

MO Studies on Palladium(0)-Derivatives of Buckminsterfullerene (C<sub>60</sub>)

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Received January 6, 1995

The electronic structures of (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) and (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>60</sub>) are calculated by using the EHMO method with modified EH parameters. Our results for Pd-derivatives show that the carbon-carbon double bonds of C<sub>60</sub> and ethene react like those of electron-poor arenes and alkenes, which are analogous with the previous results for Pt-derivatives. In Pd-C<sub>60</sub> derivative the electronic charge transferred from filled palladium *d*-orbital is localized at the two carbon atoms of the double bond to which Pd-ligand is attached.

## Introduction

The interaction of fullerenes with molecules has been of fundamental interest, so several papers showed the chemical reactivity between metal (Os, Pt, Ir) complexes and C<sub>60</sub> via solution chemistry forming metal-C<sub>60</sub> bonds. Hawkins *et al.*<sup>1</sup> have synthesized a one-to-one C<sub>60</sub>-osmium tetroxide adduct, C<sub>60</sub>(OsO<sub>4</sub>)(4-*tert*-butylpyridine)<sub>2</sub>. Balch *et al.*<sup>2</sup> have shown that addition of an equimolar amount of a purple solution of C<sub>60</sub> in benzene to a yellow benzene solution of Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub> immediately forms a deep brown solution from which black-brown crystals of (η<sup>2</sup>-C<sub>60</sub>)Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>·5C<sub>6</sub>H<sub>6</sub> precipitate. It has been reported that, for the platinum complex [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Pt(η<sup>2</sup>-C<sub>60</sub>), the reactivity of C<sub>60</sub> is not like that of relatively electron-rich planar aromatic molecules such as benzene, that is, the carbon-carbon double bonds of C<sub>60</sub> behave chemically like those of very electron-deficient arenes and alkenes.<sup>3</sup> In terms of the platinum coordination sphere, it was found that this C<sub>60</sub> complex formed at the junction of two fused 6-membered rings (6-MRs) in C<sub>60</sub> closely resembles the structures seen for another platinum alkene complex, [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Pt(η<sup>2</sup>-ethylene). Also, using NMR spectra and X-ray crystallographic results of the hexa-substituted platinum derivative [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Pt<sub>6</sub>C<sub>60</sub>, Fagan *et al.*<sup>4</sup> have shown that the molecule has a multiply-substituted buckminsterfullerene with an octahedral array of platinum atoms. And they have investigated the electrochemical properties of the complexes (Ph<sub>3</sub>P)<sub>2</sub>Pt(η<sup>2</sup>-C<sub>60</sub>), (Et<sub>3</sub>P)<sub>2</sub>M(η<sup>2</sup>-C<sub>60</sub>), [(Et<sub>3</sub>P)<sub>2</sub>M]<sub>n</sub>C<sub>60</sub> (M = Ni, Pd, Pt; Et = ethyl, Ph = phenyl), and [(Et<sub>3</sub>P)<sub>2</sub>Pt]<sub>n</sub>C<sub>60</sub> (n = 2-4). Bashilov *et al.*<sup>5</sup> have shown the synthesis and molecular structure of the Palladium(0)-fullerene derivative (η<sup>2</sup>-C<sub>60</sub>)Pd(PPh<sub>3</sub>)<sub>2</sub>. Their structural studies for metal complexation suggest that the bonds between two fused six-membered rings in C<sub>60</sub> are the most reactive, these bonds being shorter and having the most double bond character. The fact that low-valent metal centers like Ir(I) and Pt(0) add to the carbon atoms at 6-6 membered ring fusions in C<sub>60</sub> was consistent with the predictions of bond localization energy calculations.<sup>6</sup>

*Ab initio* results<sup>7</sup> for (H<sub>3</sub>P)<sub>2</sub>Pt(η<sup>2</sup>-C<sub>60</sub>) have shown that the charge transfer from Pt fragment is 0.926 and the binding energy between fragments (Pt(PH<sub>3</sub>)<sub>2</sub> and C<sub>60</sub>) is 0.95 eV. Fann *et al.*<sup>8</sup> have used the EHMO method to calculate the electronic correlation between C<sub>60</sub> and the bunnyballs (Os-C<sub>60</sub>, Ru-C<sub>60</sub> and Mn-C<sub>60</sub> complexes). The energy level correlation of C<sub>60</sub> in their EH work is different from those of 3D-Hückel,<sup>9</sup>

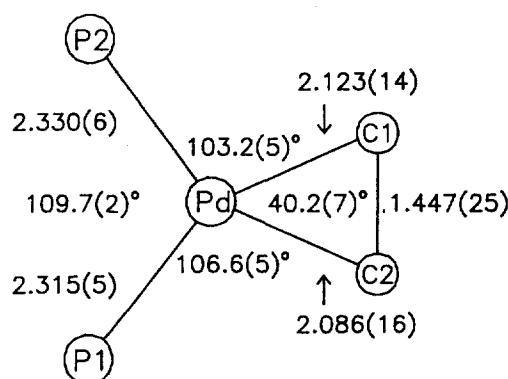


Figure 1. Geometry of the Pd coordination spheres in (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>60</sub>).<sup>7</sup>

DV-Xα,<sup>10</sup> and CNDO/S.<sup>11</sup> Lee *et al.*<sup>13</sup> have used the EHMO method to calculate the electron energy level correlation of C<sub>60</sub> and C<sub>60</sub>-Pt derivative. Results with modified parameter set in our previous work reasonably represent *ab initio* result of Morokuma and Koga.<sup>7</sup>

## Model and Calculation

We have calculated the electronic structure and properties of (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>60</sub>) and (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) using the EHMO method. The previous parameter set (parameter set 1) and the modified parameter set (parameter set 2) for carbon and the Hückel constant are used. The parameters of the other atoms (H, P and Pd) in these complexes are not changed in this work (see APPENDIX).<sup>12</sup> The results are compared with those for the Pt-derivatives. For the sake of simplifying the calculations, we substitute hydrogens for the phenyl groups of Pd-ligands. The distances and the bond angles around palladium in Pd-C<sub>60</sub> derivative are obtained from reference [7] and shown in Figure 1, and those in Pd-C<sub>2</sub>H<sub>4</sub> derivative are taken from those of Pt-C<sub>2</sub>H<sub>4</sub> derivative.<sup>3</sup> But as far as we know both experimental and theoretical studies of the complex formed by addition of Pd-ligand to a junction of 5- and 6-MRs of C<sub>60</sub> were not reported. The difference of structure between two types of Pd-C<sub>60</sub> complex, and the variation of bond lengths around the fusion of 5-6MRs of C<sub>60</sub> affected by Pd-ligand are not considered.

The fragment molecular orbital (FMO) calculations for

**Table 1.** Results from EH-FMO Calculations for (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) and (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>60</sub>) with Each Parameter Set

	Parameter sets	HOMO-LUMO gap (eV)			Charge of Pd(PH <sub>3</sub> ) <sub>2</sub>	Charge variation of Pd, Δq	Relative BE (eV) <sup>a</sup>
		(H <sub>3</sub> P) <sub>2</sub> Pd	R	(H <sub>3</sub> P) <sub>2</sub> Pd(η <sup>2</sup> -R)			
(H <sub>3</sub> P) <sub>2</sub> Pd(η <sup>2</sup> -C <sub>2</sub> H <sub>4</sub> )	1	6.02	3.98	4.04	0.395	0.349	0.00
	2	6.23	4.94	4.27	0.624	0.546	0.00
(H <sub>3</sub> P) <sub>2</sub> Pd(η <sup>2</sup> -C <sub>60</sub> ), (at 6-6MR)	1	6.05	1.46	1.36	0.427	0.369	0.07
	2	6.20	1.95	0.15	1.113	0.983	1.09
(H <sub>3</sub> P) <sub>2</sub> Pd(η <sup>2</sup> -C <sub>60</sub> ), (at 5-6MR)	1	6.05	1.60	0.96	0.305	0.295	-0.42
	2	6.20	2.06	0.33	1.741	1.587	-0.45

R=C<sub>2</sub>H<sub>4</sub> or C<sub>60</sub>; Δq=Charge of Pd in (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-R)-Charge of Pd in Pd(PH<sub>3</sub>)<sub>2</sub>; a=(the sum of Energies of (H<sub>3</sub>P)<sub>2</sub>Pd and R-Energy of Complex)-BE of (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)

**Table 2.** The Net Charges of The Carbon Atoms of C<sub>2</sub>H<sub>4</sub> and C<sub>60</sub> Attached by Pd-ligand

Complex	Parameter sets	Net charge of carbons			
		Fragment		Complex	
		C1	C2	C1	C2
(H <sub>3</sub> P) <sub>2</sub> Pd(η <sup>2</sup> -C <sub>2</sub> H <sub>4</sub> )	1	-0.08	-0.08	-0.24	-0.25
	2	-0.18	-0.18	-0.47	-0.47
(H <sub>3</sub> P) <sub>2</sub> Pd(η <sup>2</sup> -C <sub>60</sub> ), (at 6-6MR)	1	-0.08	-0.08	-0.12	-0.12
	2	-0.05	-0.05	-0.20	-0.21
(H <sub>3</sub> P) <sub>2</sub> Pd(η <sup>2</sup> -C <sub>60</sub> ), (at 5-6MR)	1	0.00	0.00	0.03	0.03
	2	0.00	0.00	-0.04	-0.06

(H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>60</sub>) with fragments, η<sup>2</sup>-C<sub>60</sub> and Pd(PH<sub>3</sub>)<sub>2</sub>, and for (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) with fragments, η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub> and Pd(PH<sub>3</sub>)<sub>2</sub> give orbital interaction diagrams as shown in Figures 2, 3 and 4.

## Results and Discussion

Table 1 shows the energy differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in complexes and each fragment, the charges of Pd(PH<sub>3</sub>)<sub>2</sub> fragment in each complex, the charge variations of Pd between Pd-ligand and Pd-derivatives, and the relative binding energies (BE) of each complex from the two fragments.

The relative BE of parameter set 2 is reasonable, not absolute. Here the BE means the negative formation energy of complex from fragments. (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>60</sub>) (complex type 1) formed by addition of Pd-ligand to a junction of 6-6MRs of C<sub>60</sub> is the most stable. The relative BE of the cases in parameter set 2 are higher than those in parameter set 1. And the relative BE for (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) is higher than that for Pd-C<sub>60</sub> derivative (complex type 2) formed with Pd-ligand attaching to a junction of 5- and 6-MRs of C<sub>60</sub>. These results are almost the same as our earlier results of Pt-derivatives.<sup>13</sup> The exception is that the absolute value of complex formation energy of Pd-ethylene derivative with parameter set 1 is smaller than that of Pd-C<sub>60</sub> complex type 1, but vice versa in the results of Pt-complexes.

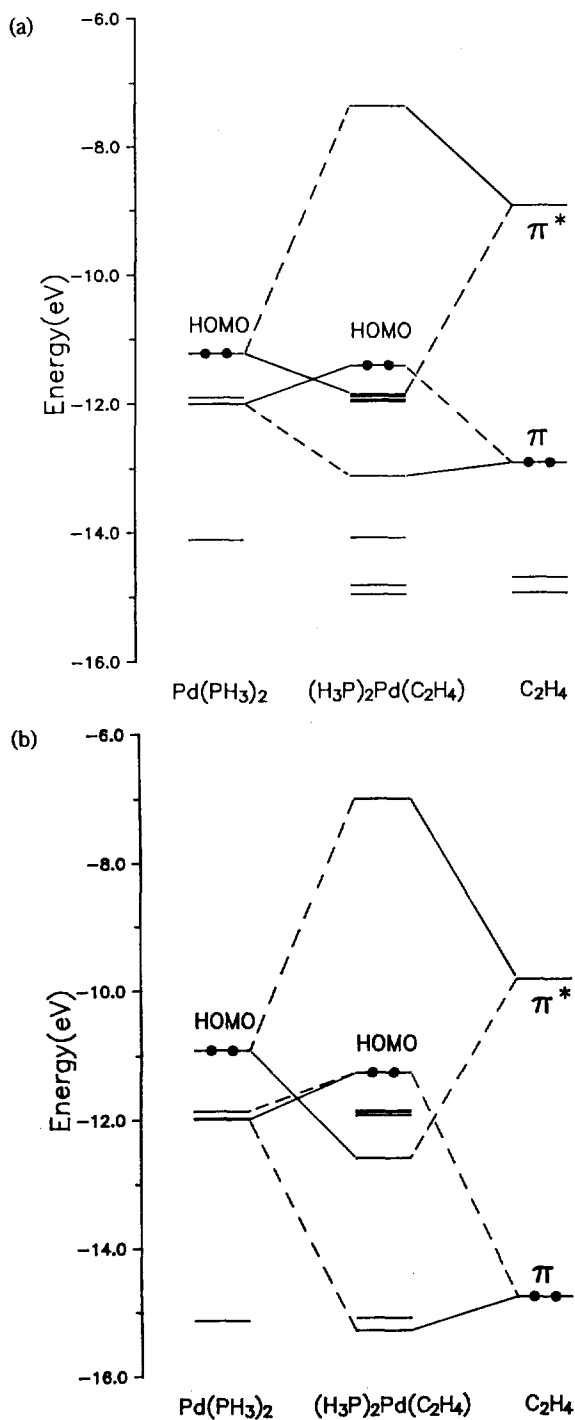
The electron acceptivity of C<sub>2</sub>H<sub>4</sub> or C<sub>60</sub> is stronger in param-

eter set 2 than set 1. In parameter set 2 case, the electron acceptance of C<sub>60</sub> in Pd-C<sub>60</sub> derivatives is stronger in type 2 than type 1. The electron acceptivity in Pd-derivatives is stronger in C<sub>60</sub> than ethylene. But in parameter set 1 case, the electron acceptivity of C<sub>60</sub> in Pd-C<sub>60</sub> complex is stronger in type 1 than type 2. In Pd-derivatives, the strength of the electron acceptance of ethylene is between those of C<sub>60</sub> in type 1 and type 2.

Table 2 shows the net charges of the carbon atoms of C<sub>2</sub>H<sub>4</sub> and C<sub>60</sub>, which are the carbon sites attached by Pd-ligand in fragments and complex. In the results of EH calculations for Pd-C<sub>2</sub>H<sub>4</sub> with each parameter set, the net charges of the carbon atoms at the interacting carbons become larger in complex than in fragment, and the charges of the interacting carbons are larger for parameter set 2 than for set 1. In Pd-C<sub>60</sub> complex type 1, the electron charges of the two carbon sites attached by Pd-ligand are larger in parameter set 2 than set 1. The electron at the sites in the double bond of C<sub>60</sub> is more localized in Pd-C<sub>60</sub> than that in Pt-C<sub>60</sub>. But in the case of Pd-C<sub>60</sub> complex type 2, the electron charges of the two carbon atoms are small, in comparison with the electron acceptivity of C<sub>60</sub> from Pd-ligand (Table 1).

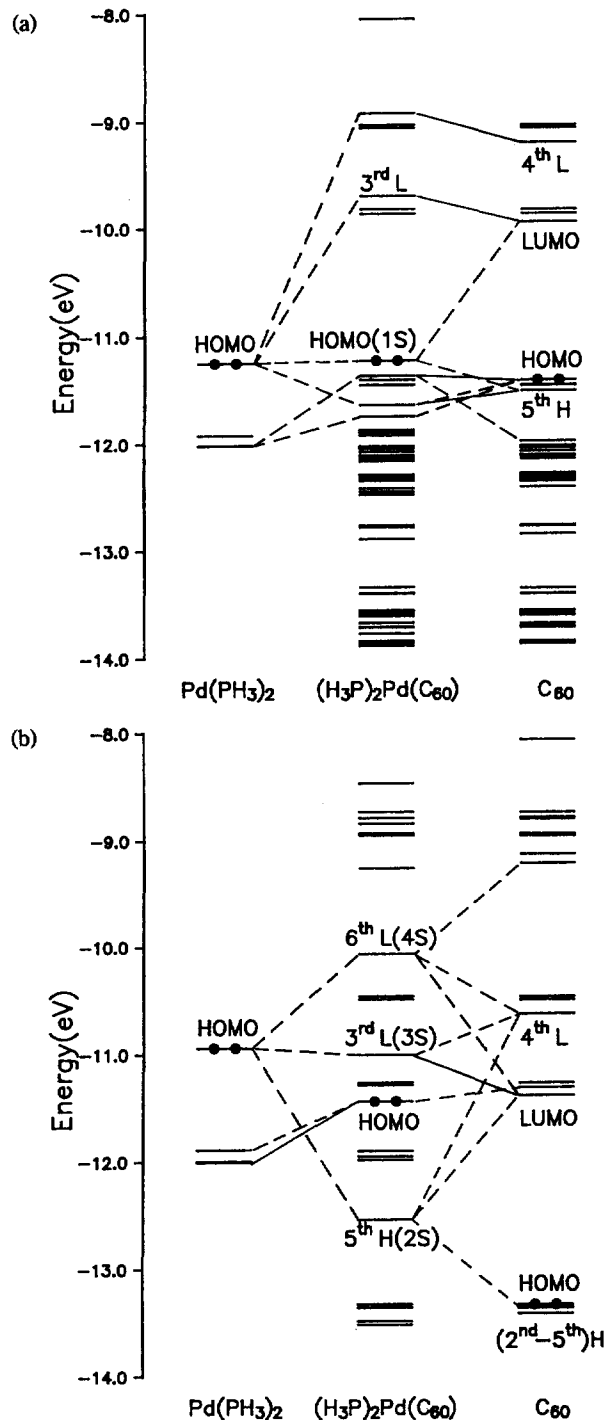
The HOMO-LUMO energy gap for the fragment C<sub>60</sub> and C<sub>2</sub>H<sub>4</sub> is larger in parameter set 2 than in set 1. As shown in Figures 2, 3 and 4, the orbital interaction of the HOMO of Pd-ligand and the LUMO of C<sub>60</sub> (or C<sub>2</sub>H<sub>4</sub>) is larger in parameter set 2 than in set 1. In both of two Pd-C<sub>60</sub> type complexes the energy gap is smaller than fragment C<sub>60</sub>.

At first, Figure 2 shows the orbital interaction diagrams by the calculations of (H<sub>3</sub>P)<sub>2</sub>Pd(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) in which phosphorus, palladium, and carbon atoms are closely associated with C<sub>2v</sub> point group symmetry. Figure 2(a) is the results with the parameter set 1. The fragment orbitals from the HOMO to 5<sup>th</sup> HOMO of Pd-ligand have strong nonbonding metal orbital character. There is an interaction between the LUMO (π\*) of the ethylene-fragment and the HOMO orbital of Pd-fragment, in which the HOMO of d<sub>xy</sub> character is stabilized by a symmetrically matched π\* orbital as electron acceptor. This interaction forms the LUMO and the 2<sup>nd</sup> HOMO of this complex. But the interaction between the 5<sup>th</sup> HOMO of d<sub>xy</sub> character of Pd-fragment and π-orbital of ethylene has little of effect on the stabilization of complex. Figure 2(b) shows the orbital interaction diagrams with the parameter set 2. As in the Figure 2(a), the HOMO of Pd-fragment interacts with



**Figure 2.** Molecular orbital interaction diagrams of  $(\text{H}_3\text{P})_2\text{Pd}(\eta^2\text{-C}_2\text{H}_4)$ , (a) with the (previous) parameter set 1 and (b) with the (modified) parameter set 2.

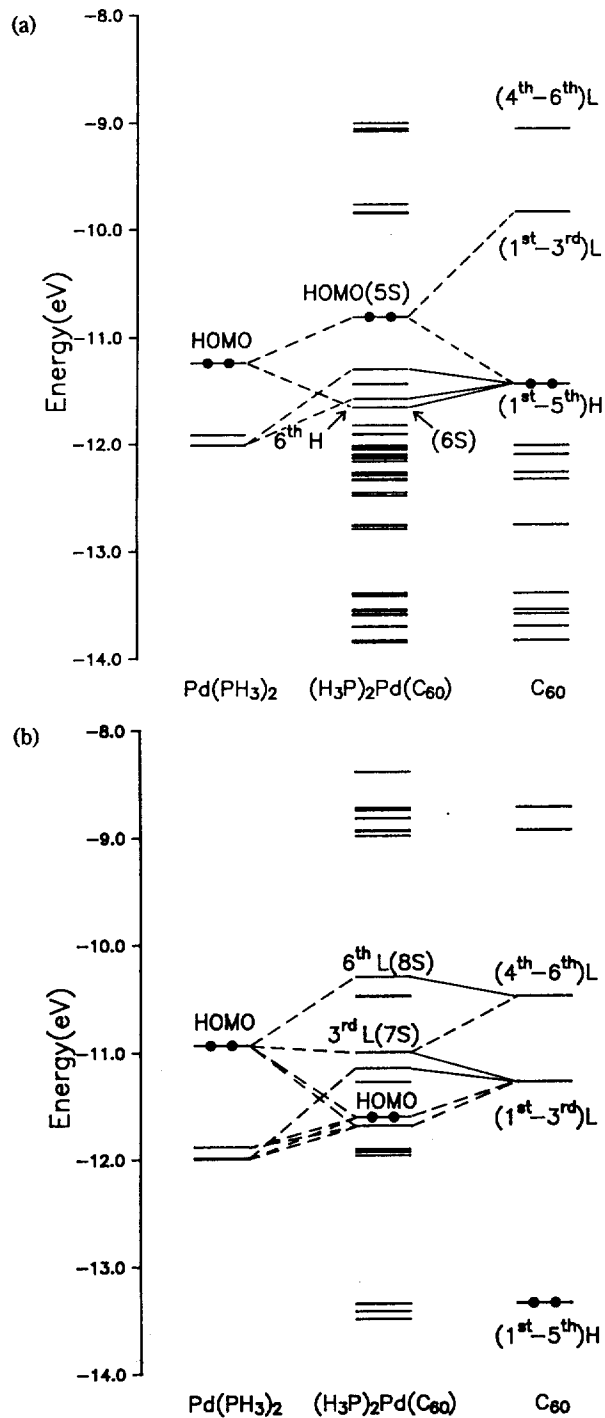
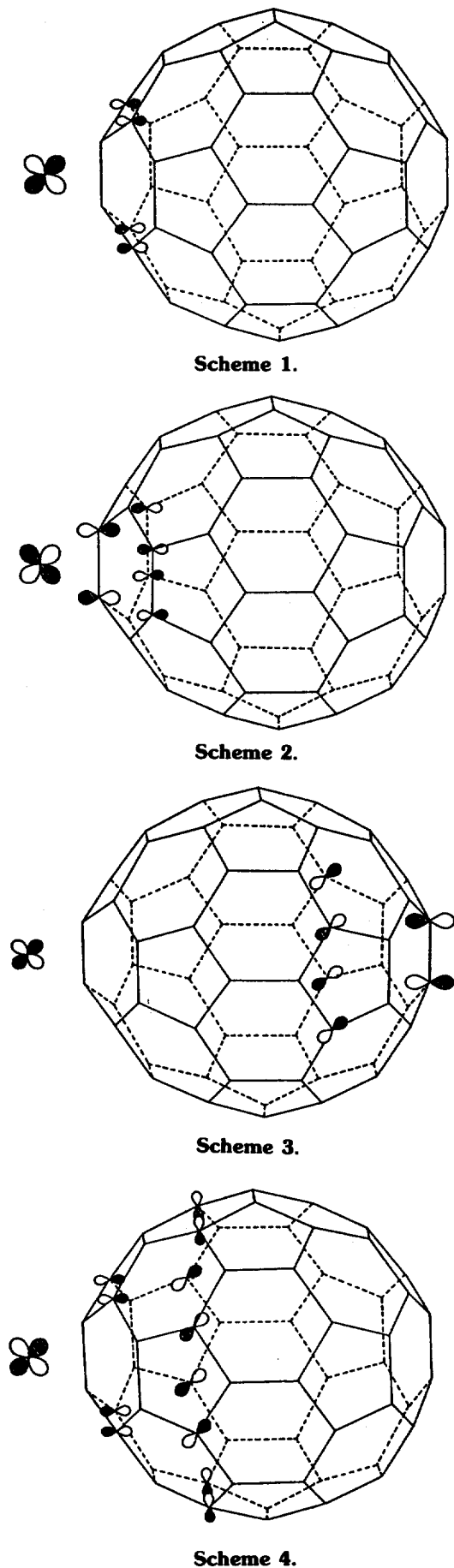
$\pi^*$  (LUMO) of ethylene, forms a stabilized molecular orbital ( $5^{\text{th}}$  HOMO of complex), and transfers electron to ethylene analogous with Pt- $\text{C}_2\text{H}_4$  derivative.<sup>13</sup> Also, there is an interaction between the  $5^{\text{th}}$  HOMO of Pd-ligand and  $\pi$ -orbital of ethylene fragment. But the energy difference of the HOMO of Pd-fragment and the LUMO of ethylene in Figure 2(b) is smaller than that in Figure 2(a), and then the interaction



**Figure 3.** Molecular orbital interaction diagrams of  $(\text{H}_3\text{P})_2\text{Pd}(\eta^2\text{-C}_{60})$  formed by addition of Pd-ligand to a junction of two 6-MRs of  $\text{C}_{60}$ , (a) with the (previous) parameter set 1 and (b) with the (modified) parameter set 2. Here numbered H(L) means  $n^{\text{th}}$  HOMO (LUMO), and (numbered S) means the MO energy level of Scheme number.

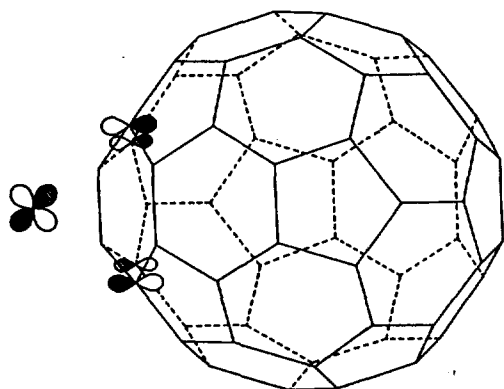
and the electron acceptance of ethylene in Figure 2(b) is larger than in Figure 2(a).

The molecular orbital interaction diagrams by the EHMO calculations for Pd- $\text{C}_{60}$  complex type 1,  $(\text{H}_3\text{P})_2\text{Pd}(\eta^2\text{-C}_{60})$ , are

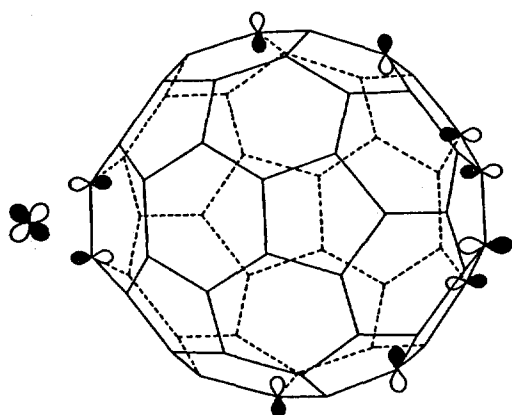


**Figure 4.** Molecular orbital interaction diagrams of  $(\text{H}_3\text{P})_2\text{Pd}(\eta^2\text{-C}_{60})$  formed by addition of Pd-ligand to a junction of 5- and 6-MRs of  $\text{C}_{60}$ , (a) with the (previous) parameter set 1 and (b) with the (modified) parameter set 2. Here numbered H(L) means  $n^{\text{th}}$  HOMO (LUMO), and (numbered S) means the MO energy level of Scheme number.

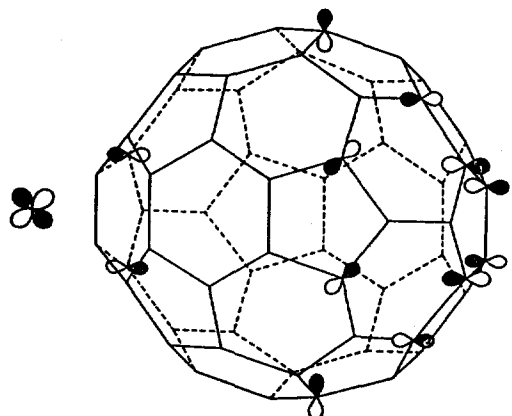
exhibited in Figure 3. The results with the parameter set 1 are shown in Figure 3(a), the results with set 2 are in Figure 3(b). From calculations of  $(\text{H}_3\text{P})_2\text{Pd}(\eta^2\text{-C}_{60})$  with parameter set 1, the interactions between the HOMO of  $d_{z^2}$  character of Pd-fragment and both the LUMO and 3<sup>rd</sup> HOMO



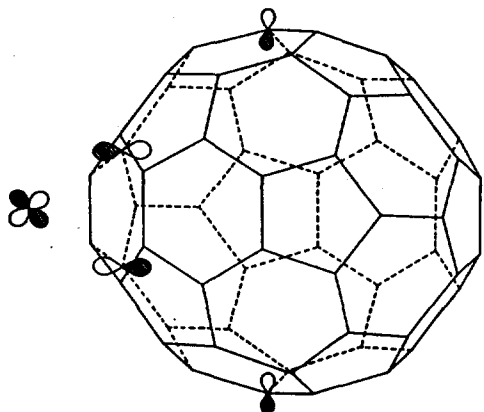
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

of  $C_{60}$  produce three molecular orbitals (one bonding and two antibonding) of Pd-derivative of this type 1. The 3<sup>rd</sup> LUMO of Pd-complex comes mainly from nonbonding MO of  $C_{60}$  fragment. But the HOMO of Pd-derivative has antibonding character as shown in Scheme 1. In Figure 3(b), which is the result with parameter set 2, it is different from the  $(H_3P)_2Pd(\eta^2-C_2H_4)$  in that the HOMO of Pd-ligand has higher energy than the LUMO of  $C_{60}$ -fragment. But the energy difference between the HOMO of  $d_{xz}$  character of Pd-fragment and the LUMO of  $C_{60}$  is much smaller than that in the case with parameter set 1. The fragment HOMO of Pd-ligand is stabilized by both the LUMO and the 4<sup>th</sup> LUMO of  $C_{60}$  fragment. These fragment orbitals make one bonding molecular orbital (the 5<sup>th</sup> HOMO) and two antibonding molecular orbitals (the 3<sup>rd</sup> and the 6<sup>th</sup> LUMOs of Pd-derivative). Scheme 2 shows the 5<sup>th</sup> HOMO of Pd-derivative. The LUMO and the 4<sup>th</sup> LUMO of  $C_{60}$  fragment are hybridized to form the 3<sup>rd</sup> LUMO of this type complex with the HOMO of Pd-fragment. The orbital lobes in the opposite of the attached position of  $C_{60}$  are larger in the 3<sup>rd</sup> LUMO of Pd-complex as shown in Scheme 3. Scheme 4 of the 6<sup>th</sup> LUMO of this complex shows antibonding character. But the orbital coefficients of the attached carbon atoms of  $C_{60}$  is very small. In the result (Figure 3(a)) with parameter set 1, the 3<sup>rd</sup> LUMO is alike with Scheme 3 and the HOMO alike with Scheme 4. In this way electron is transferred to  $C_{60}$ -fragment from Pd-ligand. These interactions between Pd-ligand and  $C_{60}$  in the diagrams of Figure 3 are analogous to those<sup>13</sup> of Pt-ligand and  $C_{60}$ .

Figure 4 shows the results from the calculations for Pd- $C_{60}$  complex of type 2. Figure 4(a) is the results with parameter set 1. The HOMO of Pd-fragment and the HOMO of  $C_{60}$  fragment interact to make the unstable antibonding MO (HOMO) and the bonding MO (6<sup>th</sup> HOMO) of Pd- $C_{60}$  derivative. Schemes 5 and 6 represent the HOMO and 6<sup>th</sup> HOMO of Pd-complex of this type. In Scheme 5 of antibonding character the orbital lobes of the next ones to the attached carbon atoms of  $C_{60}$  are considerably large. In Scheme 6 of the 6<sup>th</sup> HOMO of Pd-derivative the interaction analogy to the Scheme 2 of Pd-complex type 1 appears, and the orbital lobes of the opposite ones of the attached sites of  $C_{60}$  are appropriately large. Figure 4(b) as the results of parameter set 2 shows interactions between nonbonding metal orbitals of  $Pd(PH_3)_2$ -fragment and unoccupied fragment orbitals of  $C_{60}$ . The 6<sup>th</sup> and 3<sup>rd</sup> LUMOs of this Pd- $C_{60}$  complex are displayed in Schemes 7 and 8 which are antibonding, but the orbital coefficients of the carbon atoms bonded to the Pd-ligand are disappeared. The HOMO of Pd-ligand is stabilized to make the HOMO and unoccupied MOs of this type 2 of Pd- $C_{60}$  derivative. This fragment orbital interaction diagram is more a little complicate than that of Pt- $C_{60}$  complex.

## Conclusion

From EH-FMO calculations using the modified parameter, the HOMO of Pd-fragment interacts with electron-empty fragment orbitals of  $C_{60}$  or ethylene. The HOMO is stabilized by transferring its electrons to the empty orbitals of  $C_{60}$  or  $C_2H_4$ . Our results show that carbon-carbon double bonds of  $C_{60}$  and  $C_2H_4$  react like those of electron-poor arenes and alkenes, and also that  $C_{60}$  is more electron-susceptible than

## APPENDIX; Parameters used in EHMO Calculation

Atom	s			p			d						
	n	-IP	ζ	n	-IP	ζ	n	-IP	ζ <sub>1</sub>	ζ <sub>2</sub>	c <sub>1</sub>	c <sub>2</sub>	
H	1	13.6	1.30										
C(set 1)	2	21.4	1.625	2	11.4	1.625							
C(set 2)	2	21.4	1.92	2	12.67	1.92							
P	3	18.6	1.75	3	14.0	1.30							
Pd	5	7.32	2.19	5	3.75	2.152	4	12.02	5.983	2.613	0.5535	0.6701	

Here, the Hückel constant, K is 1.75 and 2.35 in parameter set 1 and 2, respectively.

C<sub>2</sub>H<sub>4</sub>. In Pd-C<sub>60</sub> derivative type 1, two carbon sites of the double bond of C<sub>60</sub> localize electrons transferred from Pd-ligand.

**Acknowledgment.** This research was supported through KOSEF grant 94-080011013. We are grateful to Professor Y. Lee, KAIST, for his comment.

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Electrical Properties of TiO<sub>2-x</sub> Thin Films by Thermal Oxidation

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Received February 23, 1995

The electrical properties of the TiO<sub>2-x</sub> thin films prepared by thermal oxidation from titanium sheets have been studied. The films by water vapor oxidation are oxidized more homogeneously than those by air oxidation. The electrical contact to measure the electrical conductivity of the TiO<sub>2-x</sub> electrodes is improved when the electrode surface is plated with silver. The hysteresis of the electrical conductivity curves is improved by applying alternating current rather than direct current on both sides of the electrode. The observed energy gap,  $E_d$  are 0.05-0.16 and 0.11-0.76 eV, respectively, at low and high temperatures region. These values of the TiO<sub>2-x</sub> electrode prepared by water vapor oxidation are similar to those of single crystal TiO<sub>2</sub>. The values of donor concentration,  $N_D$ , are observed about 10<sup>15</sup>-10<sup>19</sup> and 10<sup>17</sup>-10<sup>21</sup> cm<sup>-3</sup>, respectively, at low and high temperatures region. These values obtained at high temperature region are consistent with the values obtained from Mott-Schottky plot.

## Introduction

The electrical and photo-electrochemical properties of

semiconductor electrodes have been studied for the purpose of changing the solar energy into an electrochemical energy.<sup>1-35</sup> Many semiconductor materials have been used as