

Synthesis, Characterization, and Electrochemical Properties of Novel Transition Metal–Fullerene Complexes Containing Di- and Tetraphosphane Ligands

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This paper reports the synthesis, characterization, and some properties of transition metal–fullerene complexes containing *trans*-1,1'-bis(diphenylphosphanyl)ethylene (dppet, *trans*-Ph₂PCH=CHPPh₂) and *N,N,N',N'*-tetra(diphenylphosphanylmethyl)ethylene diamine (dppeda, [(Ph₂PCH₂)₂-NCH₂]₂), including [(η²-C₆₀M)(dppet)₂] (M = Pt **1**, Pd **2**), [(η²-C₆₀M)(dppet)₂] (M = Pt **3**, Pd **4**), [(η²-C₆₀Pd)(η²-C₆₀Pt)(dppet)₂] (**5**), [(η²-C₆₀Pd)(η²-C₇₀Pd)(dppet)₂] (**6**), [(η²-C₇₀Pd)(dppet)₂] (**7**), [(η²-C₆₀M)(dppeda)] (M = Pt **8**, Pd **9**), and [(η²-C₆₀M)₂(dppeda)] (M = Pt **10**, Pd **11**). Interestingly, while complexes

1, **2**, **8**, and **9** are the first examples of metallacyclopropafullerene diphosphane ligands containing fullerene cores, complexes **3–7**, **10**, and **11** are the first group 10 metal-containing, dumbbell-shaped bisfullerenes. All the complexes **1–11** were characterized by elemental analysis, spectroscopy, and, particularly for **4** and **5**, by X-ray crystallography and cyclic voltammetry. Pathways for the formation of **1–11** are suggested.

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Introduction

Since the isolation and characterization of the first transition metal–fullerene complex [(η²-C₆₀)Pt(PPh₃)₂],^[1] a large number of such complexes with unique structures and novel properties have been prepared and structurally characterized.^[2–6] Previously, we have reported several series of transition metal–fullerene complexes that contain various phosphane ligands, such as Ph₂PCH₂CH₂PPh₂ (dppe),^[7] 1,2-(Ph₂P)₂C₆H₄ (dppb),^[8] DIOP,^[9] Ph₂PCH₂(CH₂OCH₂)_n-CH₂PPh₂,^[10] [(η⁵-Ph₂PC₅H₄)₂Fe] (dppf),^[11] and [(η⁵-Ph₂PC₅H₄)₂Ru] (dppr).^[12] Now, as a continuation of this research program, we report other types of transition metal–fullerene complexes that contain either the diphosphane ligand *trans*-1,1'-bis(diphenylphosphanyl)ethylene (dppet) or the tetraphosphane ligand *N,N,N',N'*-tetra(diphenylphosphanylmethyl)ethylene diamine (dppeda). It should be noted that although some of the dppet-containing complexes were preliminarily reported in our recent communication,^[13] this paper systematically describes both the dppet- and dppeda-containing fullerene complexes and includes new results, such as the crystal structure of [(η²-C₆₀Pd)(η²-C₆₀Pt)(dppet)₂], the electrochemical properties of [(η²-C₆₀Pd)(dppet)₂] and [(η²-C₆₀Pd)(η²-C₆₀Pt)(dppet)₂], as well as the synthesis and characterization of the dppet-con-

taining [70]fullerene complexes [(η²-C₆₀Pd)(η²-C₇₀Pd)(dppet)₂] and [(η²-C₇₀Pd)(dppet)₂] along with the dppeda-containing [60]fullerene complexes [(η²-C₆₀M)(dppeda)] and [(η²-C₆₀M)₂(dppeda)] (M = Pt, Pd).

Results and Discussion

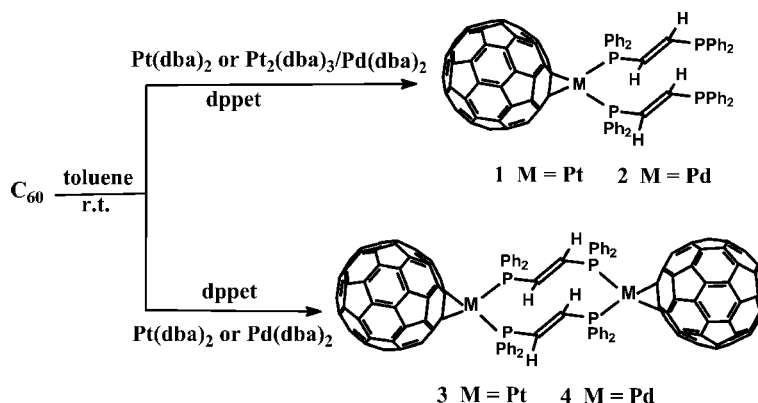
Synthesis and Characterization of Dppet-Containing Fullerene Complexes

A toluene solution of C₆₀ was treated with [M(dba)₂] or [Pt₂(dba)₃] (M = Pt, Pd; dba = dibenzylideneacetone) and dppet in a 1:1:2 molar ratio at room temperature to give the metallacyclopropa[60]fullerene complex [(η²-C₆₀Pt)(dppet)₂] (**1**) in 35–58% yield and complex [(η²-C₆₀Pd)(dppet)₂] (**2**) in 75% yield. The two different starting materials [Pt(dba)₂] and [Pt₂(dba)₃] can be used interchangeably, although [Pt₂(dba)₃] is much more reactive than [Pt(dba)₂], as judged by the rapidity of the development of the green color characteristic of product **1**, and when used in a slight excess this starting material gives the highest yield. Similarly, a toluene solution of C₆₀ was treated with [Pt(dba)₂] and dppet in a 1:1:2 ratio or with [Pd(dba)₂] and dppet in a 1:2:1 molar ratio at room temperature to give the homodinuclear bismetallacyclopropa[60]fullerene complexes [(η²-C₆₀M)(dppet)₂] (M = Pt **3**, Pd **4**) in 82% and 92% yields, respectively (Scheme 1).

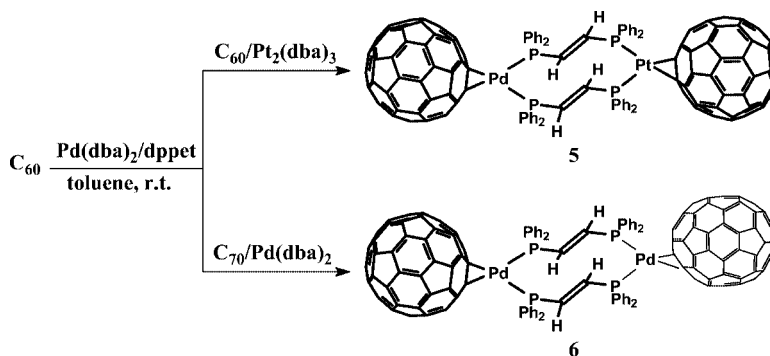
We further found that treatment of a toluene solution of C₆₀ with [Pd(dba)₂] and dppet in a 1:1:2 molar ratio at room temperature, followed by treatment with a mixture of C₆₀ and [Pt₂(dba)₃] in a 2:1 molar ratio or C₇₀ and [Pd-

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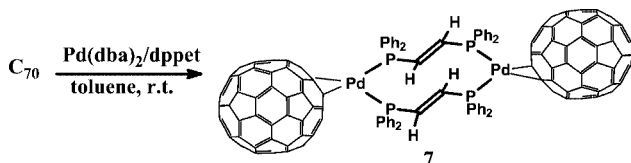
Scheme 1.



Scheme 2.

(dba)₂] in a 1:1 molar ratio, gave the heterodinuclear bismetallacyclopropa[60]fullerene complex $[(\eta^2\text{-C}_{60}\text{Pd})(\eta^2\text{-C}_{60}\text{Pt})(\text{dppet})_2]$ (**5**) and the homodinuclear bismetallacyclopropa[60]/[70]fullerene complex $[(\eta^2\text{-C}_{60}\text{Pd})(\eta^2\text{-C}_{70}\text{Pd})(\text{dppet})_2]$ (**6**) in 65% and 37% yields, respectively (Scheme 2).

Similarly, the homodinuclear bismetallacyclopropa[70]-fullerene complex $[(\eta^2\text{-C}_{70}\text{Pd})(\text{dppet})_2]$ (**7**) could be prepared by treatment of C₇₀ in toluene with [Pd(dba)₂] and dppet in a 1:1:2 molar ratio at room temperature in 44% yield (Scheme 3).



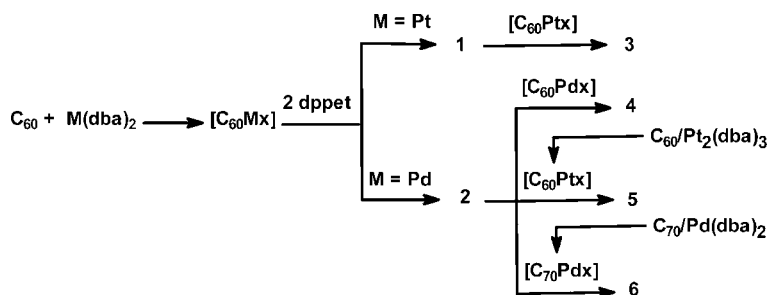
Scheme 3.

Interestingly, the above-mentioned dinuclear bisfullerene complexes **3–6** can be also prepared by another method in which the [60]fullerene-derived diphosphanes **1** and **2** were used as starting materials. Thus, treatment of **1** in toluene with C₆₀ and [Pt(dba)₂] in a 1:1:1 molar ratio at room temperature gave **3** in 59% yield, whereas treatment of **2** with C₆₀ and [Pd(dba)₂] under similar conditions gave **4** in 53% yield. In addition, while **2** reacts with C₆₀ and [Pt(dba)₂] in toluene at room temperature to produce the heterodinuclear

bisfullerene **5** in 55% yield, the reaction of **2** with C₇₀ and [Pd(dba)₂] under similar conditions gives rise to the homodinuclear bisfullerene complex **6** in 38% yield.

It follows that the possible pathways for the formation of **1–7** might be as suggested in Scheme 4. That is: (i) **1** and **2** are produced by η^1 -coordination of two molecules of dppet with the polymeric species $[\text{C}_{60}\text{M}_x]$ (M = Pt, Pd; $x = 1$) formed in situ from C₆₀ and [Pd(dba)₂], [Pt(dba)₂], or [Pt₂(dba)₃],^[14,15] (ii) subsequent chelation of **1** as a bidentate ligand with $[\text{C}_{60}\text{Pt}_x]$ gives **3**, (iii) subsequent chelation of **2** with $[\text{C}_{60}\text{M}_x]$ affords **4** and **5**, and (iv) subsequent chelation of **2** with the polymeric species $[\text{C}_{70}\text{Pd}_x]$ formed in situ from C₇₀ and [Pd(dba)₂]^[14,15] produces **6**. Apparently, **7** can be formed through similar elementary steps to those indicated in Scheme 4.

The dppet-containing fullerene complexes **1–7** were characterized by elemental analysis and spectroscopic methods. For example, the IR spectra of **1–5** display four absorption bands in the range 1434–513 cm^{−1} for their C₆₀ cores,^[16] whereas the IR spectrum of **6** exhibits nine absorption bands in the region 1433–456 cm^{−1} for its C₆₀ and C₇₀ spheres,^[16] and that of **7** shows nine absorption bands in the range 1432–457 cm^{−1}^[16] for its C₇₀ cores. In addition, the ³¹P NMR spectra of **1** and **2** show one singlet and one triplet or two singlets at $\delta \approx -7$ and 20 ppm for their two identical uncoordinated P atoms and two identical coordinated P atoms, respectively, whereas the spectra of **3–7** display the corresponding signals for their four coordinated P atoms. That the chemical shifts of the coordinated P atoms



Scheme 4.

lie at much lower field relative to the corresponding free P atoms can be ascribed to transfer of electron density from the P atom to the metal center, which is consistent with other phosphane-coordinated fullerene complexes.^[1,9,12] It is well-known that in single addition of a transition metal to fullerenes the C_{60} ligand is bonded to the metal center in an η^2 -fashion through its single C–C 6:6 bond, whereas the C_{70} ligand is preferentially bonded to a metal center in an η^2 -manner through one Ca–Cb 6:6 bond at the poles of the C_{70} ligand.^[3] Therefore, the structures of 1–7 are most

likely as shown in Schemes 1, 2, and 3. The structures of 4 and 5 were unequivocally confirmed by X-ray crystal diffraction analysis.

Crystal Structures of 4 and 5

The molecular structures of 4 and 5, as determined by X-ray diffraction techniques, are presented in Figures 1 and 2, respectively; selected bond lengths and angles are given in Tables 1 and 2, respectively. The X-ray diffraction analysis

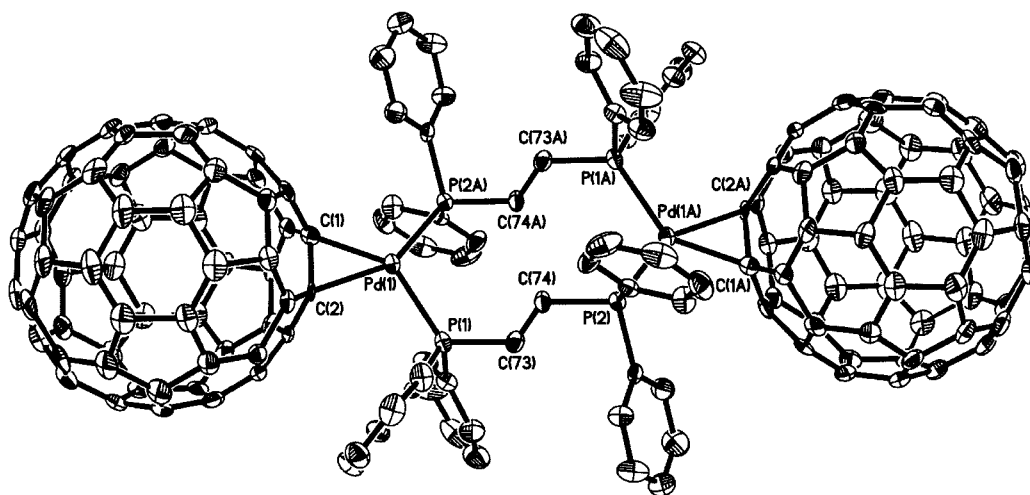


Figure 1. ORTEP drawing of 4 (30% thermal ellipsoids).

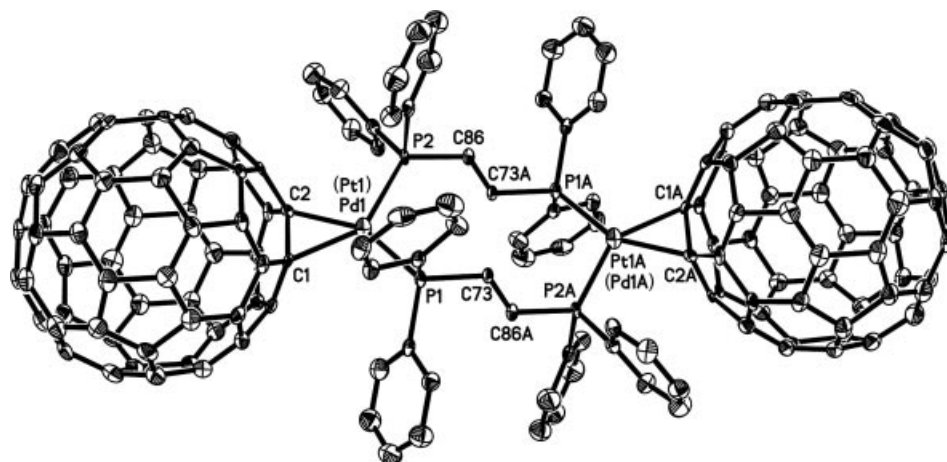


Figure 2. ORTEP drawing of 5 (30% thermal ellipsoids).

revealed that **4** (Figure 1) and **5** (Figure 2) are isostructural; they both consist of two C_{60} spheres that are ligated to two metal centers of a ten-membered metallacycle in which two *trans*-dppet ligands are coordinated to Pd/Pd or Pd/Pt metal centers, respectively. It is worth pointing out that the Pd/Pt atoms in the structure of **5** are 50% disordered and therefore the geometric parameters associated with Pd/Pt atoms cannot be distinguished. In addition, the solvent molecules C_6H_5Cl and C_6H_5Me present in the crystal of **5** are also disordered, which might be responsible for the relatively high *R* value for the structure of **5**. Interestingly, **4** and **5** are the first structurally characterized group 10 metal-containing homo- and heterodinuclear fullerene complexes. The fullerene center-to-center separations of 16.869 Å for **4** and 16.807 Å for **5** are close to that of 16.559 Å in the dinuclear Ir_2 complex. However, the non-bonded metal-to-metal distances (6.83 Å for **4** and 6.82 Å for **5**) are much shorter than the corresponding intermetallic distance of 8.104 Å in the Ir_2 complex.^[17] The two C–C double bonds [C(73)–C(74) = C(73A)–C(74A) = 1.290(14) Å for **4** and C(73)–C(86A) = C(73A)–C(86) = 1.26(2) Å for **5**] are slightly shorter than the common C–C double bond (1.34 Å). Each of the zero-valent metal centers has a square-planar geometry. For example, all the five atoms Pd(1), C(1), C(2), P(1), and P(2A) in **4** and Pt(1A), C(1A), C(2A), P(1A), and P(2A) in **5** are nearly coplanar, with a mean deviation of 0.0528 and 0.0483 Å, respectively. The η^2 -coordinated 6:6 bonds [C(1)–C(2) = 1.473(14) Å for **4** and C(1)–C(2) = 1.50 (2) Å for **5**] are obviously longer than the other 58 uncoordinated 6:6 bonds in each C_{60} sphere due to the metal-to- C_{60} π back-donation.^[5]

Table 1. Selected bond lengths [Å] and angles [°] for **4**.

Pd(1)–C(1)	2.137(11)	P(1)–C(73)	1.826(11)
Pd(1)–C(2)	2.130(9)	C(73)–C(74)	1.290(14)
Pd(1)–P(1)	2.326(3)	P(2)–C(74)	1.820(10)
Pd(1)–P(2A)	2.323(3)	C(1)–C(2)	1.473(14)
C(2)–Pd(1)–C(1)	40.4(4)	P(2A)–Pd(1)–P(1)	109.06(10)
C(2)–Pd(1)–P(2A)	147.0(3)	C(73)–P(1)–Pd(1)	123.9(4)
C(1)–Pd(1)–P(2A)	107.4(3)	C(74)–P(2)–Pd(1A)	118.4(4)
C(2)–Pd(1)–P(1)	101.8(3)	C(2)–C(1)–Pd(1)	69.5(5)
C(1)–Pd(1)–P(1)	141.9(3)	C(1)–C(2)–Pd(1)	70.1(6)

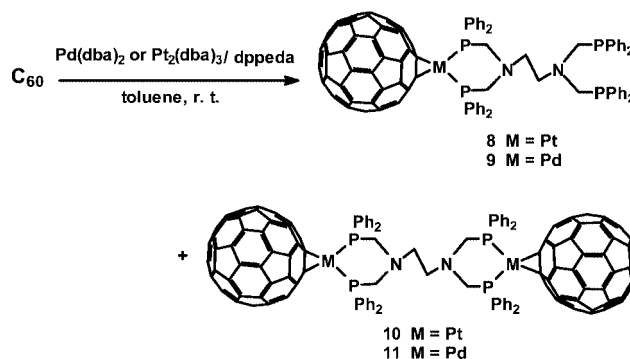
Table 2. Selected bond lengths [Å] and angles [°] for **5**.

Pd(1)–C(1)	2.169(17)	P(1)–C(73)	1.822(17)
Pd(1)–C(2)	2.115(17)	C(73)–C(86A)	1.26(2)
Pd(1)–P(1)	2.311(5)	C(86)–P(2)	1.846(18)
Pd(1)–P(2)	2.309(5)	C(1)–C(2)	1.50(2)
C(2)–Pd(1)–C(1)	41.1(6)	P(2)–Pd(1)–P(1)	108.99(17)
C(2)–Pd(1)–P(2)	101.7(4)	C(73)–P(1)–Pd(1)	118.4(6)
C(1)–Pd(1)–P(2)	142.5(4)	C(86)–P(2)–Pd(1)	124.0(6)
C(2)–Pd(1)–P(1)	147.6(4)	C(2)–C(1)–Pd(1)	67.5(9)
C(1)–Pd(1)–P(1)	107.1(4)	C(1)–C(2)–Pd(1)	71.4(9)

Synthesis and Characterization of Dppeda-Containing Fullerene Complexes

More interestingly, the first examples of a tetraphosphane ligand-containing metallacyclopentafullerene com-

plexes [$(\eta^2-C_{60}M)(dppeda)$] ($M = Pt$ **8**, Pd **9**) and bimetal-lacyclopentafullerene complexes [$(\eta^2-C_{60}M)_2(dppeda)$] ($M = Pt$ **10**, Pd **11**) were synthesized by treatment of a toluene solution of C_{60} with $[Pt_2(dba)_3]$ and the tetraphosphane ligand dppeda or with $[Pd(dba)_2]$ and dppeda in 1:1:1 molar ratio at room temperature in ca. 26% and 45% yields, respectively (Scheme 5).



Scheme 5.

It is apparent that complexes **8–11** are produced through similar pathways to those mentioned above for the production of **1–7**. Complexes **8–11** are air-stable, green solids, which were characterized by elemental analysis and IR, 1H NMR, and ^{31}P NMR spectroscopy. For example, the IR spectra of **8–11** show four absorption bands in the range 1434–526 cm^{-1} characteristic of their C_{60} spheres.^[16] In addition, the ^{31}P NMR spectra of **8** and **9** display one singlet and one triplet or two singlets at $\delta \approx -28$ and 6 ppm for their two identical uncoordinated P atoms and two identical coordinated P atoms, respectively, whereas the spectra of **10** and **11** exhibit one triplet and one singlet at $\delta \approx 6$ ppm for their four identical coordinated P atoms. In fact, the ^{31}P NMR behavior of the tetraphosphane-containing complexes **8–11** is very similar to that of the diphosphane-containing complexes **1–7**, as well as that of the other phosphane-containing fullerene complexes.^[1,9,12] Interestingly, while the 1H NMR spectrum of the free ligand dppeda shows one singlet at $\delta = 3.50$ ppm for its four CH_2 groups attached to P atoms and one singlet at $\delta = 2.88$ ppm for its two CH_2 groups attached to N atoms, the spectra of **8–11** display two broad singlets or multiplets at $\delta = 3.75$ –3.35 ppm for their CH_2 groups attached to P atoms and one multiplet at $\delta = 2.45$ –2.28 ppm for their CH_2 groups bound to N atoms.

Electrochemical Study of **4** and **5**

In order to ascertain if the presence of the p- π conjugated P=C–C–P structural units in the dppet ligands of the dinuclear bisfullerenes **3–7** could trigger inter-fullerene electronic communication, we examined the electrochemical behavior of the representative complexes **4** and **5**. Figure 3 shows the cyclic voltammetric profiles exhibited by complexes **4** and **5** in 1,2-dichlorobenzene solution.^[18]

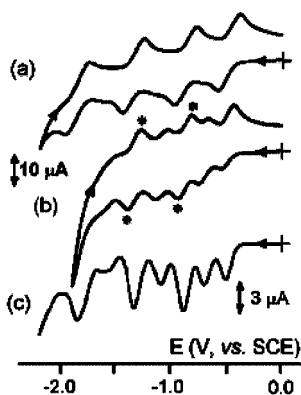


Figure 3. Cyclic voltammograms recorded at a platinum electrode in 1,2-Cl₂C₆H₄ solutions of (a) complex **4** (1.1×10^{-3} M) and (b) complex **5** (1.1×10^{-3} M). (c) Osteryoung square-wave voltammogram of **5** (1.1×10^{-3} M). *n*Bu₄NClO₄ (0.2 M) supporting electrolyte. Scan rates: (a, b) 0.2 V s⁻¹; (c) 0.1 V s⁻¹.

As Figure 3a illustrates, the homodinuclear complex **4** exhibits four fullerene-centered reductions possessing features of chemical reversibility on the cyclic voltammetric timescale ($E^{\circ'} = -0.48, -0.87, -1.34$, and -1.85 V, vs. SCE). Controlled potential coulometry ($E_w = -0.65$ V) proved that the first cathodic process involves two electrons per molecule, thus indicating that the stepwise addition of four electrons to each fullerene moiety proceeds simultaneously. As happens for most bisfullerene systems,^[19] this suggests that no mutual electronic interaction exists between the two metallofullerene subunits. It should be noted that the mentioned processes take place at potential values essentially coincident with those of free fullerene. Cyclic voltammetry in chlorobenzene solution affords a quite similar profile ($E^{\circ'} = -0.52, -0.93$, and -1.46 V vs. SCE), but in such a solvent the difference with respect to free fullerene is better defined ($E^{\circ'} = -0.49, -0.86$, and -1.35 V, vs. SCE). Therefore, since the instantaneous complete decomposition of the original complex can be reasonably ruled out – the original green color of the solution ($\lambda_{\text{max}} = 602$ and 656 nm) does not change with time – such an uncommon result can be likely accounted for by assuming that the cathodic shift induced by the η^2 -coordinated C–C double bond of the [60]-fullerene, which is directly linked to the coordinating power of the metal ion, is just compensated by the anodic shift caused by the electron-withdrawing effects of the phosphane substituents.^[19]

As Figure 3 (b) shows, a different reduction pattern is displayed by the heterodinuclear complex **5**. In fact, the sequential reductions appearing in correspondence of the preceding profile ($E^{\circ'} = -0.49, -0.88$, and -1.33 V, respectively) are followed by an interposed series of further cathodic steps ($E^{\circ'} = -0.71, -1.08$, and -1.6 V, respectively). Coulometric measurements showed that the first two processes involve one-electron additions (exhaustive electrolysis at $E_w = -0.75$ V consumed 1.8 electrons per molecule). The fact that the height of the starred peak-systems is somewhat higher than that of the respective interposed peak-systems (as better seen from the square-wave voltammogram shown

in Figure 3c) has to be attributed to slow release of free fullerene (two mols per mol of decomposed complex) following the concomitant addition of the first electron to each metallofullerene subunit, which is reflected in the high peak-height of the return peak associated with the first step. It seems that the appearance of separate sequential reductions in **5** has to be attributed to the higher coordination ability of Pt with respect to Pd towards fullerene, which renders the two metallofullerene subunits inequivalent, rather than the eventual presence of intramolecular electronic communication, as, in contrast, happens in [Rh₆(CO)₅(dppm)(CNR)(μ_3 - η^2 , η^2 , η^2 -C₆₀)₂] (dppm = diphenylphosphanylmethane; R = CH₂C₆H₅).^[20]

It follows that complexes **4** and **5** display no intramolecular electronic communication even though two p- π -conjugated P=C=C-P structural units are present in the sandwiched metallacycle. However, it can be expected that bismetallofullerenes having electronic communication could be obtained by variation of the spacer between the two metallofullerene subunits.

In summary, we have prepared the first diphosphane (dppet)- and tetraphosphane (dppeda)-containing transition metal–fullerene complexes **1–11** by simple and convenient synthetic methods in satisfactory yields. While complexes **1, 2, 8**, and **9** are diphosphane ligands with fullerene cores, complexes **3–7, 10**, and **11** are bisfullerene complexes in which either a 10-membered metallacycle or two six-membered metallacycles are sandwiched between two fullerene spheres. Possible pathways for production of complexes **1–11** have been preliminarily proposed, and the crystal structures of **4** and **5** along with their electrochemical properties have been determined by X-ray diffraction and cyclic voltammetry. It is worth pointing out that in view of the widespread uses of phosphorus-donor ligands in transition metal chemistry,^[21] the fullerene-containing diphosphane ligands **1, 2, 8**, and **9** can be expected to play an important role in the development of transition metal and fullerene chemistry.

Experimental Section

General: All reactions were carried out under highly purified nitrogen 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 15 min before use. [Pd(dba)₂],^[22] [Pt(dba)₂],^[23] [Pt₂(dba)₃],^[23] and [(Ph₂PCH₂)₂NCH₂]₂ (dppeda)^[24] were prepared according to literature methods. C₆₀ (99.9%) and *trans*-Ph₂PCH=CHPPh₂ (dppet) were available commercially. ¹H and ³¹P NMR spectra were recorded with a Bruker Avance 300 spectrometer, whereas IR spectra were taken on a Bio-Rad FTS 135 spectrophotometer. Elemental analysis was performed with an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

Preparation of [(η^2 -C₆₀Pt)(dppet)]₂ (1**):** A 100-mL, three-necked flask equipped with a magnetic stir-bar, a rubber septum, and a nitrogen inlet tube was charged with C₆₀ (0.072 g, 0.10 mmol), [Pt(dba)₂] (0.066 g, 0.10 mmol) or [Pt₂(dba)₃] (0.056 g, 0.10 mmol), and toluene (50 mL) to form a brown solution. *trans*-Dppet (0.078 g, 0.20 mmol) was added to this solution and then the mix-

ture was stirred at room temperature for 1.5 h. The resulting green mixture was filtered and the green filtrate was layered with 60 mL of hexane overnight to give a green precipitate. The precipitate was washed with hexane (2 × 5 mL) and diethyl ether (2 × 5 mL) sequentially, and then was dried in vacuo to afford 0.060 g (35%) of **1** from [Pt(dba)₂] or 0.098 g (58%) of **1** from [Pt₂(dba)₃] as a green solid. M.p. > 300 °C. ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 7.24–7.60 (m, 44 H, 8 C₆H₅ + 4 CH) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃, H₃PO₄): δ = –7.24 (s, 2 P, 2 PPh₂), 19.88 (t, J_{Pt,P} = 3682 Hz, 2 P, 2 PPt) ppm. IR (KBr disk): ν̄ = 1434 (s), 1184 (m), 577 (m), 524 (vs) (C₆₀), 1571 (m), 967 (m) (C=C) cm^{–1}. C₁₁₂H₄₄P₄Pt (1708.6): calcd. C 78.73, H 2.60; found C 78.75, H 2.41.

Preparation of [(η²-C₆₀Pd)(dppet)₂] (2): The same procedure as that for the preparation of **1** was followed, but [Pd(dba)₂] (0.057 g, 0.10 mmol) was used instead of [Pt(dba)₂] or [Pt₂(dba)₃] to give 0.123 g (75%) of **2** as a green solid. M.p. > 300 °C. ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 7.09–7.63 (m, 44 H, 8 C₆H₅ + 4 CH) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃, H₃PO₄): δ = –7.48 (s, 2 P, 2 PPh₂), 20.21 (s, 2 P, 2 PPd) ppm. IR (KBr disk): ν̄ = 1434 (s), 1183 (m), 578 (m), 513 (vs) (C₆₀), 1570 (m), 966 (m) (C=C) cm^{–1}. C₁₁₂H₄₄P₄Pd (1619.9): calcd. C 83.04, H 2.74; found C 82.87, H 2.75.

Preparation of [(η²-C₆₀Pt)(dppet)₂] (3): Method (i): The flask described above was charged with C₆₀ (0.072 g, 0.10 mmol), [Pt(dba)₂] (0.066 g, 0.10 mmol), *trans*-dppet (0.078 g, 0.20 mmol), and toluene (50 mL). The mixture was stirred at room temperature for 5 h to give a green precipitate. The precipitate was washed with toluene (2 × 10 mL), hexane (2 × 10 mL), and diethyl ether (2 × 10 mL), and finally dried in vacuo to afford 0.108 g (82%) of **3** as a dark-green solid. M.p. > 300 °C. ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 6.90–7.60 (m, 44 H, 8 C₆H₅ + 4 CH) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃, H₃PO₄): δ = 19.71 (t, J_{Pt,P} = 3794 Hz, 4 P) ppm. IR (KBr disk): ν̄ = 1434 (s), 1183 (m), 577 (m), 524 (vs) (C₆₀), 1571 (m), 969 (m) (C=C) cm^{–1}. C₁₇₂H₄₄P₄Pt₂ (2624.3): calcd. C 78.72, H 1.69; found C 78.71, H 1.70.

Method (ii): A mixture of diphosphane **1** (0.086 g, 0.05 mmol), C₆₀ (0.036 g, 0.05 mmol), and [Pt(dba)₂] (0.034 g, 0.05 mmol) in toluene (20 mL) was stirred at room temperature for 5 h to give a precipitate. The same workup as that in method (i) gave 0.078 g (59%) of **3**.

Preparation of [(η²-C₆₀Pd)(dppet)₂] (4): Method (i): The flask described above was charged with C₆₀ (0.072 g, 0.10 mmol), [Pd(dba)₂] (0.114 g, 0.20 mmol), *trans*-dppet (0.039 g, 0.10 mmol), and toluene (50 mL). The mixture was stirred at room temperature for 5 h. The resulting mixture was filtered to give a green precipitate, which was purified by the same method used above for **3** to afford 0.112 g (92%) of **4** as a dark-green solid. M.p. > 300 °C. ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 7.20–7.66 (m, 44 H, 8 C₆H₅ + 4 CH) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃, H₃PO₄): δ = 20.22 (s, 4 P) ppm. IR (KBr disk): ν̄ = 1432 (m), 1183 (m), 577 (m), 524 (vs) (C₆₀), 1571 (m), 964 (m) (C=C) cm^{–1}. C₁₇₂H₄₄P₄Pd₂ (2447.0): calcd. C 84.43, H 1.81; found C 84.16, H 2.00.

Method (ii): A mixture of diphosphane **2** (0.080 g, 0.05 mmol), C₆₀ (0.036 g, 0.05 mmol), and [Pd(dba)₂] (0.029 g, 0.05 mmol) in toluene (20 mL) was stirred at room temperature for 5 h to give a precipitate. The same workup as that in method (i) produced 0.064 g (53%) of **4**.

Preparation of [(η²-C₆₀Pd)(η²-C₆₀Pt)(dppet)₂] (5): Method (i): A mixture of C₆₀ (0.036 g, 0.05 mmol), [Pd(dba)₂] (0.029 g, 0.05 mmol), *trans*-dppet (0.039 g, 0.10 mmol), and toluene (25 mL) was stirred at room temperature for 1 h to give a green solution.

C₆₀ (0.036 g, 0.05 mmol) and [Pt₂(dba)₃] (0.028 g, 0.025 mmol) were added to this solution. The new mixture was stirred at room temperature for 5 h to give a green precipitate. The precipitate was purified by the same method used for **3** to give 0.085 g (65%) of **5** as a green solid. M.p. > 300 °C. ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 7.08–7.60 (m, 44 H, 8 C₆H₅ + 4 CH) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃, H₃PO₄): δ = 19.79 (s, 2 P, 2 PPd), 20.12 (t, J_{Pt,P} = 3848 Hz, 2 P, 2 PPt) ppm. IR (KBr disk): ν̄ = 1434 (s), 1183 (m), 579 (m), 523 (vs) (C₆₀), 1571 (m), 967 (m) (C=C) cm^{–1}. C₁₇₂H₄₄P₄PdPt (2535.6): calcd. C 81.47, H 1.75; found C 81.40, H 2.00.

Method (ii): A mixture of diphosphane **2** (0.080 g, 0.05 mmol), C₆₀ (0.036 g, 0.05 mmol), and [Pt(dba)₂] (0.034 g, 0.05 mmol) in toluene (20 mL) was stirred at room temperature for 5 h to give a precipitate. The same workup as that in method (i) afforded 0.070 g (55%) of **5**.

Preparation of [(η²-C₆₀Pd)(η²-C₇₀Pd)(dppet)₂] (6): Method (i): A mixture of C₆₀ (0.036 g, 0.05 mmol), [Pd(dba)₂] (0.029 g, 0.05 mmol), and *trans*-dppet (0.039 g, 0.10 mmol) in toluene (25 mL) was stirred at room temperature for 1 h to give a green solution. C₇₀ (0.042 g, 0.05 mmol) and [Pd(dba)₂] (0.029 g, 0.05 mmol) were then added to this solution. The new mixture was stirred at room temperature for 5 h to give a green precipitate. The precipitate was purified by the same method as that utilized for **3** to give 0.048 g (37%) of **6** as a brown solid. M.p. > 300 °C. ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 7.09–7.54 (m, 44 H, 8 C₆H₅ + 4 CH) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃, H₃PO₄): δ = 25.64–27.50 (m, 4 P) ppm. IR (KBr disk): ν̄ = 1433 (s), 1183 (m), 576 (m), 510 (vs) (C₆₀), 1130 (w), 1097 (m), 793 (m), 673 (m), 640 (w), 456 (s) (C₇₀), 1569 (w), 967 (m) (C=C) cm^{–1}. C₁₈₂H₄₄P₄Pd₂ (2567.09): calcd. C 85.15, H 1.72; found C 84.95, H 1.88.

Method (ii): A mixture of diphosphane **2** (0.080 g, 0.05 mmol), C₇₀ (0.042 g, 0.05 mmol), and [Pd(dba)₂] (0.029 g, 0.05 mmol) in toluene (20 mL) was stirred at room temperature for 5 h. The same workup as that in method (i) afforded 0.049 g (38%) of **6**.

Preparation of [(η²-C₇₀Pd)(dppet)₂] (7): A mixture of C₇₀ (0.042 g, 0.05 mmol), [Pd(dba)₂] (0.029 g, 0.05 mmol), and *trans*-dppet (0.039 g, 0.10 mmol) in toluene (25 mL) was stirred at room temperature for 1.5 h. The resulting mixture was filtered to give a brown precipitate, which was purified by the method used for purification of **3** to afford 0.023 g (44%) of **7** as a dark-green solid. M.p. > 300 °C. ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 7.15–7.67 (m, 44 H, 8 C₆H₅ + 4 CH) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃, H₃PO₄): δ = 21.15, 22.77 (2s, 4 P) ppm. IR (KBr disk): ν̄ = 1432 (vs), 1129 (w), 1097 (m), 794 (m), 673 (s), 641 (w), 577 (m), 534 (s), 457 (s) (C₇₀), 1567 (m), 967 (m) (C=C) cm^{–1}. C₁₉₂H₄₄P₄Pd₂ (2687.2): calcd. C 85.82, H 1.65; found C 85.60, H 1.73.

Preparation of [(η²-C₆₀Pt)(dppeda)] (8) and [(η²-C₆₀Pt)₂(dppeda)] (10): A brown mixture of C₆₀ (0.036 g, 0.05 mmol) and [Pt₂(dba)₃] (0.028 g, 0.05 mmol) in toluene (25 mL) was stirred at room temperature for 15 min, and then dppeda (0.043 g, 0.05 mmol) was added to cause an immediate color change from brown to green. The green mixture was stirred at room temperature for 5 h and was then filtered to give a green filtrate and a green precipitate. Whereas the green filtrate was treated by a procedure similar to that used in the preparation of **1** to afford 0.025 g (28%) of **8**, the precipitate was purified by the method used for purification of **3** to afford 0.033 g (49%) of **10**.

8: Green solid. M.p. 300 °C (dec.). ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 2.37–2.45 (m, 4 H, NCH₂CH₂N), 3.35–3.47, 3.70–3.75 (2m, 8 H, 4 CH₂P), 7.27–7.74 (m, 40 H, 8 C₆H₅) ppm. ³¹P NMR

(121.48 MHz, CS₂/CDCl₃, H₃PO₄): δ = -27.68 (s, 2 P, 2 PPh₂), 6.67 (t, $J_{\text{Pt,P}}$ = 3575 Hz, 2 P, 2 Ppt) ppm. IR (KBr disk): $\tilde{\nu}$ = 1434 (s), 1184 (m), 577 (m), 526 (vs) (C₆₀) cm⁻¹. C₁₁₄H₅₂N₂P₄Pt (1768.7): calcd. C 77.42, H 2.96, N 1.58; found C 77.49, H 2.77, N 1.72.

10: Green solid. M.p. 290 °C (dec.). ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 2.28–2.33 (m, 4 H, NCH₂CH₂N), 3.39–3.42, 3.71–3.75 (2m, 8 H, 4 CH₂P), 7.23–7.59 (m, 40 H, 8 C₆H₅) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃): δ = 6.66 (t, $J_{\text{Pt,P}}$ = 3571 Hz, 4 P) ppm. IR (KBr disk): $\tilde{\nu}$ = 1434 (s), 1184 (m), 577 (m), 526 (vs) (C₆₀) cm⁻¹. C₁₇₄H₅₂N₂P₄Pt₂ (2684.4): calcd. C 77.85, H 1.95, N 1.04; found C 77.75, H 2.04, N 1.11.

Preparation of [(η^2 -C₆₀Pd)(dppeda)] (9) and [(η^2 -C₆₀Pd)(dppeda)] (11): Similar to the preparation of 8 and 10, 0.021 g (25%) of 9 and 0.027 g (43%) of 11 were prepared from C₆₀ (0.036 g, 0.05 mmol), [Pd(dba)₂] (0.029 g, 0.05 mmol), dppeda (0.043 g, 0.05 mmol), and toluene (20 mL).

9: Green solid. M.p. 295 °C (dec.). ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 2.30–2.34 (m, 4 H, NCH₂CH₂N), 3.54, 3.71 (2 br.s, 8 H, 4 CH₂P), 7.13–7.63 (m, 40 H, 8 C₆H₅) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃): δ = -28.01 (s, 2 P, 2 PPh₂), 5.39 (s, 2 P, 2 PPd) ppm. IR (KBr disk): $\tilde{\nu}$ = 1434 (s), 1184 (m), 578 (m), 526 (vs) (C₆₀) cm⁻¹. C₁₁₄H₅₂N₂P₄Pd (1680.00): calcd. C 81.50, H 3.12, N 1.67; found C 81.70, H 3.16, N 1.69.

11: Green solid. M.p. 280 °C (dec.). ¹H NMR (300 MHz, CS₂/CDCl₃): δ = 2.29–2.34 (m, 4 H, NCH₂CH₂N), 3.57, 3.72 (2 br.s, 8 H, 4 CH₂P), 7.09–7.65 (m, 40 H, 8 C₆H₅) ppm. ³¹P NMR (121.48 MHz, CS₂/CDCl₃): δ = 5.55 (s, 4 P) ppm. IR (KBr disk): $\tilde{\nu}$ = 1434 (s), 1183 (m), 576 (m), 527 (vs) (C₆₀) cm⁻¹. C₁₇₄H₅₂N₂P₄Pd₂ (2507.1): calcd. C 83.36, H 2.09, N 1.12. found C 83.25, H, 2.08, N 1.15.

Table 3. Crystal data and structural refinements details for 4 and 5.

	4	5
Empirical formula	C ₁₇₂ H ₄₄ P ₄ Pd ₂ ·3C ₆ H ₅ Cl·0.5C ₆ H ₅ Me·H ₂ O	C ₁₇₂ H ₄₄ P ₄ PdPt·3C ₆ H ₅ Cl·C ₆ H ₅ Me
Formula mass	2848.49	2965.23
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	13.9731(13)	13.941(7)
<i>b</i> [Å]	13.6933(13)	13.638(7)
<i>c</i> [Å]	34.671(3)	32.772(16)
α [°]	90	90
β [°]	109.149(5)	94.634(10)
γ [°]	90	90
<i>V</i> [Å ³]	6266.8(10)	6210(5)
<i>Z</i>	2	2
<i>D</i> _{calcd.} [g cm ⁻³]	1.510	1.586
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.469	1.454
Crystal size [mm]	0.26 × 0.20 × 0.16	0.32 × 0.20 × 0.16
<i>F</i> (000)	2874	2968
2 θ _{max} [°]	45.00	50.00
Unique reflections	18461	30013
Observed reflections	8160	10922
Index ranges	-10 ≤ <i>h</i> ≤ 15 -14 ≤ <i>k</i> ≤ 11 -37 ≤ <i>l</i> ≤ 36	-15 ≤ <i>h</i> ≤ 16 -15 ≤ <i>k</i> ≤ 16 -38 ≤ <i>l</i> ≤ 35
Goodness of fit on <i>F</i> ²	1.082	1.139
<i>R</i>	0.0803	0.1544
<i>R</i> _w	0.1855	0.3186
Largest diff. peak and hole [e Å ⁻³]	0.886 and -0.804	1.086 and -1.513

X-ray Crystal Structure Determinations of 4 and 5: Single-crystals of 4 and 5 suitable for X-ray diffraction analyses were obtained by slow diffusion of hexane into their C₆H₅Cl/CS₂ solutions at room temperature. A single crystal of 4 or 5 was glued to a glass fiber and mounted on a Bruker SMART 1000 automated diffractometer. Data were collected using graphite-monochromated Mo-*K* α radiation (λ = 0.71073 Å) at room temperature in the ω -2 θ scanning mode. Absorption corrections were performed using the SADABS method. The structures were solved by direct methods using the SHELXS-97 program^[25] and refined by full-matrix least-squares techniques (SHELXL-97)^[26] on *F*². Hydrogen atoms were located by a geometric method. All calculations were performed on a Bruker Smart computer. Details of the crystals, data collections, and structure refinements are summarized in Table 3. The calculations were performed using the TEXSAN crystallographic software package.^[27]

CCDC-232273 (for 4) and -232274 (for 5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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