

Binding energies and bonding nature of $\text{MX}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ ($\text{M} = \text{Rh}$ or Ir ; $\text{X} = \text{H}$ or Cl): Theoretical study

Atsushi Ikeda^a, Yuu Kamenon^a, Yoshihide Nakao^a, Hirofumi Sato^a, Shige-yoshi Sakaki^{a,b,*}

^a Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

^b Fukui Institute for Fundamental Chemistry, Nishihiraki-chou, Takano, Sakyo-ku, Kyoto 606-8103, Japan

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Abstract

$\text{IrH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$, $\text{IrCl}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$, and $\text{RhH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ were theoretically investigated with DFT and MP2 to MP4(SDQ) methods. Because the DFT method considerably underestimates the binding energy compared to the MP2 method, their binding energies were evaluated by the ONIOM(MP4(SDQ):UFF) method. The binding energy decreases in the order $\text{IrH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ (59.4) > $\text{RhH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ (48.2) > $\text{Pt}(\text{PH}_3)_2(\text{C}_{60})$ (47.2) > $\text{IrCl}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ (43.0), where in parentheses are the binding energy (in kcal/mol) calculated with the ONIOM(MP4(SDQ):UFF) method and that of $\text{Pt}(\text{PH}_3)_2(\text{C}_{60})$ was calculated with the same method and the same basis sets in our previous work. This decreasing order is interpreted in terms of the d_π orbital energy, the d orbital expansion, the presence of the empty d_σ orbital, and the distortion energy of the metal fragment induced by the complexation; for instance, the d_π orbital is at higher energy and more expands in $\text{IrH}(\text{CO})(\text{PH}_3)_2$ than in the Rh analogue, which leads to the larger binding energy of $\text{IrH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ than that of the Rh analogue. $\text{IrCl}(\text{CO})(\text{PH}_3)_2$ is less favorable than $\text{IrH}(\text{CO})(\text{PH}_3)_2$ because of the lower energy of d_π orbital. Although the π -back donation is stronger in $\text{IrCl}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ than in $\text{RhH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$, the binding energy of $\text{IrCl}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ is smaller than that of $\text{RhH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ due to the larger distortion energy of the $\text{IrCl}(\text{CO})(\text{PH}_3)_2$ moiety. Although the d_π orbital of $\text{Pt}(\text{PH}_3)_2$ is at higher energy than that of $\text{IrH}(\text{CO})(\text{PH}_3)_2$, the binding energy of $\text{IrH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ is larger than that of $\text{Pt}(\text{PH}_3)_2(\text{C}_{60})$ because the distortion energy is large and the d_σ orbital is doubly occupied in $\text{Pt}(\text{PH}_3)_2(\text{C}_{60})$. It is also noted that these binding energies are much larger than those of the ethylene analogues like those of the $\text{Pt}(0)$ complexes, which is reasonably interpreted in terms that the LUMO of C_{60} is at much lower energy than those of ethylene.

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1. Introduction

Transition-metal complexes of fullerene are of considerable interest, because they are expected to be new materials with interesting properties [1]. Since the first syntheses of $\text{OsO}_4(\text{NC}_5\text{H}_4\text{CMe}_3)(\text{C}_{60})$ and $\text{Pt}(\text{PPh}_3)_2(\text{C}_{60})$ [2,3], various transition-metal η^2 -fullerene [1,4–7] and η^5 -fullerene complexes [8] have been reported so far. Also, several theoretical studies have been carried out; for instance, $\text{Pt}(\text{PH}_3)_2(\text{C}_{60})$ was investigated with Fenske–Hall [9], Hartree–Fock [10–12], and extended Hückel MO methods [13]

previously and with the DFT method [14] recently. Also, the possibility of the existence of η^6 - C_{60} complex was theoretically investigated with the semi-empirical and Hartree–Fock MO methods [15,16]. However, all those theoretical works of the η^2 - C_{60} complex were limited to $\text{M}(\text{PH}_3)_2(\text{C}_{60})$ type complexes ($\text{M} = \text{Ni}$, Pd , or Pt) and the other type of the η^2 - C_{60} complex has not been theoretically investigated yet, to our knowledge. For instance, no theoretical work has been reported on Vaska type complexes of C_{60} such as $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{C}_{60})$ [17] and $\text{RhH}(\text{CO})(\text{PPh}_3)_2(\text{C}_{60})$ [18], despite of the importance of Vaska type complexes in coordination and organometallic chemistries.

In this work, we theoretically investigated $\text{MH}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ and $\text{MCl}(\text{CO})(\text{PH}_3)_2(\text{C}_{60})$ ($\text{M} = \text{Rh}$ or Ir) with DFT and MP2 to MP4(SDQ) methods. Our purposes here

* Corresponding author. Address: Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan. Tel.: +81 75 383 2544; fax: +81 75 383 2799.

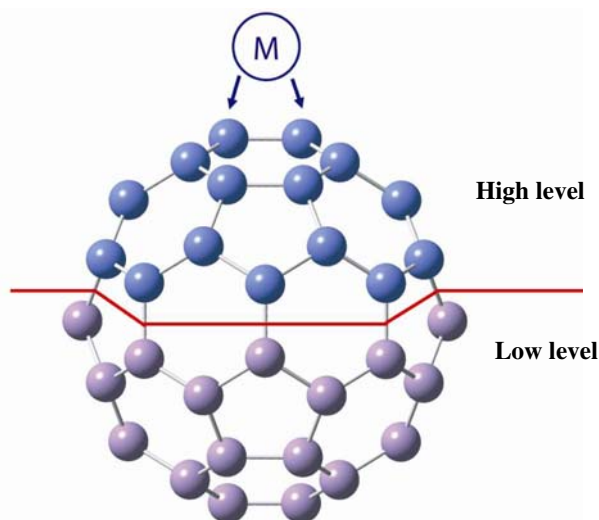
E-mail address: sakaki@moleng.kyoto-u.ac.jp (S. Sakaki).

are to evaluate binding energies of this kind of transition-metal η^2 - C_{60} complexes and to make comparisons of the binding energy of these complexes with those of ethylene complexes and $Pt(PH_3)_2(C_{60})$. From these investigations, we wish to theoretically clarify the characteristic features of $MH(CO)(PPh_3)_2(C_{60})$ and $MCl(CO)(PPh_3)_2(C_{60})$.

2. Computational details

Geometries were optimized by the DFT method with the B3LYP functional [19,20]. In the geometry optimization, LANL2DZ basis sets [21] were used for Ir and Rh and usual 6-31G basis sets [22,23] were employed for P, Cl, C, and H atoms. This basis set system is called BS-1 hereafter. The binding energy was evaluated with the MP2 and ONIOM(MP4(SDQ);UFF) [24,25] methods, because the DFT method significantly underestimated the binding energy of $Pt(PH_3)_2(C_{60})$, as reported recently by us [26]. In the ONIOM calculation, we separated high and low level regions, as shown in Scheme 1. In evaluation of the binding energy, we employed better basis set systems, BS-2 and BS-3; in BS-2, (541/541/211/1) and (541/541/111/1) basis sets were used for Rh and Ir [21,27,28], respectively, with the same effective core potentials as those of LANL2DZ. For the other atoms, usual 6-31G basis sets were employed [22,23] except for P for which LANL2DZ basis set augmented with one d polarization function was used [29,30]. In BS-3, usual 6-31G(d) basis sets were used for all atoms except for transition-metal elements for which the same basis sets and the same ECPs as those of BS-2 were used.

GAUSSIAN 98 program package was used for all calculations [31]. Orbital plots were drawn with MOLEKEL program package [32].



Scheme 1.

3. Results and discussion

3.1. Optimized Geometries of $IrH(CO)(PH_3)_2(C_{60})$ (**1**), $IrCl(CO)(PH_3)_2(C_{60})$ (**2**), and $RhH(CO)(PH_3)_2(C_{60})$ (**3**)

Experimental works reported that the transition metal interacted with C_{60} at the C–C bond between two six-member rings in these complexes [17,18]. In $Pt(PR_3)_2(C_{60})$, experimental [3] and theoretical works [10,26] showed that the Pt center interacted with C_{60} at the same C–C bond. Thus, we optimized geometries of these complexes in this coordination structure.

All these complexes take pseudo-trigonal bipyramidal structure around the metal center, in which the X (X = H or Cl) and CO ligands are at the axial positions, while two PH_3 ligands and the C–C bond of C_{60} are on the equatorial plane. This is because anion and strongly donating ligands tend to take a position on the C_{3v} axis but either electron-withdrawing ligand and less donating one tend to take a position on the equatorial plane [33]. In **2**, the optimized Ir–C¹ and C¹–C² distances agree well with the experimental values [17], as shown in Fig. 1. In **3**, the Rh–C¹ and C¹–C² distances also agree well with the experimental values [18]. The C¹–C² bond distance becomes longer in the order **3** < **2** ~ **1**. Consistent with this longer C¹–C² distances of **1** and **2** than that of **3**, the Ir–C¹ and Ir–C² distances of **1** and **2** are shorter than those of **3** [34]. Although the C¹–C² distance is similar in **1** and **2**, the Ir–C¹ and Ir–C² distances of **1** are shorter than those of **2**. These results suggest that C_{60} more strongly coordinates with the Ir center in **1** than in **3**, and in **1** than in **2**, as will be discussed below in more detail. Although moderate deviations of the optimized geometries from the experimental ones [17,18] are observed in the M–P distance [35], it is likely that reliable discussion of the coordinate bond of C_{60} can be presented on the basis of the optimized geometries here because the geometry of the M– C_{60} moiety is reproduced well by the optimization.

Geometry changes induced by the coordination with C_{60} are worthy of note. In all these complexes, the Ir–P distance becomes longer than that of $IrX(CO)(PH_3)_2$, as shown in Fig. 1. In **2**, the Ir–Cl distance becomes somewhat longer than that of $IrCl(CO)(PH_3)_2$, while the Ir–CO distance little changes by the coordination with C_{60} . The similar geometry changes are observed in the ethylene analogue. In **1** and **3**, on the other hand, the M–H distance becomes moderately shorter than those of $MH(CO)(PH_3)_2$, while the M–P and M–CO distances become longer by the coordination with C_{60} . The lengthening of the M–P distance by the C_{60} coordination is easily understood in terms of the interaction between the lone pair orbital of PH_3 and the d orbital of the metal center in the trigonal bipyramidal d^8 metal complex, as follows: in the trigonal bipyramidal d^8 metal complex, only one d_{z^2} orbital along the C_{3v} axis is empty and the others are doubly occupied, as shown in Scheme 2a. The lone pair orbital of phosphine overlaps

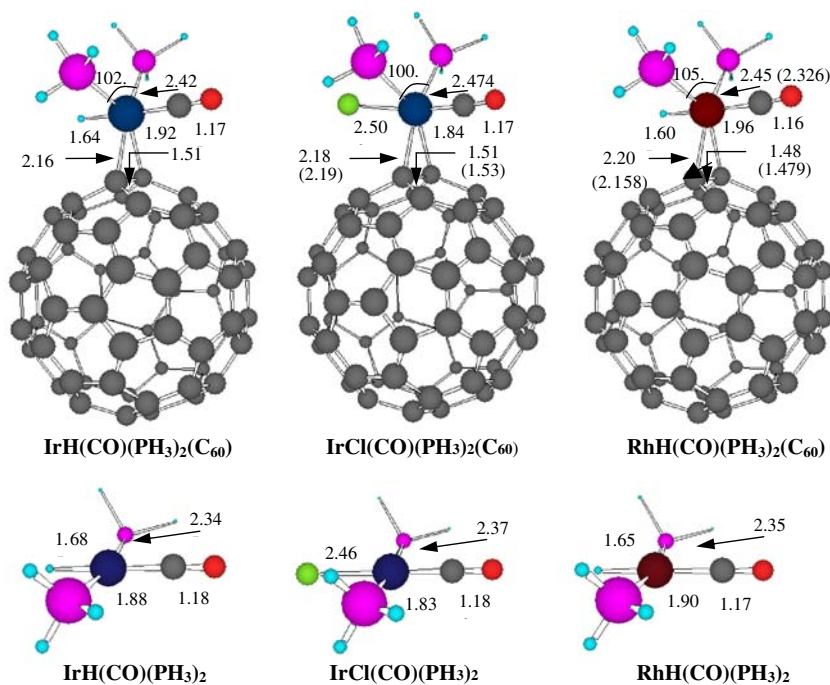


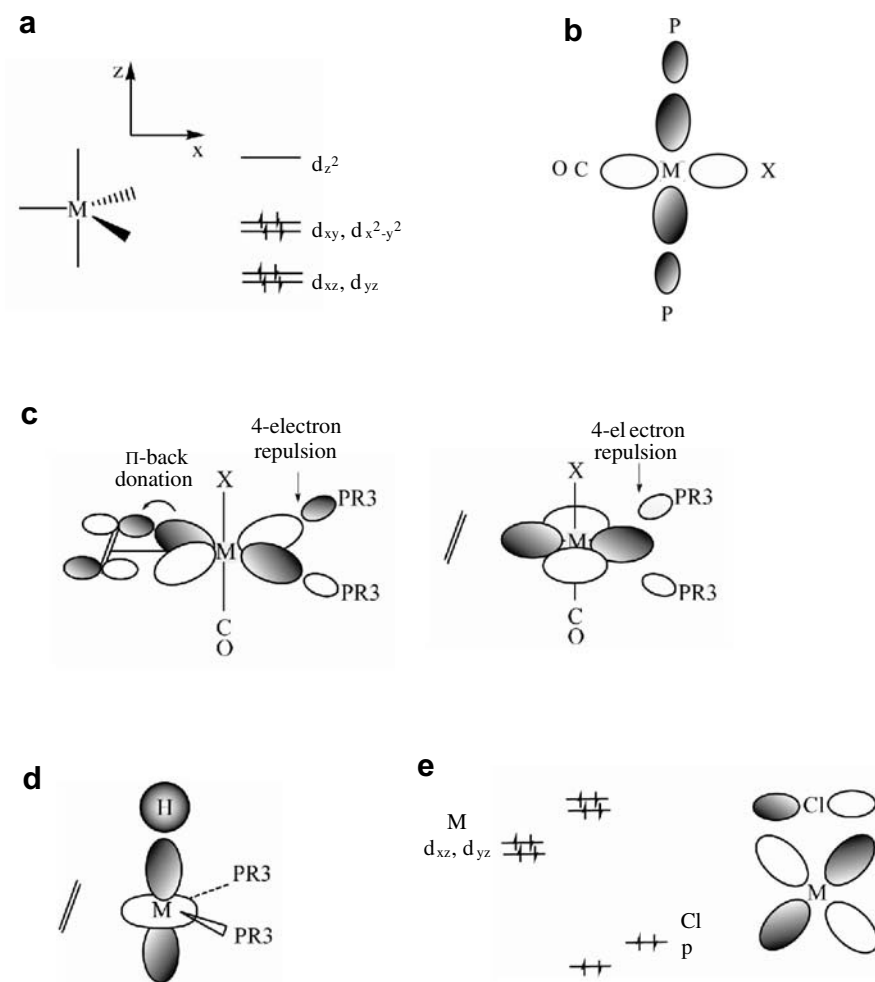
Fig. 1. Optimized structures of IrH(CO)(PH₃)₂(C₆₀), IrCl(CO)(PH₃)₂(C₆₀), RhH(CO)(PH₃)₂(C₆₀), IrH(CO)(PH₃)₂, IrCl(CO)(PH₃)₂ and RhH(CO)(PH₃)₂(C₆₀). Bond length in Å and bond angle in degree. In parentheses are experimental values.

with the empty d_{σ} orbital in square planar structure, as shown in Scheme 2b, but it must overlap well with the doubly-occupied d_{xy} and $d_{x^2-y^2}$ orbitals in the trigonal bipyramidal structure, to induce four-electron repulsion with these occupied d orbitals, as shown in Scheme 2c. As a result, the M–P distance becomes longer in the trigonal bipyramidal d^8 metal complex. The lengthening of the M–CO distance by the C₆₀ coordination in **1** and **3** is also interpreted in terms that the strong π -back donation from the M center to C₆₀ weakens the π -back donation from the M center to CO; see the discussion below for the strong π -back donation to C₆₀. In **2**, however, the Ir–CO distance little changes upon the coordination with C₆₀ unlike those of **1** and **3**. This unexpected result is related to the Ir–Cl bond lengthening in **2**, as follows: The lengthening of the M–Cl bond of **2** is in contrast to the shortening of the M–H bonds of **1** and **3**. In the trigonal bipyramidal d^8 metal complex, one d_{σ} orbital interacts with two axial ligands, as shown in Scheme 2d, while it interacts with four ligands in the square planar structure (Scheme 2b). As a result, the M–H distance becomes shorter in the trigonal bipyramidal d^8 complex than in the square planar complex. Contrary to the above discussion, the Ir–Cl distance becomes longer in the trigonal bipyramidal C₆₀ complex than in the square planar complex. The similar lengthening of the Ir–Cl bond is observed in IrCl(CO)(PH₃)₂(C₂H₄) in which the Ir–Cl distance lengthens by 0.06 Å. The Cl ligand is different from the H ligand in the larger size and the presence of doubly-occupied p_{π} orbitals. Considering that the doubly-occupied p_{π} orbitals of Cl overlap with the doubly-occupied d_{xz} and d_{yz} orbitals in an anti-bonding way (see Scheme 2e) but not with the d_{xy} orbital which mainly

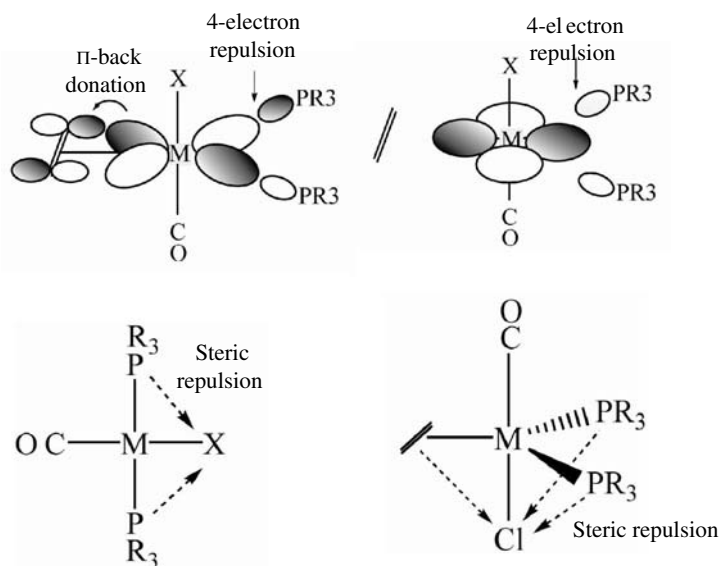
participates in the π -back donation from the M center to C₆₀, the π -back donation does not influence very much the M–Cl bond distance. This means that the other factor should be responsible for the lengthening of the M–Cl bond. One of such candidates is the steric repulsion of the large Cl ligand with the other ligands; Cl suffers from steric repulsion with two phosphine ligands in the square planar complex but from steric repulsion with C₆₀ (or C₂H₄) in addition to two phosphine ligands in the trigonal bipyramidal complex, as shown in Scheme 3. In the case of the less bulky H ligand, on the other hand, it is likely that the bonding interaction with the d_{σ} orbital plays more important role to shorten the Ir–H bond rather than the steric repulsion lengthens the Ir–H bond in the trigonal bipyramidal structure. Such Ir–Cl bond lengthening of **2** leads to the strengthening of the Ir–CO bond, which compensates the Ir–CO bond weakening by the π -back donation to C₆₀. As a result, the Ir–CO bond distance little changes by coordination with C₆₀ in **2**.

3.2. Binding energies of IrH(CO)(PH₃)₂(C₆₀) (**1**), IrCl(CO)(PH₃)₂(C₆₀) (**2**), and RhH(CO)(PH₃)₂(C₆₀) (**3**)

As shown in Table 1, the DFT-calculated binding energies (BE) are much smaller than the MP2-calculated ones in all these complexes, as reported previously [26]. Although the basis sets used here are not extremely good, the BE values are not different very much between the MP2/BS-2 and MP2/BS-3 calculations. In our previous theoretical work, the basis set effects on the BE value were carefully examined in Pt(PH₃)₂(C₂H₄), which indicated that



Scheme 2. (a) d orbital occupation of d^8 trigonal bipyramidal complex. (b) Bonding interaction of phosphine lone pair orbitals with empty d_σ orbital. (c) Anti-bonding overlap of phosphine lone pair orbitals with doubly-occupied d_{xy} and $d_{x^2-y^2}$ orbitals in d^8 trigonal bipyramidal complex. (d) Bonding interaction between H $1s$ and M d_{z^2} orbitals. (e) The d_π - p_π anti-bonding interaction between M and Cl in trigonal bipyramidal d^8 complex.



Scheme 3.

Table 1

Binding energy (BE in kcal/mol) of IrH(CO)(PH₃)₂(C₆₀) (**1**), IrCl(CO)(PH₃)₂(C₆₀) (**2**), RhH(CO)(PH₃)₂(C₆₀) (**3**), and their ethylene analogues

	1	2	3	Pt(PH ₃) ₂ (C ₆₀)
C₆₀ complexes				
B3LYP/BS-2	16.1	2.5	8.3	14.2
B3LYP/BS-3	16.9	3.1	8.8	14.9
MP2/BS-2	63.1	49.3	57.2	50.0
MP2/BS-3	68.0	53.4	60.2	55.0
ONIOM(MP2/BS-2:UFF)	61.3	47.4	55.8	48.5
ONIOM(MP4(SDQ)/BS-2:UFF)	54.9	39.9	45.5	42.8
ONIOM(MP2/BS-3:UFF)	65.9	51.1	58.6	53.2
ONIOM(MP4(SDQ)/BS-3:UFF)	[59.4] ^a	[43.5] ^a	[48.2] ^a	[47.5] ^a
	1^b	2^b	3^b	Pt(PH ₃) ₂ (C ₂ H ₄)
C₂H₄ complexes				
B3LYP/BS-2	16.5	8.8	7.9	13.0
B3LYP/BS-3	18.4	10.6	9.1	15.0
MP2/BS-2	37.5	27.5	28.6	33.2
MP2/BS-3	44.7	34.3	33.2	33.5
MP3	26.1	17.6	12.8	19.7
MP4(DQ)	34.3	24.6	23.3	23.2
MP4(SDQ)	33.8	24.9	24.2	24.2
CCSD(T)	32.4	24.1	–	24.3

^a The binding energy at the ONIOM(MP4(SDQ)/BS-3:UFF) level was estimated from the ONIOM(MP4(SDQ)/BS-2:UFF)-calculated binding energy by adding the basis set effects on the binding energy (ΔE) which was evaluated at the MP2 level, as follows: $\Delta E = \text{BE}[\text{ONIOM}(\text{MP2}/\text{BS-3}:\text{UFF})] - \text{BE}[\text{ONIOM}(\text{MP2}/\text{BS-2}:\text{UFF})]$.

^b Abbreviations, **1'**, **2'**, and **3'** represent ethylene analogues of **1**, **2**, and **3**, respectively.

the BE value little changed upon going to BS-3 from BS-2 [26]. Also, we found that the MP4(SDQ)/BS-3 and CCSD(T)/BS-3 methods presented almost the same BE value in Pt(PH₃)₂(C₂H₄) [26]. As shown in Table 1, the BE values of IrH(CO)(PH₃)₂(C₂H₄) **1'**, IrCl(CO)(PH₃)₂(C₂H₄) **2'**, and RhH(CO)(PH₃)₂(C₂H₄) **3'** moderately fluctuate at MP2/BS-3 and MP3/BS-3 levels but converge upon going to MP4(SDQ)/BS-3 from MP3/BS-3 and almost the same binding energy was calculated with the MP4(SDQ)/BS-3 and CCSD(T)/BS-3 methods, as reported previously in Pt(PH₃)₂(C₂H₄) [26]. From these results, it is reasonably concluded that the MP4(SDQ)/BS-3 method presents reliable BE values in these Ir(I) and Rh(I) complexes.

However, we could not perform MP4(SDQ)/BS-3 calculations of MX(CO)(PH₃)₂(C₆₀) because of the very large size. Although the ONIOM method is useful to evaluate the binding energy of large system, the ONIOM(MP4(SDQ)/BS-3:UFF) method could not be applied to these complexes due to their large sizes, too. Thus, we evaluated the binding energies of these complexes with the ONIOM(MP4(SDQ)/BS-2:UFF) method and then made correction of basis set effects by considering the difference in the BE value between ONIOM(MP2/BS-2:UFF) and ONIOM(MP2/BS-3:UFF) calculations. The reliability of this procedure was clearly shown in our previous work [26]. Thus-calculated BE values are given in brackets of Table 1. Apparently, the BE values of these Ir and Rh complexes of C₆₀ are much larger than those of the ethylene analogues. This is because the π^* orbital of C₆₀ is at much lower energy than that of ethylene, as reported [26]. Also, it is noted that the BE value decreases in the order **1** > **3** > **2**;

in other words, the hydride complex and the Ir complex yields larger BE value than the chloride complex and the Rh complex, respectively. The factors to determine the BE values will be discussed below.

3.3. Electron population changes by coordination with C₆₀

The electron population of the metal moiety considerably decreases and that of the C₆₀ moiety considerably increases (see Table 2). In particular, the metal d orbital population considerably decreases. On the other hand, the atomic population of metal center considerably increases. These population changes clearly show that the π -back donation predominantly participates in the coordinate bond of C₆₀, as reported previously in M(PH₃)₂(C₆₀) and also that the σ -donation from CO and PH₃ to the s and p orbitals of the metal center is enhanced by the coordination of C₆₀. The importance of the π -back donation is clearly shown by the orbital picture, as shown in Fig. 2, in which the π^* orbital of C₆₀ overlaps well with the d _{π} orbital of the metal center in these complexes.

Table 2
Population changes^a by coordination of C₆₀ with the Ir center

	1	2	3
C ₆₀	0.162	0.092	0.214
Ir	0.258	0.269	0.234
d	-0.149	-0.113	-0.198
CO	-0.146	-0.158	-0.115
H or Cl	-0.110	-0.070	-0.101
PH ₃	-0.091	-0.067	-0.116

^a Relative to MX(CO)(PH₃)₂ with distorted geometry taken in the total complex.

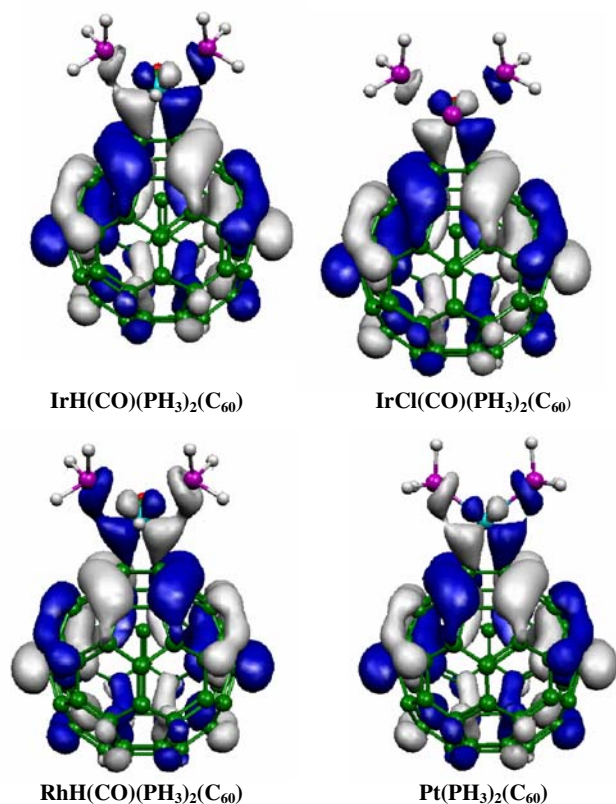


Fig. 2. Orbital pictures of π -back donation. Note: Kohn–Sham orbital (DFT/BS-III).

The charge transfer from the metal moiety to C_{60} decreases in the order $3 > 1 > 2$, which is parallel to the decreasing order of the metal d orbital population. How-

ever, it is somewhat different from the decreasing order of the BE value and the d_{π} orbital energy, unexpectedly; see Tables 1 and 3 for the BE value and d_{π} orbital energy, respectively. These results request us to investigate the relation between the binding energy and the coordinate bonding nature, in more detail.

3.4. Relation between binding energy (BE) and d orbital energy

The binding energy (BE) decreases in the order $1 > 3 > 2$, as mentioned above, which agrees with the decreasing order of the d_{π} orbital energy $\varepsilon(d_{\pi})$ of $MX(CO)(PH_3)_2$ taking the same structure as that in the total complex, as shown in Table 3. This result seemingly indicates that the π -back donation from the metal center to C_{60} plays an important role and the d_{π} orbital energy is a key factor to determine the binding energy. However, the discrepancy between the trend of the BE value and that of the electron population of C_{60} is observed, as discussed above.

Here, the intrinsic binding energy (E_{INT}) is defined as stabilization energy by the interaction between C_{60} and $MX(CO)(PH_3)_2$ taking the distorted geometry in the total complex, and the distortion energy (E_{DIST}) is defined as destabilization energy of $MX(CO)(PH_3)_2$ upon going from the equilibrium geometry to the distorted one taken in the total complex. The BE value is the sum of E_{INT} and E_{DIST} , $BE = E_{INT} + E_{DIST}$. The E_{INT} value directly relates to the d_{π} orbital energy of the distorted $MX(CO)(PH_3)_2$, if the π -back donation predominantly contributes to the coordinate bond. However, the E_{INT} value decreases in the order $1 > 2 > 3$, whereas the d_{π} orbital lowers in energy in the

Table 3
Intrinsic interaction energy (E_{INT})^a of $MX(CO)(PH_3)_2(C_{60})$, and distortion energy (E_{DIST})^b and d_{π} orbital energy^c of $MX(CO)(PH_3)_2$

	IrH(CO)(PH ₃) ₂	IrCl(CO)(PH ₃) ₂	RhH(CO)(PH ₃) ₂	Pt(PH ₃) ₂
E_{INT} ^a	97.0	90.0	75.8	83.4
E_{DIST} ^b	37.6	46.5	27.6	35.9
$\varepsilon(d_{\pi})$	−7.04	−7.76	−7.66	−6.72
	(−4.51)	(−4.98)	(−4.71)	(−4.37)
$\varepsilon(d_{\sigma})$	1.15	0.79	1.34	1.46
	(−2.32)	(−2.87)	(−1.98)	(−1.73)
Square of LCMO coefficient in the occupied space of $MX(CO)(PH_3)_2(C_{60})$ ^d				
π HOMO − 6	0.888	0.877	0.924	0.909
	(0.952)	(0.945)	(0.984)	(0.961)
HOMO − 9	0.903	0.884	0.933	0.926
	(0.915)	(0.911)	(0.949)	(0.941)
π^* LUMO	0.152	0.129	0.107	0.135
	(0.130)	(0.104)	(0.077)	(0.120)
LUMO + 3	0.061	0.056	0.045	0.058
	(0.068)	(0.058)	(0.044)	(0.064)
LUMO + 6	0.030	0.031	0.023	0.031
	(0.042)	(0.039)	(0.029)	(0.043)

^a Stabilization energy (in kcal/mol) of $MX(CO)(PH_3)_2(C_{60})$ relative to the sum of C_{60} and the distorted $MX(CO)(PH_3)_2$ taken in the total complex, where the MP4(SDQ) method was employed.

^b Destabilization energy (in kcal/mol) of $MX(CO)(PH_3)_2$ is the energy difference between the equilibrium structure and the distorted one taken in the total complex, where the MP4(SDQ) method was employed.

^c Hartree–Fock orbital energy (in eV) of $MX(CO)(PH_3)_2$ with the distorted structure taken in the total complex. In parentheses are Kohn–Sham orbital energies.

^d Kohn–Sham orbitals were analyzed. In parentheses are results from Hartree–Fock orbitals.

order $1 > 3 > 2$. This disagreement indicates that not only d_π orbital energy but also the other factor is responsible for the interaction. One of the candidates is the orbital overlap $S(d_\pi-\pi^*)$ between the d orbital of the metal center and the π^* orbital of C_{60} [36]. Actually, the $S(d_\pi-\pi^*)$ value of **3** is much smaller than those of **1** and **2**; $S(d_\pi-\pi_1^*)$ is 0.146, 0.131, and 0.111 for **1**, **2**, and **3**, respectively, where π_1^* is LUMO of C_{60} . This is because the 5d orbital more expands than the 4d orbital in general [37]. The larger $S(d_\pi-\pi^*)$ value of **2** leads to the stronger coordinate bond of **2** than that of **3**. As a result, the E_{INT} value of **2** is much larger than that of **3**. In spite of this large E_{INT} value of **2**, the BE value of **2** is smaller than that of **3**. This is because E_{DIST} value of **2** is much larger than that of **3**. Although the details are ambiguous, it is likely that the large E_{DIST} value in **2** is attributed to the considerable lengthening of the Ir–Cl bond upon going to the distorted geometry in **2** from the equilibrium one; remember that the M–H bond moderately shortens in **1** and **3** but the Ir–Cl bond considerably lengthens in **2** compared to that of $IrCl(CO)(PH_3)_2$.

Summarizing the above discussion, the E_{INT} value of **2** is considerably larger than that of **3** because of the large overlap $S(d_\pi-\pi^*)$, despite of the low d_π orbital energy. However, the large E_{DIST} value decreases very much the BE value. The BE and E_{INT} values of **1** are the largest in these complexes because of the highest d_π orbital energy, the largest $S(d_\pi-\pi_1^*)$ value, and the smallest E_{DIST} value which arises from the small size of H.

It is necessary to clarify the reason that the population increase of C_{60} is the largest in **3** but the E_{INT} value is the smallest in **3**, whereas the d_π orbital of $RhH(CO)(PH_3)_2$ is at much lower energy than that of $IrH(CO)(PH_3)_2$. This means that not the back donation but the other factor leads to the largest negative charge of C_{60} in **3**. One important characteristic features of $MX(CO)(PH_3)_2$ is the presence of the unoccupied d_σ orbital unlike $M(PH_3)_2$. This d_σ orbital contributes to the σ donation from C_{60} to the M center in $MX(CO)(PR_3)_2(C_{60})$. We evaluated how much π and π^* orbitals of C_{60} participate in the occupied space of $MX(CO)(PH_3)_2(C_{60})$ by representing the molecular orbitals of $MX(CO)(PH_3)_2(C_{60})$ as linear combinations of molecular orbitals of fragments, $MX(CO)(PH_3)_2$ and C_{60} [38]. As shown in Table 3, the sum of the squares of coefficients of the π^* orbital decreases in the order $1 > 2 \gg 3$, and the sum of the squares of coefficients of the π orbital increases in the order $2 < 1 \ll 3$. These results suggest that the π -back donation is the strongest in **1** but the σ -donation of **2** is moderately stronger than that of **1** [39]. This is because the d_π and d_σ orbitals of $IrH(CO)(PH_3)_2$ are at higher energies than those of the Cl analogue, as shown in Table 3. The larger E_{INT} value of **1** than that of **2** indicates that the π -back donation is more important than the σ -donation. Interestingly, both the σ -donation and the π -back donation are the weakest in **3**. This means that the large electron population of C_{60} in **3** results from the weakest σ -donation from C_{60} to the M center, which leads to the smallest E_{INT} value of **3**. The weakest π -back donation

arises from the facts that $S(d_\pi-\pi^*)$ value of **3** is smaller than those of **1** and **2** and the d_π orbital is at lower energy in **3** than in **1**. The weakest σ -donation is interpreted in terms of the d_σ orbital at high energy and the small overlap between the d_σ orbital and the p orbital of C_{60} ; note that the $S(d_\sigma-\pi)$ value is parallel to the $S(d_\pi-\pi^*)$ value; $S(d_\sigma-\pi_1)$ is 0.114, 0.112, and 0.090 for **1**, **2**, and **3**, respectively, where π_1 is HOMO of C_{60} .

Also, this analysis clearly shows the interesting difference between $M(PH_3)_2(C_{60})$ and $MX(CO)(PH_3)_2(C_{60})$, as follows: Interestingly, the E_{INT} value of $Pt(PH_3)_2(C_{60})$ is smaller than that of $IrX(CO)(PH_3)_2(C_{60})$ despite of the d_π orbital of $Pt(PH_3)_2$ at higher energy than that of $IrX(CO)(PH_3)_2$. Apparently, the sum of the squares of the π orbitals in $Pt(PH_3)_2(C_{60})$ are much larger than those in **1** and **2**, indicating the very weak σ -donation from C_{60} to $Pt(PH_3)_2$. This is because $Pt(PH_3)_2$ does not have empty d_σ orbital unlike $IrX(CO)(PH_3)_2$. The presence of doubly-occupied d_σ orbital also disfavors the coordination of C_{60} with the Pt center due to four-electron repulsion between d_σ orbital of Pt and π orbital of C_{60} . In other words, the smaller E_{INT} value of $Pt(PH_3)_2(C_{60})$ than that of $IrX(CO)(PH_3)_2(C_{60})$ is attributed to the absence of empty d_σ orbital.

4. Conclusions

The MP2 to MP4(SDQ) and DFT methods were applied to $IrH(CO)(PH_3)_2(C_{60})$ (**1**), $IrCl(CO)(PH_3)_2(C_{60})$ (**2**), and $RhH(CO)(PH_3)_2(C_{60})$ (**3**), to estimate their binding energies and clarify the bonding nature. The DFT method presents much smaller binding energies than the MP2 method, as reported previously [26]; for instance, the binding energy of **1** was evaluated to be 16.9 kcal/mol with the DFT/BS-3 method but 68.0 kcal/mol by the MP2/BS-3 method [26].

The binding energies of **1**, **2**, and **3** were evaluated to be 59.4, 43.5, and 48.2 kcal/mol, respectively, with the ONIOM(MP4(SDQ)/BS-3:UFF) method, where the basis set effects upon going to BS-3 from BS-2 were evaluated at the MP2 level. This decreasing order is different from that of the E_{INT} value $1 > 2 > 3$. The E_{INT} value is easily interpreted in terms of π -back donation and σ -donation; in **3**, both π -back donation and σ -donation are the weakest, which leads to the smallest E_{INT} value. The weakest π -back donation of **3** arises from the less expansion of the d orbital and the d_π orbital at the low energy. The weakest σ -donation is due to the d_σ orbital at the high energy and the less expansion of the d orbital. The E_{INT} value of **2** is much larger than that of **3**, which arises from the larger expansion of the d orbital. However, the larger E_{DIST} value leads to the smaller BE value of **2** than that of **3**. The largest BE and E_{INT} values of **1** are interpreted in terms of the d_π orbital at the highest energy and the largest overlap $S(d_\pi-\pi^*)$ value. The smaller BE and E_{INT} values of $Pt(PH_3)_2(C_{60})$ than that of **1** is interpreted in terms of the presence of the doubly-occupied d_σ orbital in the Pt(0) center.

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