large.

Binding Energies of d^8 and d^6 Transition-Metal Complexes. We investigated here d^8 metal complexes, $[PtCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$ ($n = 0-4$). Because of the presence of one unoccupied d orbital, both the σ-donation and the π-back-donation interactions participate in the coordinate bond of these complexes, as will be discussed below. Thus, their coordinate bonds are different from those of the d^{10} metal complexes $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ in which the π-back-donation largely participates in the coordinate bond. From this investigation, we clarify whether the DFT method presents a reliable binding energy when both the σ-donation and the π-back-donation interactions participate in the coordinate bond.

Optimized structures of these complexes are shown in Figure 2. The Pt−C bond distance becomes longer as the size of the π-conjugate system increases. This bond lengthening is greater than in $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$. Also, it is noted that the C=C double bond is shorter in these complexes than in $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$. This is consistent with the fact that the π-back-donation is weaker in these complexes than in $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$, as will be discussed below in detail. The MP4(SDQ)-calculated binding energy decreases as the number of vinyl group increases by more than 2, as shown in Figure 3. On the other hand, the DFT-calculated binding energy decreases much more. Thus, it is concluded that the DFT method underestimates the binding energies of these d^8 metal complexes when the π-conjugate system is large; for instance, the ΔBE(B3LYP) value is 25.2 kcal/mol for $[PtCl_3\{C_2(CH{=}CH_2)_4\}]^-$, which is almost the same as that for $Pt(PH_3)_2\{C_2(CH{=}CH_2)_4\}$. Similar results are observed in the Pd analogues $[PdCl_3\{C_2(CH{=}CH_2)_4\}]^-$; see Supporting Information Figures S3 and S4 for their optimized geometries and binding energies, respectively.

In $[PtCl_5\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$ ($n = 0-4$), the Pt center takes the +4 oxidation state with the d^6 electron configuration.

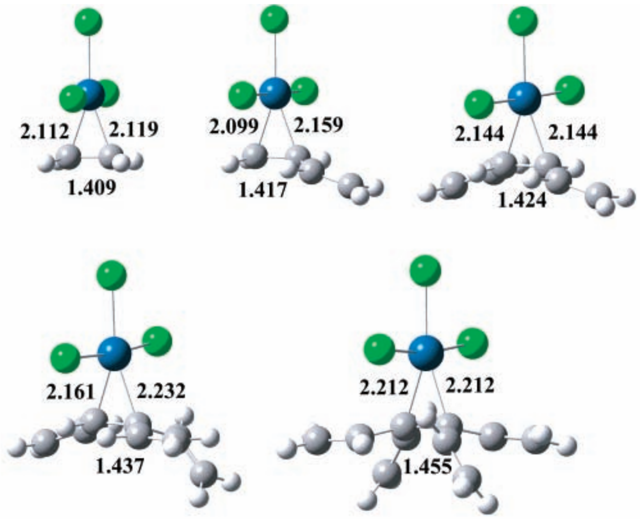


Figure 2. B3PW91-optimized structure of $[\mathrm{PtCl_3\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$ (bond lengths in angstroms).

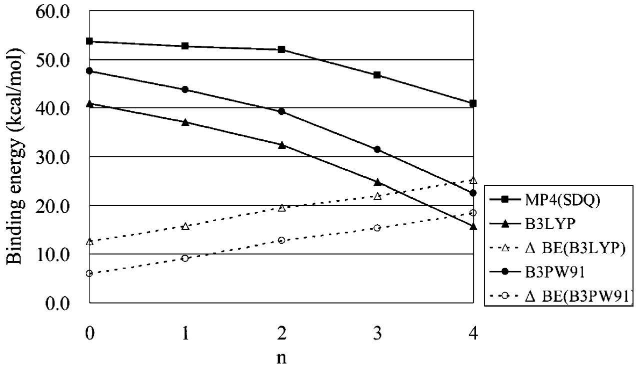


Figure 3. Binding energies of $[\mathrm{PtCl_3\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$.

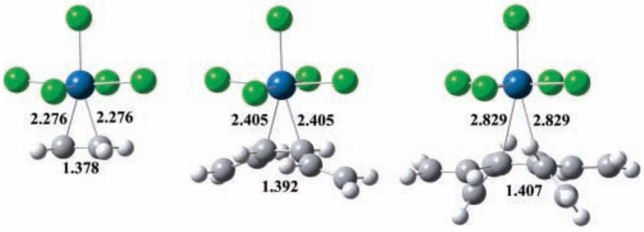


Figure 4. B3PW91-optimized structure of $[\mathrm{PtCl_5\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$ (bond lengths in angstroms).

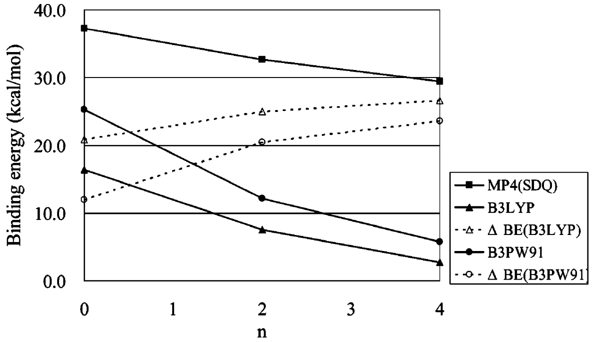


Figure 5. Binding energies of $[\mathrm{PtCl_5\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$.

This suggests that the σ-donation interaction becomes more important in these complexes than in the Pt(II) complexes, as will be discussed below. The Pt−C bond distance is considerably longer in these complexes than in $\mathrm{Pt(PH_3)_2\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}$ and $[\mathrm{PtCl_3\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$; for instance, it is 2.829 Å in $[\mathrm{PtCl_5\{C_2(CH{=}CH_2)_4\}}]^-$, as shown in Figure 4, indicating that the coordinate bond is weak. These results would arise from the weak π-back-donation and the large steric repulsion between the four Cl ligands and the π-conjugate system, as will be discussed below. In $[\mathrm{PtCl_5\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$, both the DFT- and MP4(SDQ)-calculated binding energies decrease as the size of the π-conjugate system increases. However, it is noted that the DFT-calculated binding energy decreases more than the MP4(SDQ)-calculated value; actually, the ΔBE(B3LYP) and ΔBE(B3PW91) values of $[\mathrm{PtCl_5\{C_2(CH{=}CH_2)_4\}}]^-$ are very large, 26.6 and 23.6 kcal/mol, respectively, as shown in Figure 5. Thus, it is concluded that the DFTmethod underestimates the binding energies of these d^6 metal complexes, too, when the π-conjugate system is large.

Coordinate Bonding Nature and Electron Distribution. Table 4 shows the natural atomic orbital (NAO) charge evaluated by the MP4(SDQ) and DFT(B3LYP) methods. The π-conjugate system is negatively charged, and its negative charge increases as the size of the π-conjugate system increases. These results clearly show that the π-back-donation interaction plays a more important role in $\mathrm{Pt(PH_3)_2\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}$ than the σ-donation interaction and becomes stronger with an increase of the size of the π-conjugate system. The DFT-calculated negative charge is slightly larger than the MP4(SDQ)-calculated value, indicating that the DFT method evaluates slightly stronger π-back-donation than the MP4(SDQ) method. It is noted that the difference in negative charge between the DFT and MP4(SDQ) calculations increases with an increase of the size of the π-conjugate system.

In the d^8 metal complex $[\mathrm{PtCl_3\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$, the π-conjugate systems are almost neutral, indicating that both the π-back-donation and the σ-donation interactions comparably participate in the coordinate bond of these complexes. In the d^6 metal complex $[\mathrm{PtCl_5\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$, the π-conjugate system is positively charged, indicating that the σ-donation participates more in the coordinate bond than the π-back-donation, as expected. In the d^8 and d^6 metal complexes, the DFT method tends to present a slightly less negative or a slightly more positive NAO charge of the π-conjugate system, respectively. This suggests that the σ-donation is calculated to be slightly stronger by the DFT method than by the MP4(SDQ) method.

To present more detailed information about the coordinate bonding nature, the molecular orbitals (MOs) of $\mathrm{Pt(PH_3)_2\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}$, $[\mathrm{PtCl_3\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$, and $[\mathrm{PtCl_5\{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}\}}]^-$ are represented by linear combination of the MOs of the fragments, as follows:[42]

$$\psi_i(\mathrm{A{-}B}) = \sum_k c_{i,k}\phi_k(\mathrm{A}) + \sum_j d_{i,j}\varphi_j(\mathrm{B}) \qquad (3)$$

where $\phi_k(\mathrm{A})$ is the kth MO of such a metal fragment A as $\mathrm{Pt(PH_3)_2}$, $[\mathrm{PtCl_3}]^-$, and $[\mathrm{PtCl_5}]^-$, $\varphi_j(\mathrm{B})$ is the jth MO of such a π-conjugate system B as $\mathrm{C_2H_{4-\mathit{n}}(CH{=}CH_2)_\mathit{n}}$, and $c_{i,k}$ and $d_{i,j}$ are their expansion coefficients, respectively. The Mulliken-like population of each fragment MO is represented by eqs 4 and 5.

$$\rho_k(\mathrm{A}) = \sum_i^{\mathrm{occ}}[c_{i,k}^{\;2} + \sum_j c_{i,k}d_{i,j}S_{k,j}] \qquad (4)$$

$$\rho_j(\mathrm{B}) = \sum_i^{\mathrm{occ}}[d_{i,j}^{\;2} + \sum_k c_{i,k}d_{i,j}S_{k,j}] \qquad (5)$$

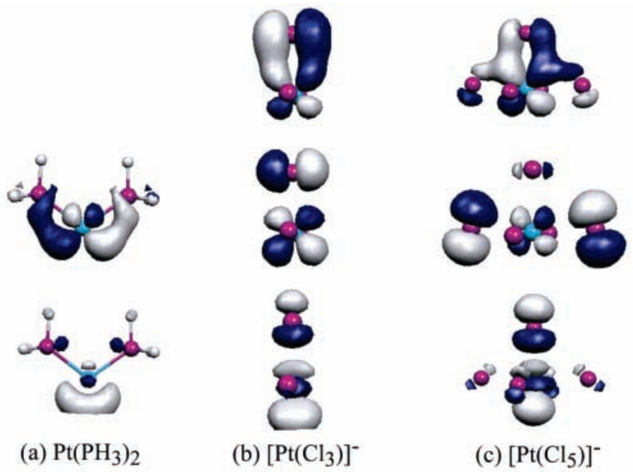
TABLE 4: NAO Charges of $C_2H_{4-n}(CH{=}CH_2)_n$ in $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$, $[PtCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$, and $[PtCl_5\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$

	$Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$		$[PtCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$		$[PtCl_5\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$	
n	MP4(SDQ)	B3LYP	MP4(SDQ)	B3LYP	MP4(SDQ)	B3LYP
1	−0.356	−0.359	0.003	−0.002	0.184	0.209
2	−0.384	−0.393	−0.025	−0.013		
3	−0.419	−0.424	−0.041	−0.034	0.180	0.226
4	−0.436	−0.456	−0.065	−0.056		
5	−0.459	−0.470	−0.090	−0.074	0.171	0.199

TABLE 5: Mulliken-like Populations of Fragment MOs in $Pt(PH_3)_2(C_2H_4)$, $[PtCl_3(C_2H_4)]^-$, and $[PtCl_5(C_2H_4)]^-$

	$Pt(PH_3)_2(C_2H_4)$	$[PtCl_3(C_2H_4)]^-$	$[PtCl_5(C_2H_4)]^-$
Pt Moiety			
d_π-type orbital[a]		1.962	1.938
d_π-type orbital[b]	1.461	1.675	1.977
σ-type unoccupied orbital[c]	0.310	0.474	0.560
C_2H_4 Moiety			
π orbital	1.652	1.558	1.510
π* orbital	0.556	0.390	0.174

[a] This molecular orbital mainly consists of a d_π orbital which does not interact with the π* orbital of the π-conjugate system. [b] This molecular orbital mainly consists of a d_π orbital which interacts with the π* orbital of the π-conjugate system. [c] This molecular orbital mainly consists of a Pt 6s-like orbital in $Pt(PH_3)_2(C_2H_4)$ and a d_σ orbital in $[PtCl_3(C_2H_4)]^-$ and $[PtCl_5(C_2H_4)]^-$, where both interact with the π-orbital of the π-conjugate system.



(a) $Pt(PH_3)_2$ (b) $[Pt(Cl_3)]^-$ (c) $[Pt(Cl_5)]^-$

Figure 6. d_π- and d_σ-type orbitals of (a) $Pt(PH_3)_2$, (b) $[PtCl_3]^-$, and (c) $[PtCl_5]^-$.

where $S_{k,j}$ is the overlap integral between the *k*th MO of fragment A and the *j*th MO of fragment B. It is noted that the sum of these populations of the fragment is the same as the sum of the Mulliken atomic populations of fragment A. Table 5 summarizes the DFT(B3LYP)-evaluated Mulliken-like populations of the d_π occupied and σ-type unoccupied MOs of $Pt(PH_3)_2$, $[PtCl_3]^-$, and $[PtCl_5]^-$ and those of the π and π* MOs of C_2H_4 in $Pt(PH_3)_2(C_2H_4)$, $[PtCl_3(C_2H_4)]^-$, and $[PtCl_5(C_2H_4)]^-$; see Figure 6 for these MOs. In the d^{10} metal complex $Pt(PH_3)_2(C_2H_4)$, the population (1.461e) of the d_π MO is significantly small, while it is 1.675e in the d^8 metal complex $[PtCl_3(C_2H_4)]^-$ and 2.00e in the d^6 metal complex $[PtCl_5(C_2H_4)]^-$. These results clearly show that the π-back-donation interaction is considerably strong in the d^{10} metal complex but becomes weaker in the d^8 metal complex than in the d^{10} metal complex and is not formed at all in the d^6 metal complex. On the other hand, the population of the σ-type unoccupied MO increases in the order $d^{10} < d^8 < d^6$. This result indicates that the σ-donation interaction becomes stronger in the order $d^{10} < d^8 < d^6$. Consistent with these results, the populations of the π and π* MOs decrease in the order $d^{10} > d^8 > d^6$. All these results indicate that the π-back-donation is stronger than the σ-donation in the d^{10} metal complex, both are comparable in the d^8 metal complex, and only the σ-donation participates in the coordinate bond of the d^6 metal complex. Of course, we must consider the possibility that these population changes arise from polarization interaction. In these systems, however, the population changes in the d_π occupied and σ-type unoccupied MOs are similar to the population changes in the π* and π MOs of the π-conjugate system, respectively. These results indicate that the population changes are induced by the CT interactions such as the σ-donation and the π-back-donation. From these results, it is concluded that the coordinate bonding nature is much different among these d^{10}, d^8, and d^6 metal complexes and that the DFT method underestimates the binding energies independently of the bonding nature when the π-conjugate system is large.

Why Does the DFT Method Underestimate Binding Energies When the π-Conjugate System Is Large? It is important to clarify the reason why the DFT method underestimates the binding energy when the π-conjugate system is large. We must remember that the DFT method tends to overestimate the charge delocalization and cannot calculate well the dispersion interaction.[1−4] Here, we examine whether these tendencies lead to the underestimation of the binding energy.

(1) Charge Delocalization. As well-known, the DFT method overestimates electron delocalization. If the DFT method overestimated the CT interaction between the metal center and the π-conjugate system, it overestimated the binding energy and vice versa. In the Pt(0) complexes, the population analysis shows that the DFT method presents slightly stronger π-back-donation from the Pt center to the π-conjugate system than the MP4(SDQ) method, though the difference is not large. In the Pt(II) and Pt(IV) complexes, the DFT method moderately overestimates the σ-donation from the π-conjugate system to the Pt center, compared to the MP4(SDQ) method. These results suggest that the DFT method tends to overestimate the CT interaction in these complexes, as expected. This tendency would lead to the overestimation of the binding energy by the DFT method, which is not consistent with the underestimation of the binding energy by the DFT method.

Thus, we must consider another factor responsible for the underestimation of the binding energy. If the DFT method overestimated the delocalization of negative charge on the π-conjugate system which was induced by the π-back-donation,

SCHEME 1: Delocalization Effect

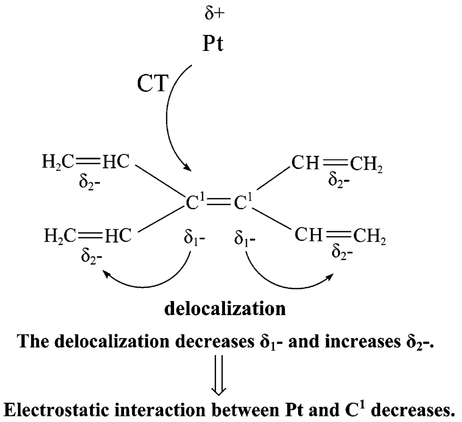


TABLE 6: Interaction Energies (kcal/mol) between the Radical Anion $[\bullet C_2H_{4-n}(CH{=}CH_2)_n]^-$ and a Positive Charge

	$n = 0$	$n = 2$	$n = 4$
MP4(SDQ)	196.4	168.6	157.3
B3LYP	195.9	166.6	155.4
B3PW91	197.3	168.3	157.5

the DFT method underestimated the electrostatic interaction between the positive charge on Pt and the negative charge on the π-conjugate system, as shown in Scheme 1. Certainly, the coordinating C atoms are calculated to be more negatively charged and the C atoms of the vinyl groups are calculated to be less negatively charged by the MP4(SDQ) method than by the DFT method, though the differences are small; see Supporting Information Figure S5. Using these negative charges, we approximately evaluated the Coulomb interaction between the π-conjugate system and the positively charged Pt atom. When a +1 positive charge is placed on the Pt atom, the Coulomb interaction is −89.9 kcal/mol for the MP4(SDQ)-calculated electron distribution and −90.3 kcal/mol for the DFT(B3LYP)-calculated electron distribution. The difference is much smaller than that between the MP4(SDQ)- and DFT-(B3LYP)-calculated binding energies.

We also evaluated the interaction energy between a radical anion, $[\bullet C_2H_{4-n}(CH{=}CH_2)_n]^-$ (n = 0, 2, or 4), and a positive charge using the DFT and MP4(SDQ) methods, where the geometry of $C_2H_{4-n}(CH{=}CH_2)_n$ was taken to be the same as that in $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ and a positive charge was placed at the position of the Pt center. If the DFT method overestimated the delocalization of negative charge, the negative charge on the C1 atom decreased, where the C1 atom coordinates with the Pt center (Scheme 1), which led to underestimation of the electrostatic interaction by the DFT method. As shown in Table 6, the energy difference between the DFT-(B3LYP) and MP4(SDQ) methods is less than 2 kcal/mol and that between the DFT(B3PW91) and MP4(SDQ) methods is less than 1 kcal/mol. These differences are much smaller than the difference between the DFT- and MP4(SDQ)-calculated binding energies; remember that the ΔBE(B3LYP) value is 22.2 kcal/mol and the ΔBE(B3PW91) value is 13.3 kcal/mol for $C_2(CH{=}CH_2)_4$. Moreover, the difference between the DFT- and MP4(SDQ)-calculated electrostatic interaction energies changes little as the size of the π-conjugate system increases. From these results, it is concluded that the delocalization of the negative charge in the π-conjugate system is not responsible for the underestimation of the binding energy by the DFT method.

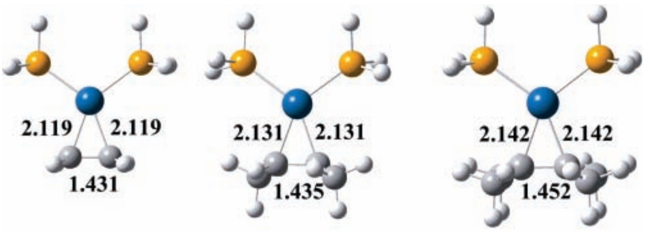


Figure 7. B3PW91-optimized structure of $Pt(PH_3)_2\{C_2H_{4-n}(CH_3)_n\}$ (bond lengths in angstroms).

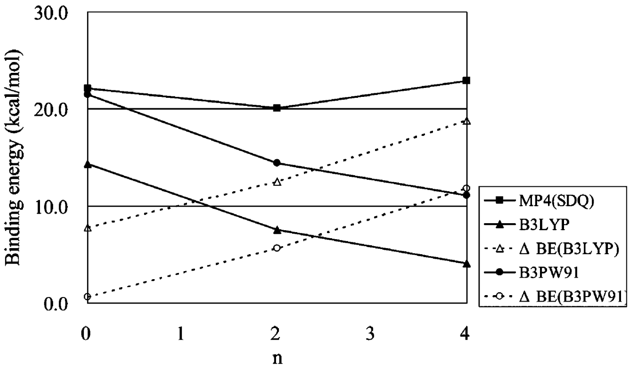
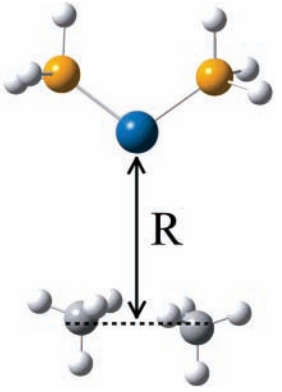


Figure 8. Binding energies of $Pt(PH_3)_2\{C_2H_{4-n}(CH_3)_n\}$.

SCHEME 2: System Which Consists of $Pt(PH_3)_2$ and Two Methane Molecules



(2) Dispersion Interaction. If the dispersion interaction contributed to the binding energy,[1−5] the DFT method underestimated the binding energy. Here, we investigate whether the dispersion interaction contributes to the binding energy. However, we cannot estimate the energy stabilization by the dispersion interaction between $Pt(PH_3)_2$ and the vinyl group, because the vinyl group contributes not only to the dispersion interaction but also to the CT interaction with the Pt center. We investigated here $Pt(PH_3)_2\{C_2H_{4-n}(CH_3)_n\}$ in which methyl groups are introduced to the C═C double bond, because the methyl group forms a dispersion interaction but not a CT interaction with the Pt moiety. The optimized geometries and binding energies of these complexes are shown in Figures 7 and 8, respectively. In these complexes, the ΔBE value increases, in other words, the DFT-calculated binding energy decreases, as the number of methyl groups increases, whereas the MP4(SDQ)-calculated value decreases little. This behavior is similar to that of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$.

If this underestimation arises from the poor description of the dispersion interaction, a similar underestimation should occur in the interaction between $Pt(PH_3)_2$ and the methyl substituents. We evaluated the interaction energy between $Pt(PH_3)_2$ and two methane molecules, as shown in Scheme 2, where we employed methane instead of the methyl substituent because the methyl radical would form a covalent interaction with $Pt(PH_3)_2$. The

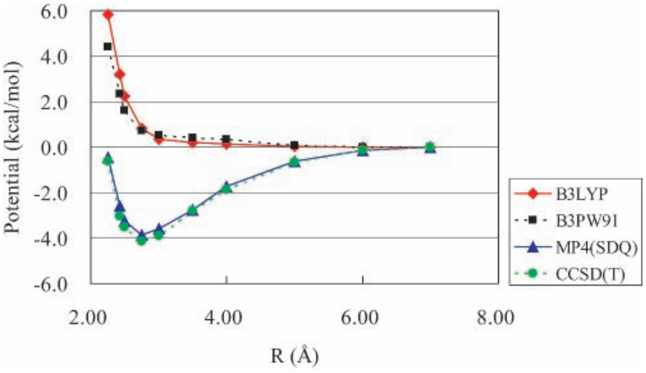


Figure 9. Potential energy curves in $Pt(PH_3)_2(CH_4)_2$. *R* represents the distance between Pt and the centers of the two C atoms.

positions of the methanes were taken to be the same as those of the methyl groups in $Pt(PH_3)_2$(*trans*-MeHC=CHMe). The MP4(SDQ) and CCSD(T) methods present a considerably large energy stabilization around $R = 2.8$ Å, as shown in Figure 9. However, the B3LYP and B3PW91 methods present an energy destabilization around there. The difference between the DFT- and MP4(SDQ)-calculated binding energies of $Pt(PH_3)_2$(*trans*-MeHC=CHMe) is about 12.5 kcal/mol, but we must remember that the binding energy of $Pt(PH_3)_2(C_2H_4)$ is different by 7.8 kcal/mol between these two methods. Thus, two methyl groups induce an energy difference of 4.7 kcal/mol, which is similar to the difference (5.8 kcal/mol) in the interaction energy of $Pt(PH_3)_2(CH_4)_2$ between the DFT and MP4(SDQ) calculations, where the distance between Pt and the centers of the two C atoms was taken to be the same as that of $Pt(PH_3)_2$(*trans*-MeHC=CHMe). Because the stabilization energy between $Pt(PH_3)_2$ and CH_4 is considered to arise from the dispersion interaction, these results lead to the conclusion that the insufficient description of the dispersion interaction by the DFT method is one of the reasons for the underestimation of the binding energy.[43]

(c) Other Factors. The B3PW91 functional presents energy stabilization of the methane−methane interaction like the CCSD(T) method.[4] Because methane−methane interaction mainly arises from the dispersion interaction, the B3PW91 functional is not very bad at evaluating the dispersion interaction. Nevertheless, the DFT(B3PW91)-calculated binding energy decreases as the size of the π-conjugate system increases, unlike the MP4(SDQ)-calculated value.

We investigated here the complexes of a bare Pt(0) atom with the π-conjugate systems, $Pt\{C_2H_{4-n}(CH{=}CH_2)_n\}$. In these complexes, the DFT-calculated binding energy considerably decreases to an extent similar to that of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ as the size of the π-conjugate system increases (see Table 7), while the MP4(SDQ)-calculated binding energy decreases little. Because the dispersion interaction between the ligands and substituents is not involved in $Pt\{C_2H_{4-n}(CH{=}CH_2)_n\}$, these results suggest that not only the dispersion interaction but also another factor is responsible for the underestimation.

TABLE 8: Binding Energies (kcal/mol) of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ ($n = 0-4$) Calculated with the Hartree−Fock Method

	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
BE	3.2	0.4	−2.5	−5.5	−10.8

We also evaluated the binding energy of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ at the Hartree−Fock level. Interestingly, the binding energy decreases as the size of the π-conjugate system increases, as shown in Table 8. This behavior is the same as that of the DFT method.

From all these results, it should be concluded that if the electron correlation effects are not sufficiently taken into consideration in the calculation, the binding energy decreases as the size of the π-conjugate system increases. It is likely that the use of a single-determinant wave function is one of the reasons that the DFT method underestimates the binding energy of the transition-metal complexes with a π-conjugate system when the size of the π-conjugate system is large.[44]

Conclusions

In this study, we systematically evaluated the binding energies of d^{10}, d^8, and d^6 transition-metal complexes of π-conjugate systems using the MP2 to MP4, CCSD(T), and DFT methods with triple-ζ-quality basis sets. The binding energy of $Pt(PH_3)_2\{C_2H_{4-n}\text{-}(CH{=}CH_2)_n\}$ considerably fluctuates around the MP2 and MP3 levels but much less upon going to MP4(SDQ) from MP3. The binding energy moderately increases upon going from MP4(SDQ) to MP4(SDTQ) and from CCSD to CCSD(T). The MP4(SDTQ) method tends to present a moderately larger binding energy than the CCSD(T) method. Thus, the MP4(SDQ) method presents a binding energy similar to that of the CCSD(T) method, which indicates that the MP4(SDQ) method provides a reliable binding energy from a practical point of view.

It should be noted that the MP4(SDQ)- and CCSD(T)-calculated binding energies of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ change little as the size of the π-conjugate system increases, while the DFT-calculated binding energy considerably decreases. The difference between the DFT- and MP4(SDQ)-calculated binding energies reaches about 25 kcal/mol for $n = 4$. The DFT-calculated binding energies of such d^8 and d^6 metal complexes as $[PtCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$, its Pd analogue, and $[PtCl_5\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$ decrease similarly.

Population analysis based on the fragment MOs and usual natural atomic population leads to the conclusion that the bonding nature is quite different in these complexes; the π-back-donation mainly participates in the coordinate bond of the Pt(0) complex, the σ-donation and π-back-donation comparably

TABLE 7: Binding Energies (kcal/mol) of $Pt\{C_2H_{4-n}(CH{=}CH_2)_n\}$

(A) Binding Energies Evaluated by the Post-Hartree−Fock Method

n	MP2	MP3	MP4(DQ)	MP4(SDQ)	CCSD	CCSD(T)
0	86.6	61.0	67.3	70.7	67.5	72.4
2	85.8	56.6	64.8	69.0		
4	88.5	54.8	66.0	71.1		

(B) Binding Energies Evaluated by the DFT Method with Various Functionals

n	B3LYP	B3PW91	ΔBE(B3LYP)	ΔBE(B3PW91)
0	62.8	69.6	8.0	1.2
2	55.9	63.2	13.1	5.9
4	52.1	60.0	19.0	11.1

participate in the coordinate bond of the Pt(II) complex, and the σ-donation largely participates but the π-back-donation participates little in the coordinate bond of the Pt(IV) complex. Thus, it is concluded that the DFT method underestimates the binding energy independently of the coordinate bonding nature when the π-conjugate system is large.

The reason for the underestimation was investigated with model systems $Pt(PH_3)_2\{C_2H_{4-n}(CH_3)_n\}$ and $Pt(PH_3)_2 + 2CH_4$. We found that the DFT method underestimated the interaction between $Pt(PH_3)_2$ and two methane molecules to an extent similar to that of the binding energy of $Pt(PH_3)_2$(*trans*-MeCH═CHMe). This result suggests that the dispersion interaction is one of the reasons for the underestimation of the binding energy by the DFT method.[43] However, it is noted that the DFT-calculated binding energy between the bare Pt(0) atom and the π-conjugate system decreases with an increase of the size of the π-conjugate system but the MP4(SDQ)-calculated value changes little, indicating that not only the dispersion interaction between the substituents and the metal moiety but also another factor is responsible for the underestimation.[44] The Hartree−Fock-calculated binding energy of $Pt(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ also decreases as the size of the π-conjugate system increases. From these results, we present several conclusions, as follows.

(1) The DFT method underestimates the binding energies of these d^{10}, d^8, and d^6 metal complexes with a large π-conjugate system.

(2) The DFT method tends to moderately overestimate the CT interaction, which is not responsible for the underestimation of the binding energy.

(3) One of the reasons for the underestimation is the poor description of the dispersion interaction between the substituents of the C═C double bond and the metal moiety.[43]

(4) The insufficient incorporation of the electron correlation effects is one of the reasons that the DFT method underestimates the binding energy of these complexes when the π-conjugate system is large.[44]

The present examination was made for the late-transition-metal complexes. It would be interesting to investigate the binding energies of the middle- and early-transition-metal complexes, because the electronic structure would be very different among the early-, middle-, and late-transition-metal complexes.

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Supporting Information Available: Complete ref 36, table of the Cartesian coordinates of the complexes examined, optimized geometries of $Pd(PH_3)_2\{C_2H_{4-n}(CH{=}CH_2)_n\}$ and their binding energies (two figures), optimized geometries of $[PdCl_3\{C_2H_{4-n}(CH{=}CH_2)_n\}]^-$ and their binding energies (two figures), and charge distribution of (a) the radical anion $[\bullet C_2(CH{=}CH_2)_4]^-$ and (b) $C_2(CH{=}CH_2)_4$ in $Pt(PH_3)_2\{C_2(CH{=}CH_2)_4\}$ evaluated with the MP4(SDQ) and B3LYP methods (two figures). This material is available free of charge via the Internet at http://pubs.acs.org.

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experimental value.[40b] The calculated value in this work is almost the same as the theoretical value which was previously calculated with the CCSD(T) method using a good basis set.[34] These results suggest that the CCSD(T)/BS2 and MP4(SDQ)/BS2 methods present a reliable binding energy. (b) Kirkham, W. G.; Lister, M. W.; Lister, R. B. *Thermochim. Acta* **1975**, *11*, 89. (c) Mortimer, C. T. *Rev. Inorg. Chem.* **1984**, *6*, 233. (d) Martinho Simóes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

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(44) Because the polarization is very important in the coordinate bond, it is likely that the incorrect evaluation of the polarizability and hyperpolarizability by the DFT method is another reason for the underestimation of the binding energy by the DFT method. It is likely that the electron correlation effects should be well incorporated with a multiconfiguration wave function to calculate the polarizability and hyperpolarizability.