Synthesis, Characterization and Properties of Transition Metal Pd/Pt [60]Fullerene Complexes Containing Phosphane Ligands − Crystal Structure of $[Pd(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2\}]$

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A solution of C_{60} in toluene reacts with $Pd(dba)_2$ or $Pd_2(dba)_3$ (dba = dibenzylideneacetone) and monophosphanes in a 1:1:2 molar ratio to give the corresponding Pd monophosphane fullerene derivatives $[Pd(\eta^2\text{-}C_{60})L_2]$ [L = $P(2\text{-}Fu)_3$ (Fu = furyl) **1**; L = $P(2\text{-}Fu)Ph_2$ **2**; L = PPh_2H **3**; L = $P(Fc)Ph_2$ (Fc = ferrocenyl) **4**; L = $P(Fc)_2Ph$ **5**], whereas reaction with $M(dba)_2$ (M = Pd, Pt) and subsequent treatment with diphosphanes in 1:1:1 molar ratio afforded the corresponding Pd/Pt diphosphane fullerene complexes $[Pd(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_nCH_2PPh_2\}]$ (n = 1 **6**; n = 2 **7**; n = 3 **8**) and $[Pt(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_nCH_2PPh_2\}]$ (n = 1 **9**; n = 2 **10**; n =3 **11**). All the new fullerene complexes **1**–**11** were characterized by elemental analysis, IR, ^1H NMR and ^{31}P NMR spectroscopy, as well as by X-ray diffraction analysis (for **7**). The optical limiting properties of **3**–**5** were determined and the possible pathways for the "one pot" reactions leading to **1**–**11** are briefly discussed.

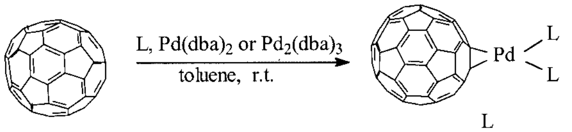
Introduction

The synthesis, structural characterization, and properties of transition metal fullerene complexes have attracted great attention,[1] since the discovery of [60]fullerene[2] and its synthesis in macroscopic quantities.[3] These complexes may be classified into two major categories: exohedral metal complexes in which the fullerene behaves mainly as an electron-deficient alkene ligand directly π-bonded to transition metal center,[1] and endohedral compounds in which the metal atom is encapsulated by the fullerene cage.[4] We are interested in exohedral transition metal fullerene complexes[5] because it can be expected that the exohedral modification of the fullerene core using different metals with ancillary ligands may change the structure and properties of the fullerene itself and allow us to obtain new transition metal fullerene derivatives, possibly with novel structures and unique properties. In this article we will describe the synthesis and spectroscopic characterization of a series of new transition metal Pd/Pt [60]fullerene complexes containing mono- and diphosphane ligands. The nonlinear optical properties of some of the new derivatives and the crystal structure of one representative fullerene complex — $[Pd(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2\}]$ — are also reported.

Results and Discussion

Synthesis and Characterization of $[Pd(\eta^2\text{-}C_{60})L_2]$

A toluene solution of C_{60} reacts with the mononuclear Pd complex $Pd(dba)_2$ (dba = dibenzylideneacetone) and the monophosphanes $P(2\text{-}Fu)_3$ (Fu = furyl), $P(2\text{-}Fu)_2Ph$, PPh_2H or $P(Fc)Ph_2$ in a 1:1:2 molar ratio at room temperature to give the corresponding monophosphane fullerene complexes **1**−**4**, respectively, in 63−93% yields, whereas it reacts with the dinuclear Pd complex $Pd_2(dba)_3$ and the monophosphane $P(Fc)_2Ph$ (Fc = ferrocenyl) under similar conditions to afford complex **5** in 76% yield (Scheme 1). Our attempts to prepare $[Pd(\eta^2\text{-}C_{60})\{P(Fc)_3\}_2]$ by the reac-



	L
1	$P(2\text{-}Fu)_3$
2	$P(2\text{-}Fu)Ph_2$
3	PPh_2H
4	$P(Fc)Ph_2$
5	$P(Fc)_2Ph$

Scheme 1

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tion of a toluene solution of C_{60} with $Pd(dba)_2$ or $Pd_2(dba)_3$ followed by treatment with the monophosphane $P(Fc)_3$ under similar conditions were unsuccessful, probably due to the very low nucleophilicity of $P(Fc)_3$ caused by the three bulky ferrocenyl groups attached to the phosphorus atom.

It is believed that the sequential "one-pot" reactions leading to **1−5** include an intermediate fullerene complex $(C_{60}Pd)_n$ generated from C_{60} and $Pd(dba)_2$ or $Pd_2(dba)_3$, which reacts further with the monophosphanes to yield **1−5**. This pathway is suggested as C_{60} is known to react with $Pd_2(dba)_3$ to produce a black, insoluble polymer $(C_{60}Pd)_n$ ($n \approx 1$),[6] which can be depolymerized by monophosphanes to give the fullerene derivatives $[PdC_{60}L_2]$ (L = PPh_3, PEt_3).[7] This pathway is consistent with our observation that C_{60} reacts with $Pd(dba)_2$ or $Pd_2(dba)_3$ in toluene to give black suspensions.

Complexes **1−5** are air-stable solids that dissolve in polar solvents such as toluene, chlorobenzene, THF and CS_2, but do not dissolve in nonpolar solvents such as petroleum ether and hexane. In solution, **1−5** are air sensitive, and can release C_{60} completely within 1−2 days.

The IR spectra of **1−5** display four absorption bands in the range $\tilde{\nu}$ = 1435−521 cm^{-1} for their C_{60} cores,[8] while the ^{31}P NMR spectra of **1−5** each exhibit one singlet in the region δ = 7−30 ppm for the two identical P atoms. The ^{1}H NMR spectra of **1−5** show the corresponding signals for their respective hydrogen-containing groups. The UV/Vis spectra of **1−5** display two intense bands between 200 and 400 nm; the new weak broad band appearing at ca. 440 nm suggests that the C_{60} ligand is coordinated to palladium in an η^2-fashion in each of the compounds.[9]

The nonlinear optical properties of [60]fullerene and its derivatives are of considerable interest, largely because of their potential applications as optical limiting materials.[10−13] We recently studied the optical limiting properties of the fullerene derivatives **3−5**. Figure 1 shows the optical limiting curves of **3−5**, from which it can be seen that the optical limiting properties of **4** and **5** are virtually the same within the experimental accuracy. They display better optical limiting characteristics than **3**, probably due to both phenyl and ferrocenyl groups having stronger electron-donating ability than that of a hydrogen atom.[14]

Synthesis and Characterization of $[Pd(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_nCH_2PPh_2\}]$ and $[Pt(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_nCH_2PPh_2\}]$

Similarly, C_{60} reacted with mononuclear complexes $M(dba)_2$ (M = Pd, Pt) in toluene, followed by in situ treatment with diphosphanes $Ph_2PCH_2(CH_2OCH_2)_nCH_2PPh_2$ (n = 1−3) in 1:1:1 molar ratio at room temperature to afford the first examples of the ether-chain-bridged diphosphane fullerene complexes **6−11** (M = Pd: n = 1 **6**, n = 2 **7**, n = 3 **8**; M = Pt: n = 1 **9**, n = 2 **10**, n = 3 **11**) in 61−94% yield (Scheme 2).

Presumably, these "one-pot" reactions for production of **6−11** also involve an intermediate polymer, either $(C_{60}Pd)_n$ or $(C_{60}Pt)_n$, generated from C_{60} and $M(dba)_2$ (M = Pd, Pt); the in situ reaction of $(C_{60}Pd)_n$ or $(C_{60}Pt)_n$ with the diphosphanes affords **6−11**. C_{60} is known to react with $Pt(dba)_2$ to give a black, insoluble polymer $(C_{60}Pt)_n$ ($n \approx 1$), and treatment of $(C_{60}Pt)_n$ with monophosphanes affords $[PtC_{60}L_2]$ (L = PPh_3, PEt_3).[15] Similarly, reaction of C_{60} with $Pd_2(dba)_3$ produces the polymer $(C_{60}Pd)_n$ ($n \approx 1$),[6] which reacts with dppe to yield $[PdC_{60}(dppe)]$.[7] We also observed the formation of black suspensions when C_{60} was reacted with $M(dba)_2$ (M = Pd, Pt) in toluene.

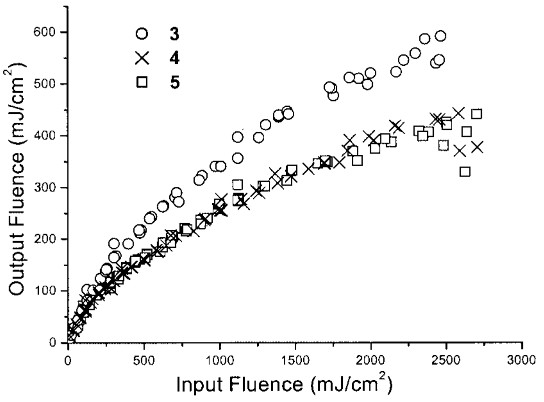
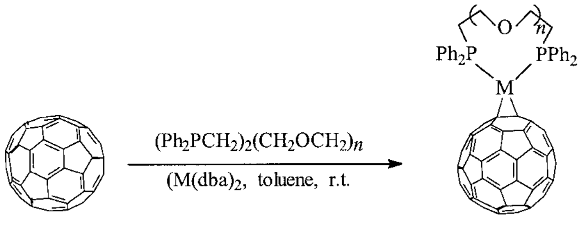


Figure 1. Optical limiting of **3−5** determined in toluene solution: **3** (6.26×10^{-5} mol/L); **4** (3.74×10^{-5} mol/L); **5** (5.10×10^{-5} mol/L)



	M	n		M	n
6	Pd	1	**9**	Pt	1
7	Pd	2	**10**	Pt	2
8	Pd	3	**11**	Pt	3

Scheme 2

Similar to **1−5**, complexes **6−11** are air-stable solids, which are soluble in polar solvents, but insoluble in nonpolar solvents. In solution, **6−11** are air sensitive, but less so than **1−5**; they release C_{60} completely after two or three days. Compounds **6−11** were fully characterized by elemental analysis and spectroscopy, and **7** by X-ray crystallography. For instance, the IR spectra of **6−11** show four bands in the range $\tilde{\nu}$ = 1434−525 cm^{-1} for their C_{60} spheres,[8] whereas the UV/Vis spectra of **6−11** display two intense bands in the 200−400 nm range and one weak broad band at ca. 440 nm, indicating that the C_{60} ligand is coordinated to Pd or Pt in an η^2-mode in each of these complexes.[9] In addition, the ^{31}P NMR spectra of **6−8** show a singlet at about δ = 16 ppm for the two identical P atoms in each of **6−8**, whereas the spectra of **9−11** exhibit a singlet at about δ = 18 ppm, along with two satellite singlets due to ^{195}Pt-

^{31}P coupling, attributed to the two identical P atoms in each of **9−11**.

Crystal Structure of 7

The molecular structure of **7** has been unequivocally confirmed by single-crystal X-ray diffraction techniques (Figure 2). Figure 3 displays its cell packing. Selected bond lengths and angles are listed in Table 1. As can be seen from Figure 2, complex **7** indeed consists of a C_{60} ligand bound to the Pd atom in an η^2-fashion by the C(1)−C(2) 6:6 bond, and a diphosphane ligand $Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2$ chelated to the Pd atom through the P(1) and P(2) atoms. In addition, from Figure 3 it can be seen that each crystal cell contains two molecules of **7** and two molecules of MeOH. The closest contact between solvent MeOH and **7** [2.467 Å, from the oxygen atom of MeOH to C(10) of the C_{60} ligand] is less than the sum of the van der Waals radii of C and O (3.22 Å),[16] which might be due to disorder of the MeOH molecule. In addition, the disordered MeOH molecule could also give rise to the relatively high *R* value (0.1426) for the structure of **7**.

To the best of our knowledge, **7** is the first crystallographically characterized transition metal fullerene complex containing an ether-chain-bridged diphosphane ligand. The Pd coordination geometry of **7** is similar to that of its monophosphane PPh_3-containing analogue $[Pd(\eta^2\text{-}C_{60})(PPh_3)_2]$.[17] Figure 4 shows that the corresponding bond lengths and angles within the coordination spheres of the Pd atoms of these two complexes are very similar.

It is noteworthy that the C(1)−C(2) bond lengths of **7** and $[Pd(\eta^2\text{-}C_{60})(PPh_3)_2]$[17] are slightly longer than the 6:6 bond length in free C_{60},[1a] due to the metal-to-C_{60} π-back-

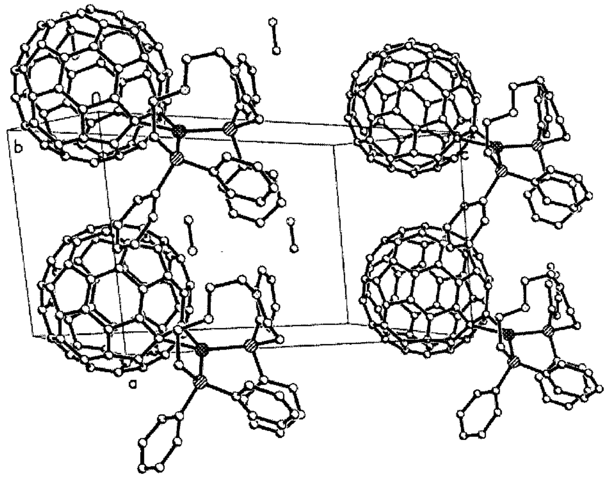


Figure 3. Cell packing of **7**

Table 1. Selected bond lengths (Å) and angles (°) for **7**

Pd(1)−C(1)	2.060(18)	P(1)−C(73)	1.80(2)
Pd(1)−C(2)	2.119(17)	P(1)−C(67)	1.83(2)
Pd(1)−P(1)	2.297(5)	P(2)−C(79)	1.77(2)
Pd(1)−P(2)	2.344(6)	P(2)−C(85)	1.81(2)
P(1)−C(61)	1.76(2)	C(1)−C(2)	1.43(3)
C(1)−Pd(1)−C(2)	40.1(7)	C(61)−P(1)−C(67)	102.8(9)
C(1)−Pd(1)−P(1)	103.2(5)	C(73)−P(1)−C(67)	100.7(9)
C(2)−Pd(1)−P(1)	143.2(5)	C(61)−P(1)−Pd(1)	117.9(6)
C(1)−Pd(1)−P(2)	150.5(5)	C(79)−P(2)−C(85)	102.1(9)
C(2)−Pd(1)−P(2)	110.4(5)	C(79)−P(2)−C(78)	101.7(10)
P(1)−Pd(1)−P(2)	106.27(19)	C(85)−P(2)−C(78)	106.9(10)
C(61)−P(1)−C(73)	103.5(10)	C(79)−P(2)−Pd(1)	113.7(6)

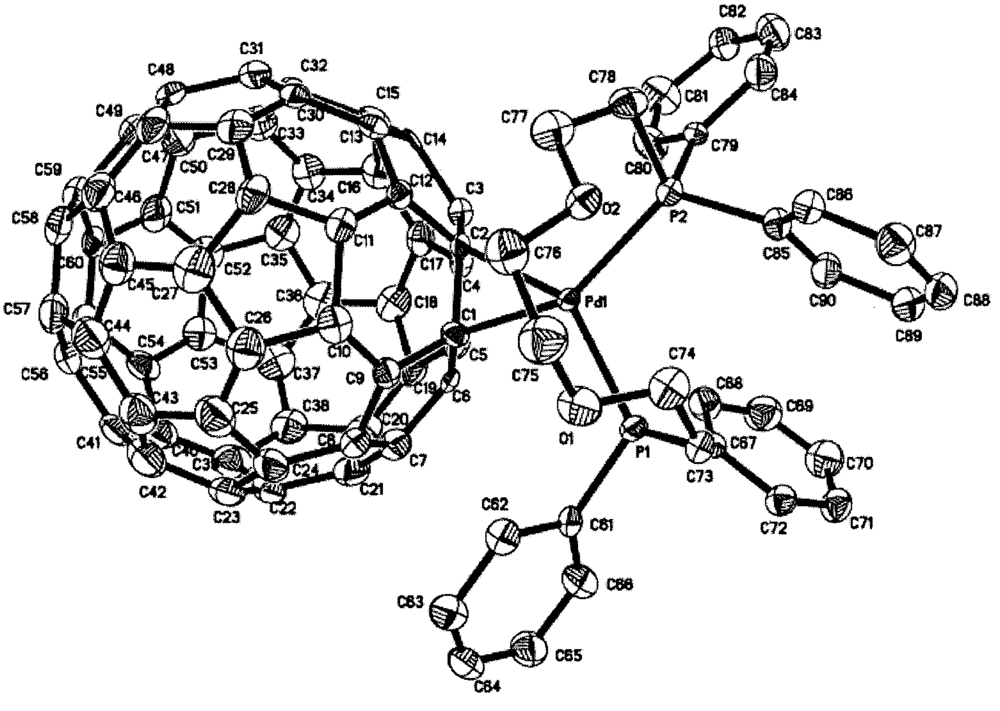


Figure 2. ORTEP diagram of **7**

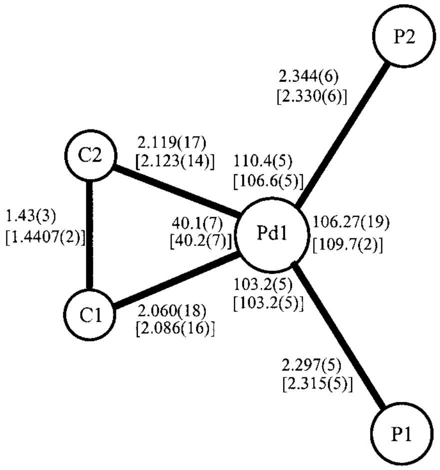


Figure 4. The Pd coordination sphere in **7** (lengths in angstroms and angles in degrees); values for its PPh_3 analogue[17] are given in brackets

donation.[1b] In addition, the Pd coordination geometries of **7** and $[Pd(\eta^2\text{-}C_{60})(PPh_3)_2]$ are square planar, the five atoms C(1), C(2), P(1), P(2) and Pd being coplanar, with deviations from the least-squares plane of less than 0.02 Å for **7** and 0.06 Å for $[Pd(\eta^2\text{-}C_{60})(PPh_3)_2]$.[17]

Interestingly, complex **7** could be regarded as a hybrid of a metallocrown ether and a fullerene, in which the Pd atom, part of an eleven-membered metallocrown ether ring [Pd(1)P(1)C(73)C(74)O(1)C(75)C(76)O(2)C(77)C(78)P(2)], is bound to the fullerene through the C(1)−C(2) 6:6 bond. In view of the unique structures and novel properties of both crown ether and fullerene, it can be expected that such modified hybrids might find practical applications in catalysis, molecular recognition and materials science.[1,18]

Experimental Section

General: All reactions were carried out under a highly purified nitrogen atmosphere using standard Schlenk or vacuum-line techniques. Toluene and hexane were distilled from Na/benzophenone ketyl. Other solvents were bubbled with nitrogen for at least 20 minutes before use. $Pd(dba)_2$,[19] $Pd_2(dba)_3$,[20] $P(Fc)_3$,[21] $P(Fc)_2Ph$,[22] $P(Fc)Ph_2$,[22] PPh_2H,[23] $P(2\text{-}Fu)_3$,[24] $P(2\text{-}Fu)Ph_2$ [25] and $Pt(dba)_2$ [26] were prepared according to literature methods. C_{60} (99.9%) is available commercially.

^1H NMR and ^{31}P NMR were recorded on a Bruker AC-P200 spectrometer, UV/Vis spectra on a Shimadzu UV-240 spectrometer and IR spectra on a Bio-Rad FTS 135 spectrometer. Elemental analysis was performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

Preparation of $[Pd(\eta^2\text{-}C_{60})\{P(2\text{-}Fu)_3\}_2]$ (1): A 50-mL three-necked flask equipped with a magnetic stir-bar, a rubber septum and a nitrogen inlet tube was charged with C_{60} (0.036 g, 0.05 mmol) and toluene (16 mL). $Pd(dba)_2$ (0.029 g, 0.05 mmol) was added to the purple toluene solution and then the mixture was stirred at room temperature for 0.5 h to give a black suspension. $P(2\text{-}Fu)_3$ (0.023 g, 0.10 mmol) was added to this suspension and the new mixture was stirred for another 0.5 h to produce a deep green solution. The solution was carefully layered with hexane (40 mL). After standing overnight, the mixture was filtered to give a precipitate, which was washed with (10 × 2 mL) of toluene and dried in vacuo. 0.054 g (84%) of **1** was obtained as a black solid. M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 6.39$ (s, 6 H, 6 H^4 of furan ring), 6.78 (s, 6 H, 6 H^3 of furan ring), 7.64 (s, 6 H, 6 H^5 of furan ring) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): $\delta = 30.04$ (s, 2 P) ppm. IR (KBr disk): $\tilde{\nu} = 2327$ (m), 1458 (m), 1427 (m) (C_{60}), 1364 (m), 1213(m), 1183 (m) (C_{60}), 1159 (m), 1122(m), 1009 (s), 906 (m), 745 (s), 592 (m), 577(m) (C_{60}), 524 (s) (C_{60}), 490 (s), 438 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 285.0 (4.93), 333.3 (5.11), 406.7 (3.85), 435.5 (3.84) nm. $C_{84}H_{18}O_6P_2Pd$ (1291.43): calcd. C 78.12, H 1.40; found C 77.95, H 1.50.

Preparation of $[Pd(\eta^2\text{-}C_{60})\{P(2\text{-}Fu)Ph_2\}_2]$ (2): This complex was prepared similarly, with $P(2\text{-}Fu)Ph_2$ (0.025 g, 0.10 mmol) instead of $P(2\text{-}Fu)_3$; 0.042 g (63%) of **2** was obtained as a black solid. M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 6.35$ (s, 2 H, 2 H^4 of furan ring), 6.78 (s, 2 H, 2 H^3 of furan ring), 7.14−7.75 (m, 22 H, 4 C_6H_5, 2 H^5 of furan ring) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): $\delta = 7.04$ (s, 2 P) ppm. IR (KBr disk): $\tilde{\nu} = 1481$ (m), 1434 (m) (C_{60}), 1356 (m), 1212 (m), 1183 (m) (C_{60}), 1120 (m), 1097 (m), 1009 (s), 904 (m), 874 (m), 742 (s), 693 (s), 577(m) (C_{60}), 524 (s) (C_{60}), 489 (m), 432 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 285.0 (4.91), 333.3 (4.93), 405.8 (4.17), 437.5(3.99) nm. $C_{92}H_{26}O_2P_2Pd$ (1331.58): calcd. C 82.98, H 1.97; found C 82.93, H 2.10.

Preparation of $[Pd(\eta^2\text{-}C_{60})(PPh_2H)_2]$ (3): This complex was prepared similarly, with PPh_2H (0.019 g, 0.10 mmol) in place of $P(2\text{-}Fu)_3$; 0.056 g (93%) of **3** was obtained as a black solid. M.p. 282−283 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 7.48$−7.74 (m, 20 H, 4 C_6H_5), 8.08 (d, $J = 484$ Hz, 2 H, 2 HP) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): $\delta = 22.50$ (s, 2 P) ppm. IR (KBr disk): $\tilde{\nu} = 2923$ (m), 1457 (m), 1435 (m) (C_{60}), 1183 (m) (C_{60}), 1107 (m), 1036 (m), 1000 (m), 821 (m), 746 (m), 696 (s), 577(m) (C_{60}), 524 (s) (C_{60}), 489 (m), 430 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 285.0 (4.50), 331.7 (4.42), 405.8 (3.85), 436.0 (3.92) nm. $C_{84}H_{22}P_2Pd$ (1199.47): calcd. C 84.11, H 1.85; found C 84.15, H 2.00.

Preparation of $[Pd(\eta^2\text{-}C_{60})\{P(Fc)Ph_2\}_2]$ (4): This complex was prepared similarly, with $P(Fc)Ph_2$ (0.037 g, 0.10 mmol) instead of $P(2\text{-}Fu)_3$; 0.053 g (68%) of **4** was obtained as a black solid. M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 3.84$ (s, 4 H, 2 H^3, 2 H^4), 4.01 (s, 10 H, 2 C_5H_5), 4.19 (s, 4 H, 2 H^2, 2 H^5), 7.25−7.75 (m, 20 H, 4 C_6H_5) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): $\delta = 17.16$ (s, 2 P) ppm. IR (KBr disk): $\tilde{\nu} = 3052$ (m), 1570 (m), 1480 (m), 1458 (m), 1434 (m) (C_{60}), 1354 (m), 1306 (m), 1185 (m) (C_{60}), 1160(m), 1098 (m), 1028 (m), 1001 (m), 820 (s), 741 (s), 696 (s), 622 (m), 579(m) (C_{60}), 524 (s) (C_{60}), 485 (s), 430 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 287.0 (4.82), 333.0 (4.73), 405.6 (4.12), 432.5 (4.04) nm. $C_{104}H_{38}Fe_2P_2Pd$ (1567.51): calcd. C 79.69, H 2.44; found C 79.50, H 2.54.

Preparation of $[Pd(\eta^2\text{-}C_{60})\{P(Fc)_2Ph\}_2]$ (5): This complex was prepared similarly, with $Pd_2(dba)_3{\cdot}C_6H_6$ (0.026 g, 0.025 mmol) and $P(Fc)_2Ph$ (0.048 g, 0.10 mmol) instead of $Pd(dba)_2$ and $P(2\text{-}Fu)_3$; 0.068 g (76%) of **5** was obtained as a black solid. M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 4.18$ (s, 8 H, 4 H^3, 4 H^4), 4.38 (s, 20 H, 4 C_5H_5), 4.83, 5.03 (s, s, 8 H, 4 H^2, 4 H^5), 7.30−7.95 (m, 10 H, 2 C_6H_5) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): $\delta = 13.84$ (s, 2 P) ppm. IR (KBr disk): $\tilde{\nu} = 2923$ (m), 2851(m), 1456 (m), 1434 (m) (C_{60}), 1185 (m) (C_{60}), 1161 (m), 1056 (m), 1106 (m), 1026 (m), 1002 (m), 821 (s), 740 (m), 697 (s), 578(m) (C_{60}), 521 (s) (C_{60}), 438 (s), 431 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 285.0 (4.90), 333.3 (4.91), 405.8 (4.32), 435.6 (3.88) nm. $C_{112}H_{46}Fe_4P_2Pd$ (1783.35): calcd. C 75.43, H 2.59; found C 75.49, H 2.48.

Preparation of $[Pd(\eta^2\text{-}C_{60})(Ph_2PCH_2CH_2OCH_2CH_2PPh_2)]$ (6): This complex was prepared similarly, with $Ph_2PCH_2CH_2OCH_2CH_2PPh_2$ (0.022 g, 0.05 mmol) instead of P(2-Fu)$_3$; 0.056 g (88%) of **6** was obtained as a black solid. M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.63 (s, 4 H, 2 CH_2P), 3.78−4.03 (m, 4 H, 2 CH_2O), 7.08−7.78 (m, 20 H, 4 C_6H_5) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): δ = 13.60 (s, 2 P) ppm. IR (KBr disk): $\tilde{\nu}$ = 2852 (m), 1570 (m), 1480 (m), 1459 (m), 1433 (s) (C_{60}), 1353 (m), 1183 (m) (C_{60}), 1101(s), 930 (s), 821 (m), 739 (s), 693 (s), 666 (m), 578(m) (C_{60}), 526 (s) (C_{60}), 499 (s), 438 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 290.0 (5.34), 333.3 (5.28), 405.5 (4.22), 437.5 (4.50) nm. $C_{88}H_{28}OP_2Pd$ (1269.56): calcd. C 83.25, H 2.22; found C 83.10, H 2.30.

Preparation of $[Pd(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2\}]$ (7): This complex was prepared similarly, with $Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2$ (0.024 g, 0.05 mmol) instead of P(2-Fu)$_3$; 0.040 g (61%) of **7** was obtained as a black solid. M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.50−2.70 (m, 4 H, 2 CH_2P), 3.68−3.90 (m, 8 H, 4 CH_2O), 7.10−7.75 (m, 20 H, 4 C_6H_5) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): δ = 17.95 (s, 2 P) ppm. IR (KBr disk): $\tilde{\nu}$ = 2858 (m), 1481 (m), 1460 (m), 1433 (s) (C_{60}), 1352 (m), 1184 (m) (C_{60}), 1127 (m), 1098(s), 994 (m), 739 (s), 695 (s), 578(m) (C_{60}), 525 (s) (C_{60}), 434 (m), 412 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 286.7 (5.24), 333.3 (5.13), 405.8 (4.37), 437.5 (4.24), nm. $C_{90}H_{32}O_2P_2Pd$ (1313.61): calcd. C 82.29, H 2.46; found C 82.42, H 2.45.

Preparation of $[Pd(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_3CH_2PPh_2\}]$ (8): This complex was prepared similarly, with $Ph_2PCH_2(CH_2OCH_2)_3CH_2PPh_2$ (0.026 g, 0.05 mmol) instead of P(2-Fu)$_3$; 0.050 g (74%) of **8** was obtained as a black solid. M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.46−2.60 (m, 4 H, 2 CH_2P), 3.70 (s, 12 H, 6 CH_2O), 7.12−7.65 (m, 20 H, 4 C_6H_5) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): δ = 13.89 (s, 2 P) ppm. IR (KBr disk): $\tilde{\nu}$ = 2865 (m), 1571 (m), 1480 (m), 1459 (m), 1433 (s) (C_{60}), 1352 (m), 1183 (s) (C_{60}), 1099 (s), 974 (m), 739 (s), 695 (s), 577(m) (C_{60}), 525 (s) (C_{60}), 486 (m), 434 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 287.0 (5.27), 333.0 (5.28), 405.5 (4.10), 438.0 (4.15) nm. $C_{92}H_{36}O_3P_2Pd$ (1357.66): calcd. C 81.39, H 2.67; found C 81.35, H 2.56.

Preparation of $[Pt(\eta^2\text{-}C_{60})(Ph_2PCH_2CH_2OCH_2CH_2PPh_2)]$ (9): This complex was prepared similarly, with Pt(dba)$_2$ (0.033 g, 0.05 mmol) and $Ph_2PCH_2CH_2OCH_2CH_2PPh_2$ (0.022 g, 0.05 mmol) instead of Pd(dba)$_2$ and P(2-Fu)$_3$; 0.064 g (94%) of **9** was obtained as a black solid. M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.60−2.85 (m, 4 H, 2 CH_2P), 3.85−4.02 (m, 4 H, 2 CH_2O), 7.23−7.70 (m, 20 H, 4 C_6H_5) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): δ = 16.59 (s, $J_{P,Pt}$ = 3876 Hz, 2 P) ppm. IR (KBr disk): $\tilde{\nu}$ = 2920 (m), 2853 (m), 1480 (m), 1459 (m), 1434 (s) (C_{60}), 1332 (m), 1280 (m), 1184 (m) (C_{60}), 1101(s), 928 (m), 906 (m), 823 (m), 741 (s), 694 (s), 577(m) (C_{60}), 527 (s) (C_{60}), 502 (s), 480 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 285.0 (4.62), 314.0 (5.10), 318.6 (5.11), 437.5(3.94) nm. $C_{88}H_{28}OP_2Pt$ (1358.22): calcd. C 77.82, H 2.08; found C 77.75, H 2.10.

Preparation of $[Pt(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2\}]$ (10): This complex was prepared similarly, with Pt(dba)$_2$ (0.033 g, 0.05 mmol) and $Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2$ (0.024 g, 0.05 mmol) instead of Pd(dba)$_2$ and P(2-Fu)$_3$; 0.066 g (94%) of **10** was obtained as a black solid, M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.50−2.75 (m, 4 H, 2 CH_2P), 3.65−3.95 (m, 8 H, 4 CH_2O), 7.10−7.70 (m, 20 H, 4 C_6H_5) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): δ = 19.34 (s, $J_{P\text{-}Pt}$ = 3949 Hz, 2 P) ppm. IR (KBr disk): $\tilde{\nu}$ = 2921 (m), 2853 (m), 1479 (m), 1459 (s), 1434 (s) (C_{60}), 1331 (m), 1279 (m), 1184 (m) (C_{60}), 1128 (s), 1099 (s), 994 (s), 743 (s), 696 (s), 673 (m), 577(m) (C_{60}), 527 (s) (C_{60}), 484 (m), 414 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 285.0 (4.69), 314.2 (5.15), 318.3 (5.16), 440 (3.84) nm. $C_{90}H_{32}O_2P_2Pt$ (1402.27): calcd. C 77.09, H 2.30; found C 76.99, H 2.38.

Preparation of $[Pt(\eta^2\text{-}C_{60})\{Ph_2PCH_2(CH_2OCH_2)_3CH_2PPh_2\}]$ (11): This complex was prepared similarly, with Pt(dba)$_2$ (0.033 g, 0.05 mmol) and $Ph_2PCH_2(CH_2OCH_2)_3CH_2PPh_2$ (0.026 g, 0.05 mmol) instead of Pd(dba)$_2$ and P(2-Fu)$_3$; 0.064 g (89%) of **11** was obtained as a black solid, M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 2.60−2.85 (m, 4 H, 2 CH_2P), 3.50−3.95 (m, 12 H, 6 CH_2O), 7.11−7.70 (m, 20 H, 4 C_6H_5) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$, H_3PO_4): δ = 19.35 (s, $J_{P\text{-}Pt}$ = 3946 Hz, 2 P) ppm. IR (KBr disk): $\tilde{\nu}$ = 2910 (m), 2853 (m), 1481 (m), 1459 (m), 1434 (s) (C_{60}), 1332 (m), 1280 (m), 1183 (m) (C_{60}), 1141 (m), 1101(s), 976 (m), 903 (m), 740 (s), 694 (s), 577(m) (C_{60}), 526 (s) (C_{60}), 489 (m) cm^{-1}. UV/Vis (PhCl): λ_{max} (log ε) = 287.0 (5.09), 333.0 (5.09), 405.0 (4.25), 438.5 (4.17) nm. $C_{92}H_{36}O_3P_2Pt$ (1446.32): calcd. C 76.40, H 2.51; found C 76.42, H 2.54.

Determination of the Optical Limiting Properties: The investigation of the optical limiting properties of the fullerene derivatives was conducted at a wavelength of 532 nm. They were housed in quartz cells with a path 2 mm long with the same linear transmittance of 83%. The laser pulses used in experiments were supplied by a frequency-doubled, Q-switched, mode-locked Continuum ns/ps Nd:YAG laser system, which provides linearly polarized 8 ns (FWHM) optical pulses at 532 nm with a repetition of 1 Hz. The transverse mode of the laser pulses is nearly Gaussian. The input laser pulses adjusted by an attenuator were split into two beams. One was employed as reference to monitor the incident laser energy, and the other was focused onto the sample cell by using a lens with 30 cm focal length. The sample was positioned at the focus. The incidence and transmitting laser pulses were monitored by utilizing two energy detectors (818J-09B, Newport Corp). The optical limiting was studied by measuring the nonlinear fluence transmittance change with input fluence.

Crystal Structure Determination of 7: Single crystals of **7** suitable for X-ray diffraction analysis were obtained by slow diffusion of MeOH into a toluene solution of **7** at room temperature. A crystal of **7** was glued to a glass fiber and mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at room temperature, using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) in the ω-2θ scanning mode. Absorption correction was performed with SADABS.[27] The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on F^2.[28] Hydrogen atoms were located by using the geometric method. The crystal data and structural refinements details are listed in Table 2. CCDC-216076 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data and structure refinements for **7**·MeOH

Empirical formula	$C_{91}H_{32}O_2P_2Pd\cdot MeOH$
Formula mass	1345.54
Temperature (K)	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.986 (7)
b (Å)	13.934(10)
c (Å)	20.089(14)
α (°)	73.834(13)
β (°)	77.823(15)
γ (°)	80.527(15)
V (Å^3)	2608(3)
Z	2
$D_{\mathrm{calcd.}}$(mg/mm^3)	1.714
μ (mm^{-1})	0.487
F (000)	1364
Unique reflections, R_{int}	10488, 0.0924
Observed reflections	6687
Goodness-of-fit on F^2	1.069
R [$I > 2\sigma(I)$]	$R_1 = 0.1426$, $wR_2 = 0.3314$

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