Synthesis and Characterization of Pentaarylated [60]Fullerene Coordinated Complexes [(η^2-$Ar_5C_{60}H$)M(PPh_3)$_2$] (M = Pt, Pd) and an ab initio Study on Their Isomerism

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This paper reports on the first examples of η^2-pentaarylated [60]fullerene organometallic complexes [(η^2-$Ar_5C_{60}H$)M(PPh_3)$_2$] (**1**: Ar = Ph, M = Pt; **2**: Ar = *m*-MeC_6H_4, M = Pt; **3**: Ar = *p*-MeC_6H_4, M = Pt; **4**: Ar = Ph, M = Pd; **5**: Ar = *m*-MeC_6H_4, M = Pd; **6**: Ar = *p*-MeC_6H_4, M = Pd), which were synthesized by treatment of [M(PPh_3)$_4$] with $Ar_5C_{60}H$ and fully characterized by elemental analyses and their ^1H NMR, ^{31}P NMR, IR, UV/Vis, and FAB-MS data. The ^1H NMR spectra displayed by the protons directly bonded to the C_{60} core and the ^{31}P NMR spectra caused by the PPh_3 ligands indicated that complexes **1**–**6** exist as mixtures of isomers. To gain insights into the isomerism of **1**–**6**, the regioselectivity of the pentaarylated derivatives $Ar_5C_{60}H$ as ligands coordinated to Pt^0 or Pd^0 has been studied by means of ab initio calculations. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

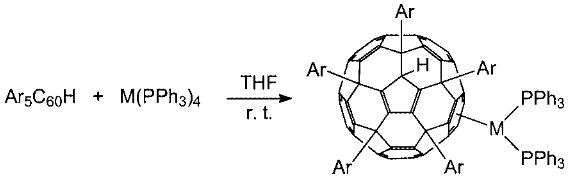
It is known that the [60]fullerene derivatives $Ar_5C_{60}H$ were first synthesized by a three-pot method starting from C_{60}, involving chlorination of C_{60} to give $C_{60}Cl_6$, arylation of $C_{60}Cl_6$ with benzene or substituted benzene, and reduction of $Ar_5C_{60}Cl$ with an excess of PPh_3.[1,2] Later on, a more convenient one-pot method for preparation of $Ar_5C_{60}H$ was discovered, involving treatment of C_{60} with organocopper/magnesium reagents $Ar_2CuMgBr$, followed by treatment of the reaction mixture with aqueous NH_4Cl.[3,4] It is conceivable that the pentaarylated [60]fullerene derivatives $Ar_5C_{60}H$ might form organometallic complexes with single, double, triple, and even multiple metal centers through their pentaarylated cyclopentadienyl rings and other sites of the C_{60} core in a variety of coordination modes from η^1 to η^6. Up to now, however, except for the η^5-pentaarylated [60]fullerene organometallic compounds such as η^5-$Ph_5C_{60}M$ (M = Li, K, Tl, CuPEt$_3$),[3] there are no other reported organometallic complexes that contain pentaarylated [60]fullerene ligands coordinated to metal centers in a mode from η^1 to η^4 or in an η^6-fashion.

During recent years we have been interested in the synthesis, structural characterization, and properties of organotransition metal fullerene derivatives.[5] As part of this project, we recently carried out an investigation into the reactions between transition metal complexes [M(PPh_3)$_4$] (M = Pt, Pd) and pentaarylated [60]fullerene derivatives $Ar_5C_{60}H$ to see which type of coordination mode might be adopted by $Ar_5C_{60}H$ in the products and whether the ligand-exchange reaction might be regioselective toward the reactive sites of pentaarylated [60]fullerene derivatives $Ar_5C_{60}H$. Here we report our results.

Results and Discussion

Synthesis and Characterization of Complexes [(η^2-$Ar_5C_{60}H$)M(PPh_3)$_2$] (1−6)

An equivalent of each transition metal complex [M(PPh_3)$_4$] (M = Pt, Pd) was treated with a pentaarylated [60]fullerene derivative $Ar_5C_{60}H$ (Ar = Ph, *m*-MeC_6H_4, *p*-MeC_6H_4) in THF at room temperature to give six products [(η^2-$Ar_5C_{60}H$)M(PPh_3)$_2$] (**1−6**) in 51−63% yields, as shown in Scheme 1.



1-6

	1	2	3	4	5	6
Ar	Ph	*m*-MeC_6H_4	*p*-MeC_6H_4	Ph	*m*-MeC_6H_4	*p*-MeC_6H_4
M	Pt	Pt	Pt	Pd	Pd	Pd
%	53	63	55	58	51	58

Scheme 1

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Apparently, products **1−6** can be formally regarded − similarly to the parent [60]fullerene metal complexes [(η^2-C_{60})M(PR_3)$_2$] (M = Pt,[6] Pd[7]) − as deriving from displacement of one PPh_3 ligand from M(PPh_3)$_3$ {generated in situ through dissociation of one PPh_3 ligand of starting material [M(PPh_3)$_4$]} by one equivalent of $Ar_5C_{60}H$. Interestingly, products **1−6** are, to the best of our knowledge, the first organometallic complexes containing pentaarylated [60]fullerene ligands $Ar_5C_{60}H$ coordinated to transition metals through their [6:6] bonds in an η^2-fashion.

Products **1−6** have been characterized by elemental (C,H,P) analysis and spectroscopic methods. In their FAB-MS spectra, while products **1−3**, **5**, and **6** show their molecular ions M^+ and their pentaarylated [60]fullerene ligand ions $Ar_5C_{60}H^+$ (Ar = Ph, *m*-MeC_6H_4, *p*-MeC_6H_4), product **4** displays the largest fragment ion [M^+ − Pd] and pentaarylated [60]fullerene ligand ion $Ph_5C_{60}H^+$. The UV/Vis spectra of **1−6** are all very similar to one another and each exhibits three absorption bands in the 239−489 nm range. In addition, the IR spectra of **1−6** each include four absorption bands, at 1431−1435, 1193−1190, 579−591, and 534−540 cm^{-1}, which resemble those of the free ligands C_{60}[8] and $Ar_5C_{60}H$ (Ar = Ph,[1] *m*-MeC_6H_4,[9] *p*-MeC_6H_4[2]).

For the ^1H NMR spectra, it should be noted that, while the hydrogen atom directly bonded to the C_{60} core in each of the free ligands $Ar_5C_{60}H$ (Ar = Ph,[3] *m*-MeC_6H_4,[9] *p*-MeC_6H_4[2]) displays only one singlet at δ = 5.2−5.3 ppm, the corresponding hydrogen atom in each of the compounds **1−6** exhibits two to four singlets at δ = 5.1−5.3 ppm. This implies that **1−6** might exist as mixtures of isomers. Similarly to the ^1H NMR spectra, the ^{31}P NMR spectra of **1−6** each show two to four singlets at δ = 29−33 ppm for the P atoms, which also suggests that compounds **1−6** exist as isomer mixtures. The ^{31}P NMR spectra of **1−3**, however, in contrast to those of **4−6**, have two groups of satellite peaks at both sides of the groups of singlets at $\delta \approx 30$ ppm, caused by ^{195}Pt-^{31}P coupling. It is worth noting that the chemical shifts ($\delta \approx 30$ pm) of **1−6** and the ^{195}Pt-^{31}P coupling constants ($J \approx 3960$ Hz) of **1−3** are similar to those of [(η^2-C_{60})Pt(PPh_3)$_2$][6,10] and [(η^2-C_{60})Pd(PPh_3)$_2$],[7] apparently due to their similar structures. Figures 1 and 2 show the partial ^1H NMR and the whole ^{31}P NMR spectra of products **2** and **4**, respectively. The four singlets at $\delta \approx 5.2$ ppm in Figure 1(a) could each be assigned to the hydrogen atom directly bonded to C_{60} core in each of four isomers of product **2**, whereas the four singlets at $\delta \approx 30$ ppm in Figure 1(b) could each be attributed to the two P atoms in each of the four isomers. Similarly, the three singlets at $\delta \approx 5.3$ ppm in Figure 2(a) and the three singlets at $\delta \approx 30$ ppm in Figure 2(b) could be assigned to the hydrogen atoms directly bonded to the C_{60} cores and to the P atoms in three isomers of product **4**, respectively. In order to obtain some further details concerning the possible isomers of **1−6**, we carried out a computational study on the simplest ligand $Ph_5C_{60}H$ and its Pt complex [(η^2-$Ph_5C_{60}H$)Pt(PPh_3)$_2$] (**1**).

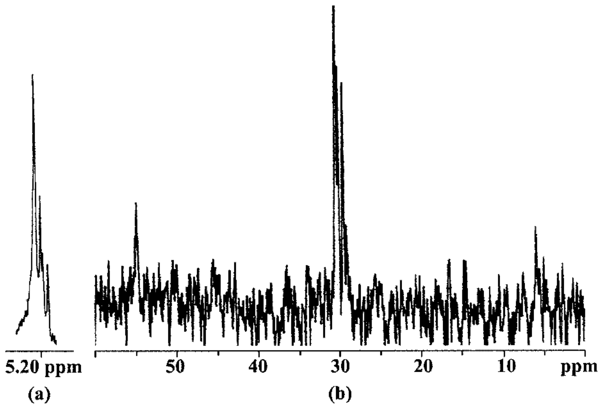


Figure 1. The partial ^1H NMR (a) and ^{31}P NMR (b) spectra of **2**

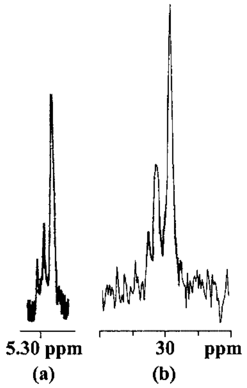


Figure 2. The partial ^1H NMR (a) and ^{31}P NMR (b) spectra of **4**

Computational Study on Possible Isomers of 1−6

As shown in Figure 3, the pentaarylated hydro[60]fullerenes $Ar_5C_{60}H$ (Ar = Ph, *m*-MeC_6H_4, *p*-MeC_6H_4), unlike the highly I_h-symmetric [60]fullerene, are C_s-symmetric molecules, each of which contains a series of carbon−carbon double bonds represented by **A−O**, **B′**, **C′**, **E′−K′** and **M′−O′**. The double bonds represented by capital letters and those represented by the corresponding capital letters with primes are located symmetrically on the two sides of the symmetrical plane of $Ar_5C_{60}H$, which are actually the same in terms of their ability to coordinate with metal atoms M (M = Pt, Pd). Hence, each of the pentaarylated $Ar_5C_{60}H$ has 14 kinds of [6:6] double bonds formed between two six-membered rings represented by **A−N** or **A**, **B′**, **C′**, **D**, **E′−K′**, **L**, **M′**, **N′** and one kind of [6:5] double bonds formed between six- and five-membered rings, represented by **O** and **O′**. However, since the **L−O** or **M′−O′** double bonds could not coordinate with metal atoms M, due to the great steric hindrance between the two large PPh_3 ligands attached to M and the five aryl groups located around the double bonds **L−O** or **M′−O′**, products [(η^2-$Ar_5C_{60}H$)M(PPh_3)$_2$] (**1−6**) each have only 11 possible structural isomers **A−K** or **A**, **B′**, **C′**, **D**, **E′−K′** generated through coordination of the remaining 11 kinds of the corresponding [6:6] double bonds. In fact, the isomers, which are derived from coordination of the [6:6] double bonds **B′**,

C′, and **E**′−**K**′ with M atoms, are the enantiomers of isomers **B**, **C**, and **E**−**K**.

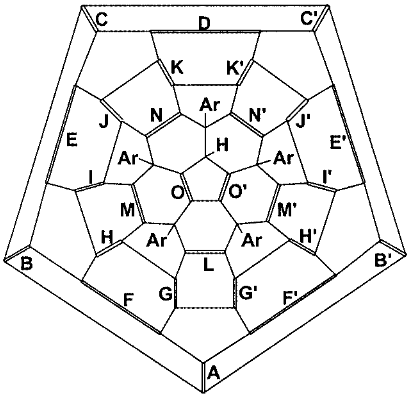


Figure 3. Possible η^2-coordinating sites of $Ar_5C_{60}H$ in a Schlegel diagram

Computational chemistry methods had previously been utilized to study [60]fullerene platinum and palladium complexes in the model complex $[(\eta^2\text{-}C_{60})Pt(PH_3)_2]$.[11−14] In order to further establish the actually existing isomers of **1**−**6** and the regioselectivity of the involved η^2-$Ar_5C_{60}H$ ligands in the products, we chose the platinum complex $[(\eta^2\text{-}Ph_5C_{60}H)Pt(PPh_3)_2]$ (**1**) as a representative with which to carry out ab initio DFT calculations on its 11 possible isomers. It is worth noting that we did not use $[(\eta^2\text{-}Me_5C_{60}H)Pt(PH_3)_2]$ as a model complex in calculations in this case, since it is oversimplified for the strong steric hindrance existing between the phenyl groups in **1**, which is very important for the isomer energies and the ^1H NMR calculations.

Density functional theory (DFT) calculations at the B3LYP level were performed in full structural optimizations. With the optimized structures, the ^1H magnetic shielding coefficients for the proton directly bonded to the C_{60} core were obtained by Hartree−Fock GIAO method. The energies and isotropic ^1H magnetic shielding coefficients are compiled in Table 1.

The reaction involved in the production of the 11 isomers is assumed to be thermodynamically controlled. Provided that a transformation equilibrium among all of the 11 isomers is present, the abundances of the isomers would be determinable only by their energy differences according to the Boltzmann distribution, as shown in Equation (1), where k, T, n_i, p_i, and E_i are the Boltzmann constant, absolute temperature, number of enantiomers of isomer i, and the abundance and energy of isomer i, respectively.

$$p_i = n_i e^{-E_i/kT} / \sum_j n_j e^{-E_j/kT} \quad (1)$$

As can be seen from Table 1, only six (namely **A**−**F**) of the 11 isomers have noticeable abundances at 298 K, the other isomers **G**−**K** derived from the corresponding double bonds **G**, **H**, **I**, **J**, and **K** having very low abundance.

The simulated partial ^1H NMR spectrum can be drawn from the isomer abundance data (peak areas) and the calculated ^1H shielding coefficients (chemical shifts). Figure 4(b) shows the calculated ^1H NMR spectrum of the isomer mixture of **1**, in which the peaks of isomers **F** and **A** or **B** and **D** are overlapped due to their very close values of the shielding coefficients. The similarity of Figure 4(b) with the actual spectrum Figure 4(a) suggests that the ab initio result is logical and acceptable. The four ^1H NMR signals of the proton directly bonded to the C_{60} core shown in Figure 4(a) can be assigned to isomers **F**+**A**, **B**+**D**, **C**, and **E**, respectively. It follows that this computational result is different from our initial assignment described above, in which each experimental singlet is related to one single isomer.

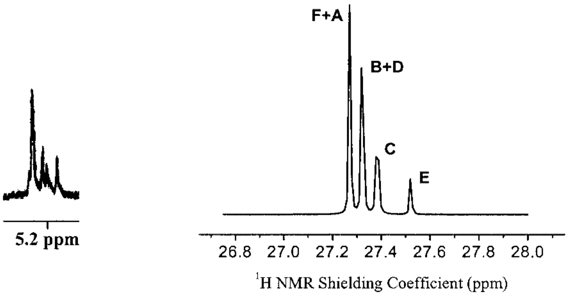
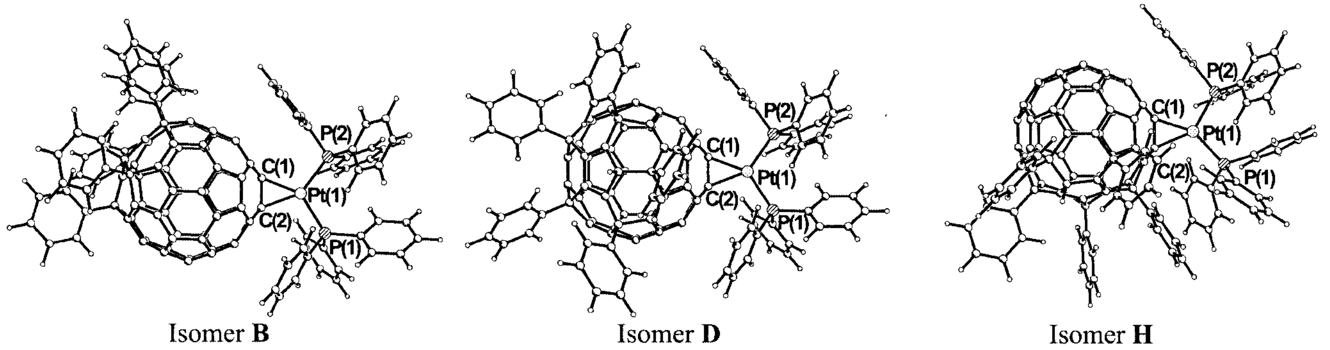


Figure 4. The partial ^1H NMR spectrum of the isomer mixture of **1**

Table 1. Calculated properties of the isomers of **1**

Coordination site of Pt	Number of enantiomer(s)	Energy [a. u.]	Estimated abundance at 298 K	^1H magnetic shielding coefficient [ppm]
B/B′	2	−4935.59686992	0.296691	27.3226
C/C′	2	−4935.59680000	0.275489	27.3849
A	1	−4935.59679828	0.137494	27.2744
F/F′	2	−4935.59637593	0.175715	27.2699
D	1	−4935.59572960	0.044272	27.3296
E/E′	2	−4935.59551091	0.070218	27.5225
H/H′	2	−4935.58867981	0.000050	27.4275
J/J′	2	−4935.58803199	0.000025	27.2833
G/G′	2	−4935.58764336	0.000017	27.2804
K/K′	2	−4935.58761027	0.000016	27.7785
I/I′	2	−4935.58735725	0.000012	27.8293



Isomer **B** Isomer **D** Isomer **H**

Figure 5. Optimized structures of isomers **B**, **D**, and **H**

Some of the structural parameters of the optimized structures for isomers **B**, **D**, and **H**, together with the corresponding values of the crystal structure of [(η^2-C_{60})Pt(PPh_3)$_2$],[10] are presented in Table 2, whereas Figure 5 shows the optimized structures of the three isomers.

As shown in Table 2, the calculated values for the optimized structures are similar to the crystal structural data of [(η^2-C_{60})Pt(PPh_3)$_2$], which indicates the accuracy of the calculation. That we chose the optimized structures of isomers **B**, **D**, and **H** is to illustrate that the stability and thus the abundance of each isomer is directly related to the steric effect. As can be seen intuitively in Figure 5, the phenyl groups in both $Ph_5C_{60}H$ and PPh_3 are most crowded in isomer **H**, then intermediate in isomer **D**, and least crowded in isomer **B**. This is consistent with the magnitudes of the abundances **B** > **D** > **H** shown in Table 1. In addition, the energy sequence **B** < **D** < **H** shown in Table 1 is also consistent with the magnitudes of the steric repulsion between the five C_{60}-bonded phenyl groups and the six phenyl groups of the two tertiary phosphane ligands in **B**, **D**, and **H**. In fact, isomers **A**, **B**/**B′**, and **C**/**C′** are the most stable ones, since the steric repulsions in these isomers are among the smallest. Finally, it can be concluded that the steric repulsion between the bulky phenyl substituents is most probably the key factor for the regioselectivity of $Ar_5C_{60}H$ ligands in coordinating with transition metals Pt and Pd in an η^2-fashion to form products **1**−**6**.

Table 2. Selected structural parameters of [(η^2-C_{60})Pt(PPh_3)$_2$] and isomers **B**, **D**, and **H**

Compound	(η^2-C_{60})Pt(PPh_3)$_2$	B	D	H
Bond lengths [Å]:				
C(1)−C(2)	1.502	1.515	1.509	1.511
Pt(1)−C(1)	2.145	2.137	2.133	2.117
Pt(1)−C(2)	2.115	2.142	2.147	2.187
Pt(1)−P(1)	2.304	2.362	2.362	2.366
Pt(1)−P(2)	2.254	2.348	2.348	2.357
Bond angles [°]:				
C(2)−C(1)−Pt(1)	68.3	69.4	69.9	72.0
C(1)−C(2)−Pt(1)	70.4	69.1	68.8	67.0
C(1)−Pt(1)−C(2)	41.3	41.5	41.3	41.1
C(2)−Pt(1)−P(1)	107.1	101.1	102.5	111.2
C(1)−Pt(1)−P(2)	109.2	105.3	104.7	101.3
P(1)−Pt(1)−P(2)	102.4	112.1	111.5	101.3

Experimental Section

General: All reactions were carried out under highly purified nitrogen by use of standard Schlenk or vacuum-line techniques. THF was distilled from Na/benzophenone ketyl. All solvents were bubbled with nitrogen for at least 15 min before use. [Pt(PPh_3)$_4$],[15] [Pd(PPh_3)$_4$],[16] $Ph_5C_{60}H$,[3] (*m*-MeC_6H_4)$_5C_{60}H$,[9] and (*p*-MeC_6H_4)$_5C_{60}H$[9] were prepared by literature methods. IR spectra were measured with a Bio-Rad FTS 135 spectrophotometer, whereas $^1H\{^{31}P\}$ NMR and UV/Vis spectra were recorded with a Bruker AC P200 and a Shimadzu UV 240 spectrometer, respectively. Elemental analysis of C and H was performed with an Elementar Vario EL analyzer, while P was determined by the vanadomolybdophosphoric acid colorimetric method. Melting points were determined with a Yanaco MP-500 apparatus.

Preparation of [(η^2-$Ph_5C_{60}H$)Pt(PPh_3)$_2$] (1): A 100-mL three-necked flask fitted with a stirrer bar, a serum cap, and an N_2 inlet tube was charged with $Ph_5C_{60}H$ (44 mg, 0.04 mmol) and THF (15 mL). Pt(PPh_3)$_4$ (50 mg, 0.04 mmol) was then added and the reaction mixture was stirred for 0.5 h at room temperature. After removal of the solvent under vacuum, the residue was chromatographed on an Al_2O_3 column with toluene/petroleum ether (3:2) as eluent, and the pink band was collected. After removal of the solvent, 42 mg (57%) of **1** was obtained as a red-brown solid. M.p. > 300°C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 5.13, 5.20, 5.22, 5.28 (4 s, 1 H, $C_{60}H$), 7.05−7.90 (m, 55 H, 11 Ph) ppm. ^{31}P NMR [81.0 MHz, toluene, $(CD_3)_2CO$ lock signal, H_3PO_4]: δ = 28.95, 29.35, 29.96, 30.24 (4 s surrounded with satellite peaks, $J_{Pt\text{-}P}$ = 3959 Hz, 2 P) ppm. IR (KBr): $\tilde{\nu}$ = 516.5 (s), 534.7 (m), 585.0 (w), 693.3 (vs), 742.4 (s), 1029.3 (w), 1094.6 (m), 1434.3 (s), 1491.9 (m), 1598.4 (w), 2863.8 (w), 2952.5 (w), 3056.7 (w) cm^{-1}. UV/Vis (THF): λ_{max} (log ε) = 239.7 (5.14), 288.7 (4.98), 488.9 (4.18) nm. FAB-MS: *m*/*z* = 1826 [($Ph_5C_{60}H$)Pt(PPh_3)$_2^+$, ^{196}Pt], 1107 [$Ph_5C_{60}H^+$]. $C_{126}H_{56}P_2Pt$ (1826.86): calcd. C 82.84, H 3.09, P 3.39; found C 82.56, H 3.35, P 3.43.

Preparation of [{η^2-(*m*-MeC_6H_4)$_5C_{60}H$}Pt(PPh_3)$_2$] (2): Similarly, when (*m*-MeC_6H_4)$_5C_{60}H$ (47 mg, 0.04 mmol) was used in place of $Ph_5C_{60}H$, **2** (48 mg, 63%) was obtained as a red-brown solid. M. p. > 300°C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.03, 2.06, 2.17 (3 s, 15 H, CH_3 + 2 CH_3 + 2 CH_3), 5.13, 5.19, 5.21, 5.26 (4 s, 1 H, $C_{60}H$), 7.00−7.90 (m, 50 H, 6 Ph + 5 C_6H_4) ppm. ^{31}P NMR

[81.0 MHz, toluene, $(CD_3)_2CO$ lock signal, H_3PO_4]: δ = 29.02, 29.43, 29.99, 30.28 (4 s surrounded with satellite peaks, $J_{Pt\text{-}P}$ = 3962 Hz, 2 P) ppm. IR (KBr): ṽ = 516.9 (s), 534.1 (m), 580.0 (w), 693.2 (vs), 747.4 (s), 1094.5 (m), 1434.1 (m), 1480.2 (m), 1603.7 (w), 2856.0 (w), 2921.6 (w), 3052.9 (w) cm^{-1}. UV/Vis (THF): λ_{max} (log ε) 240.1 (5.16), 288.3 (5.01), 489.1 (4.20) nm. FAB-MS: *m*/*z* = 1895 [$\{(MeC_6H_4)_5C_{60}H\}Pt(PPh_3)_2^+$, ^{195}Pt], 1177 [$(MeC_6H_4)_5C_{60}H^+$]. $C_{131}H_{66}P_2Pt$ (1896.99): calcd. C 82.94, H 3.51, P 3.26; found C 82.79, H 3.74, P 2.91.

Preparation of [{η²-(*p*-MeC₆H₄)₅C₆₀H}Pt(PPh₃)₂] (3): Similarly, when (p-$MeC_6H_4)_5C_{60}H$ (47 mg, 0.04 mmol) was used in place of $Ph_5C_{60}H$, **3** (42 mg, 55%) was obtained as a red-brown solid. M. p. > 300°C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.26, 2.31, 2.36 (3 s, 15 H, CH_3 + 2 CH_3 + 2 CH_3), 5.06, 5.11, 5.13, 5.20 (4 s, 1 H, $C_{60}H$), 6.95−7.85 (m, 50 H, 6 Ph + 5 C_6H_4) ppm. ^{31}P NMR [81.0 MHz, toluene, $(CD_3)_2CO$ lock signal, H_3PO_4]: δ = 29.04, 29.44, 30.01, 30.33 (4 s surrounded with satellite peaks, $J_{Pt\text{-}P}$ = 3959 Hz, 2 P) ppm. IR (KBr): ṽ = 517.0 (s), 534.9 (s), 583.0 (w), 692.8 (vs), 742.8 (s), 1095.6 (m), 1186.6 (m), 1434.6 (m), 1476.8 (m), 1509.2 (vs), 2848.3 (w), 2863.8 (w), 2952.5 (w), 3022.0 (w), 3052.9 (w) cm^{-1}. UV/Vis (THF): λ_{max} (log ε) 239.1 (5.16), 287.9 (5.00), 487.5 (4.13) nm. FAB-MS: *m*/*z* = 1895 [$\{(MeC_6H_4)_5C_{60}H\}Pt(PPh_3)_2^+$, ^{195}Pt], 1177 [$(MeC_6H_4)_5C_{60}H^+$], 720 [C_{60}^+]. $C_{131}H_{66}P_2Pt$ (1896.99): calcd. C 82.94, H 3.51, P 3.27; found C 83.17, H 3.63, P 3.18.

Preparation of [(η²-Ph₅C₆₀H)Pd(PPh₃)₂] (4): Similarly to the preparation of **1**, when [$Pd(PPh_3)_4$] (46 mg, 0.04 mmol) was used in place of [$Pt(PPh_3)_4$], **4** (40 mg, 58%) was obtained as a red-brown solid. M. p. > 300°C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 5.28, 5.30, 5.31 (3 s, 1 H, $C_{60}H$), 7.10−7.85 (m, 55 H, 11 Ph) ppm. ^{31}P NMR [81.0 MHz, toluene, $(CD_3)_2CO$ lock signal, H_3PO_4]: δ = 29.05, 31.22, 32.41 (3 s, 2 P) ppm. IR (KBr): ṽ = 486.0 (w), 513.0 (w), 540.0 (m), 692.0 (s), 739.0 (w), 1027.0 (w), 1093.0 (m), 1431.0 (m), 1490.0 (w), 1599.0 (w), 2863.0 (w), 2926.0 (w), 3058.0 (w) cm^{-1}. UV/Vis (THF): λ_{max} (log ε) 240.5 (5.04), 287.5 (4.83), 472.0 (3.99) nm. FAB-MS: *m*/*z* = 1630 [$\{(Ph_5C_{60}H)Pd(PPh_3)_2 - Pd\}^+$], 1107 [$Ph_5C_{60}H^+$]. $C_{126}H_{56}P_2Pd$ (1738.20): calcd. C 87.07, H 3.25, P 3.56; found C 87.14, H 3.51, P 3.74.

Preparation of [{η²-(*m*-MeC₆H₄)₅C₆₀H}Pd(PPh₃)₂] (5): Similarly to the preparation of **2**, when [$Pd(PPh_3)_4$] (46 mg, 0.04 mmol) was used in place of [$Pt(PPh_3)_4$], **5** (37 mg, 51%) was obtained as a red-brown solid. M. p. > 300°C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.01, 2.06, 2.17 (3 s, 15 H, CH_3 + 2 CH_3 + 2 CH_3), 5.25, 5.27 (2 s, 1 H, $C_{60}H$), 6.95−7.80 (m, 50 H, 6 Ph + 5 C_6H_4) ppm. ^{31}P NMR [81.0 MHz, toluene, $(CD_3)_2CO$ lock signal, H_3PO_4]: δ = 29.05, 31.27 (2 s, 2 P) ppm. IR (KBr): ṽ = 486.0 (w), 505.0 (w), 540.0 (s), 591.0 (w), 688.0 (s), 719.0 (s), 750.0 (m), 996.0 (w), 1027.0 (w), 1093.0 (w), 1120.0 (s), 1178.0 (m), 1435.0 (m), 1482.0 (w), 1597.0 (w), 1607.0 (m), 2856.0 (w), 2918.0 (w), 3043.0 (w) cm^{-1}. UV/Vis (THF): λ_{max} (log ε) 239.5 (5.09), 287.7 (4.93), 470.5 (4.00) nm. FAB-MS: *m*/*z* = 1806 [$\{(MeC_6H_4)_5C_{60}H\}Pd(PPh_3)_2^+$, ^{106}Pd], 1177 [$(MeC_6H_4)_5C_{60}H^+$]. $C_{131}H_{66}P_2Pd$ (1808.33): calcd. C 87.01, H 3.68, P 3.43; found C 87.06, H 3.75, P 3.48.

Preparation of [{η²-(*p*-MeC₆H₄)₅C₆₀H}Pd(PPh₃)₂] (6): Similarly to the preparation of **3**, when [$Pd(PPh_3)_4$] (46 mg, 0.04 mmol) was used in place of [$Pt(PPh_3)_4$], **6** (42 mg, 58%) was obtained as a red-brown solid. M. p. > 300°C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.26, 2.31, 2.36 (3 s, 15 H, CH_3 + 2 CH_3 + 2 CH_3), 5.20, 5.22 (2 s, 1 H, $C_{60}H$), 6.90−7.85 (m, 50 H, 6 Ph + 5 C_6H_4) ppm. ^{31}P NMR [81.0 MHz, toluene, $(CD_3)_2CO$ lock signal, H_3PO_4]: δ = 29.08, 31.08 (2 s, 2 P) ppm. IR (KBr): ṽ = 513.0 (s), 536.0 (m), 579.0 (w), 692.0 (s), 743.0 (m), 1019.0 (w), 1093.0 (w), 1190.0 (m), 1431.0 (m), 1509.0 (s), 2863.0 (w), 2926.0 (w), 2972.0 (w), 3027.0 (w), 3058.0 (w) cm^{-1}. UV/Vis (THF): λ_{max} (log ε) = 239.0 (4.85), 287.7 (4.70), 472.0 (3.89) nm. FAB-MS: *m*/*z* = 1808 [$\{(MeC_6H_4)_5C_{60}H\}Pd(PPh_3)_2^+$, ^{108}Pd], 1177 [$(MeC_6H_4)_5C_{60}H^+$]. $C_{131}H_{66}P_2Pd$ (1808.33): calcd. C 87.01, H 3.68, P 3.43; found C 86.98, H 3.70, P 3.65.

Computational Details: The geometry optimizations of the 11 isomers for [$(\eta^2\text{-}Ph_5C_{60}H)Pt(PPh_3)_2$] were performed at the DFT B3LYP hybrid functional level by use of the effective core potential basis set LANL2DZ[17−19] for Pt and P. The standard 6-31G basis sets were chosen for C and H, except for those atoms in the phenyl rings, for which STO-3G was used. A polarization function [ξd(P)= 0.387] was added for P.[20] The ^1H NMR magnetic shielding tensors were calculated by the Gauge-Including Atomic Orbital (GIAO) method[21] at the Hartree−Fock level[22] by use of the LANL2DZ basis set for Pt, the 6-31G** basis set for P and for the H atoms directly bonded to C_{60}, and the 6-31G basis set for all other atoms. All calculations were performed with the parallel version of the GAUSSIAN 98 software package[23] on a multi-nodes Beowulf Linux cluster computer system.

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