

# Synthesis and characterization of the first transition-metal fullerene complexes containing bis( $\eta^6$ -benzene)chromium moieties

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Received 2 June 2005; received in revised form 8 October 2005; accepted 13 October 2005

Available online 5 December 2005

## Abstract

While photochemical reaction of C<sub>60</sub> with an equimolar amount of Mo(CO)<sub>4</sub>( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr (**1**) in toluene at room temperature produced bimetallic Mo/Cr fullerene complex *fac/mer*-( $\eta^2$ -C<sub>60</sub>)Mo(CO)<sub>3</sub>[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**2**) in 87% yield, the thermal reaction of an equimolar mixture of C<sub>60</sub>, M(dba)<sub>2</sub> (M = Pd, Pt; dba = dibenzylideneacetone) and ( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr (**3**) in toluene at room temperature afforded bimetallic M/Cr fullerene complexes ( $\eta^2$ -C<sub>60</sub>)M[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**4**, M = Pd; **5**, M = Pt) in 88% and 92% yields, respectively. Products **2**, **4** and **5** are the first transition-metal fullerene complexes containing bis( $\eta^6$ -benzene)chromium moieties. While **2**, **4** and **5** were characterized by elemental analysis and spectroscopy, the crystal molecular structures of **4** along with the starting materials **1** and **3** have been determined by X-ray diffraction techniques.

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**Keywords:** Molybdenum; Platinum; Palladium; [60]Fullerene; Bis( $\eta^6$ -diphenylphosphinobenzene)chromium; Crystal structures

## 1. Introduction

Since the discovery of [60]fullerene [1] and its synthesis in macroscopic quantities [2], a great number of transition-metal fullerene complexes have been synthesized and structurally characterized [3–6], largely because of their unique structures, novel properties and the potential applications in various fields such as material and life sciences [7]. Recently, we reported a series of transition-metal fullerene complexes which contain a bis( $\eta^5$ -cyclopentadienyl)-type of metallocene unit, such as ( $\eta^2$ -C<sub>60</sub>)M(CO)<sub>3</sub>[( $\eta^5$ -Ph<sub>2</sub>PC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe] (M = Mo, W) [8], ( $\eta^2$ -C<sub>n</sub>)Pt[( $\eta^5$ -Ph<sub>2</sub>AsC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>-Fe] (C<sub>n</sub> = C<sub>60</sub>, C<sub>70</sub>) [9], ( $\eta^2$ -C<sub>60</sub>)M[( $\eta^5$ -Ph<sub>2</sub>PC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Ru]

(M = Pd, Pt) [10], and ( $\eta^2$ -C<sub>60</sub>)M[( $\eta^5$ -Ph<sub>2</sub>PC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Co]<sup>+</sup>(PF<sub>6</sub>)<sup>-</sup> (M = Pd, Pt) [10]. However, up to now, no report has appeared regarding another series of transition metal fullerene complexes in which a transition-metal atom is sandwiched between two parallel benzene rings, such as bis( $\eta^6$ -benzene)chromium. Now, as a continuation of our project regarding the metallocene-containing transition-metal fullerene complexes, we report a new series of transition-metal fullerene complexes, each of which contains a bis( $\eta^6$ -benzene)chromium unit, namely *fac/mer*-( $\eta^2$ -C<sub>60</sub>)Mo(CO)<sub>3</sub>[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**2**) and ( $\eta^2$ -C<sub>60</sub>)M[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**4**, M = Pd; **5**, M = Pt). Apparently, these complexes are of particular interest, since they contain both theoretically and practically important fullerene core and sandwich moiety. Furthermore, we also report the crystal molecular structure of **4**, as well as those of the starting materials Mo(CO)<sub>4</sub>[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**1**) and ( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr (**3**).

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## 2. Results and discussion

### 2.1. Synthesis and characterization of *fac*/*mer*-( $\eta^2$ -C<sub>60</sub>)Mo(CO)<sub>3</sub>[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**2**) and ( $\eta^2$ -C<sub>60</sub>)M[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**4**, M = Pd; **5**, M = Pt)

We found that the bimetallic Mo/Cr fullerene complex **2** could be obtained in 87% yield when an equimolar mixture of C<sub>60</sub> and Mo(CO)<sub>4</sub>[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**1**) was irradiated with a UV 450 W photochemical lamp in toluene at room temperature for 2 h (Scheme 1).

Compound **2** is an air-sensitive, dark green solid, which has been characterized by elemental analysis, and IR, <sup>1</sup>H NMR, <sup>31</sup>P NMR, and UV–Vis spectroscopy. The <sup>31</sup>P NMR spectrum of **2** showed it to be an isomeric mixture of the *fac* and *mer* isomers. This is because that the <sup>31</sup>P NMR spectrum (Fig. 1) displayed two doublets at 39.18 and 29.84 ppm assignable to the two different P atoms in the *mer* isomer and one singlet at 33.49 ppm attributable to the two identical P atoms in the *fac* isomer. The IR spectrum of **2** exhibited four absorption bands in the range 1433–526 cm<sup>-1</sup> for its C<sub>60</sub> core [11] and six bands in the region 2043–1889 cm<sup>-1</sup> for its terminal carbonyls. The latter is in good agreement with **2** being a mixture of the two isomers, since the number of IR active bands cannot exceed but may be less than the number of CO ligands in the complex [12]. The UV–Vis spectrum of **2** showed three intense bands between 200 and 400 nm, which are close to those of free C<sub>60</sub> [13]. Compared with that of free C<sub>60</sub>, the UV–Vis spectrum of **2** has a new weak broad band appearing at 435 nm, which might be attributed to the [60]fullerene cage being coordinated to molybdenum in an  $\eta^2$ -fashion [14]. The <sup>1</sup>H NMR spectrum of **2** displayed three sharp singlets at 3.69, 3.97 and 4.23 ppm, which can be assigned respectively to  $\gamma$ -CH,  $\beta$ -CH and  $\alpha$ -CH of the two benzene rings in the bis(benzene)chromium moiety.

We further found that the thermal reaction of an equimolar mixture of C<sub>60</sub>, M(dba)<sub>2</sub> (M = Pd, Pt; dba = dibenzylideneacetone) and ( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr (**3**) in toluene at room temperature resulted in formation of the bimetallic M/Cr fullerene complexes ( $\eta^2$ -C<sub>60</sub>)M[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr]

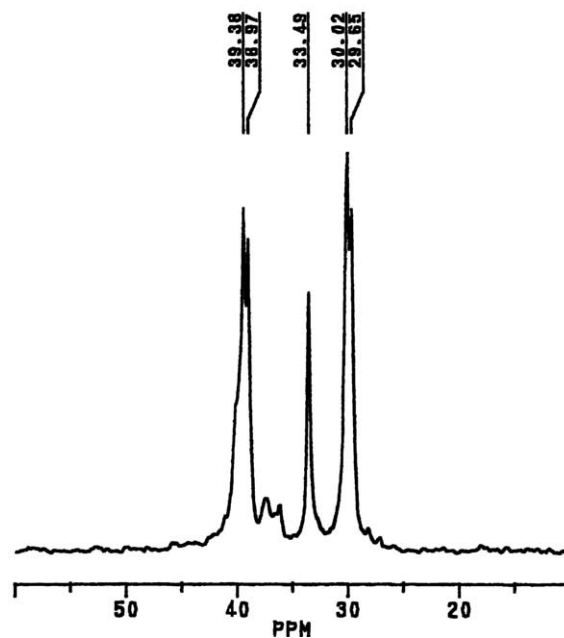


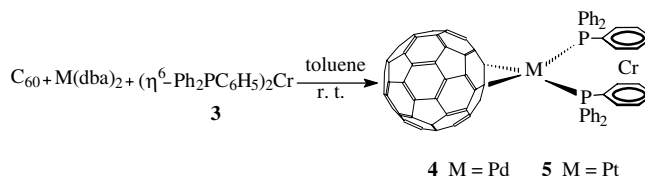
Fig. 1. <sup>31</sup>P NMR spectrum of **2**.

(**4**, M = Pd; **5**, M = Pt) in 88% and 92% yields, respectively (Scheme 2).

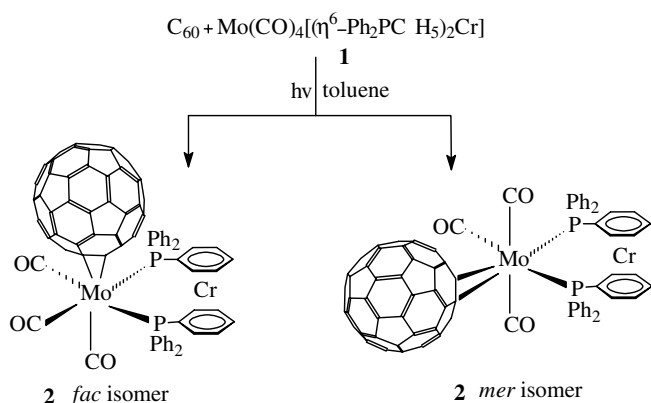
The synthetic route for formation of **4** and **5** is believed to involve an initial reaction of C<sub>60</sub> with M(dba)<sub>2</sub> to give (C<sub>60</sub>M)<sub>n</sub> (M = Pd [15], Pt [16]) and the subsequent reaction of (C<sub>60</sub>M)<sub>n</sub> with diphosphine ligand ( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr (**3**). Products **4** and **5** are air-sensitive, green solids, which were characterized by elemental analysis and spectroscopy. For example, both IR spectra of **4** and **5** (showing four absorption bands in the region 1435–523 cm<sup>-1</sup>) [11] and UV–Vis spectra of **4** and **5** (displaying three intense bands in the range 200–400 nm and one weak broad band at ca. 440 nm) are consistent with their C<sub>60</sub> ligand being coordinated to Pd or Pt in an  $\eta^2$ -mode [11,13,14]. In addition, the <sup>1</sup>H NMR spectra of **4** and **5** exhibited three singlets at 3.70, 3.97 and 4.23 ppm assigned to  $\gamma$ -CH,  $\beta$ -CH and  $\alpha$ -CH of the two benzene rings in bis(benzene)chromium unit, respectively. However, it is worth pointing out that although the <sup>31</sup>P NMR spectrum of **4** showed one singlet at 29.62 ppm for its two identical P atoms, the qualified <sup>31</sup>P NMR spectrum of **5** was not obtained due to its too little solubility in common deuterated organic solvent.

### 2.2. Crystal structures of **3**, **1** and **4**

Although the Ph<sub>2</sub>P-disubstituted bis( $\eta^6$ -benzene)chromium ( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr (**3**) and its molybdenum complex



Scheme 2.



Scheme 1.

$\text{Mo}(\text{CO})_4[(\eta^6\text{-Ph}_2\text{PC}_6\text{H}_5)_2\text{Cr}]$  (**1**) were known three decades ago [17,18], there are no crystallographic data of **3** and **1** available in the literature. Fortunately, we have succeeded in determining their molecular structures by single-crystal X-ray diffraction techniques. The molecular structures of **3** and **1** are shown in Figs. 2 and 3, whereas Tables 1 and 2 list their selected bond lengths and angles, respectively. As can be seen in Fig. 2, diphosphine ligand **3** is centrosymmetric with respect to Cr(1) atom. Therefore, the two benzene rings are parallel and staggered to each

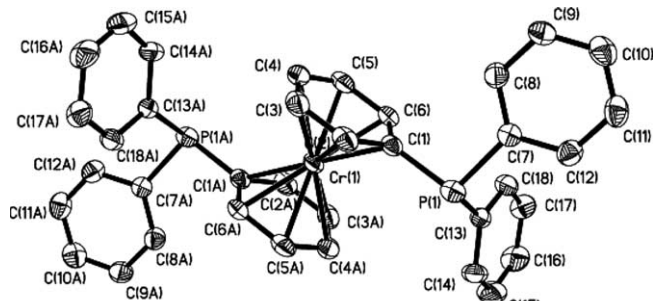


Fig. 2. ORTEP plot of **3** with the atom labeling scheme.

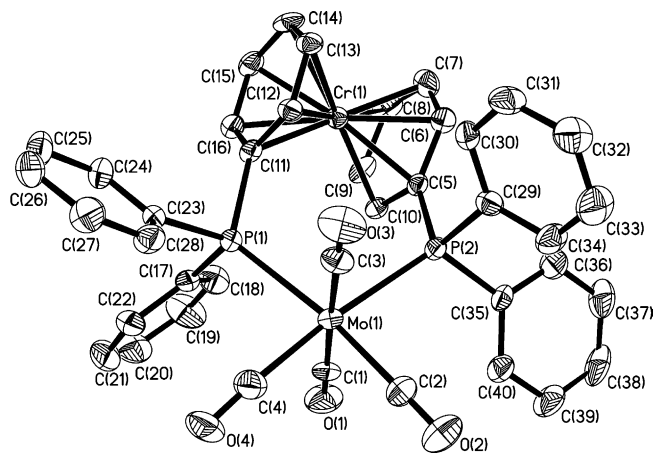


Fig. 3. ORTEP plot of **1** with the atom labeling scheme.

Table 1  
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths (Å)			
Cr(1)–C(3)	2.131(4)	P(1)–C(1)	1.821(4)
Cr(1)–C(2)	2.133(4)	P(1)–C(13)	1.828(4)
Cr(1)–C(6)	2.132(3)	P(1)–C(7)	1.836(4)
Cr(1)–C(5)	2.139(4)	C(1)–C(2)	1.420(5)
Cr(1)–C(1)	2.147(4)	C(2)–C(3)	1.395(6)
Cr(1)–C(4)	2.148(4)	C(3)–C(4)	1.395(6)
Bond angles (°)			
C(3)–Cr(1)–C(1)	69.81(16)	C(1)–P(1)–C(13)	105.94(18)
C(2)–Cr(1)–C(1)	38.76(14)	C(1)–P(1)–C(7)	100.60(17)
C(6)–Cr(1)–C(1)	38.53(14)	C(6)–C(1)–C(2)	118.4(4)
C(5)–Cr(1)–C(1)	69.63(16)	C(6)–C(1)–P(1)	125.6(3)
C(1)–Cr(1)–C(4)	82.14(16)	C(2)–C(1)–P(1)	115.9(3)
C(5)–C(4)–C(3)	120.3(5)	C(3)–C(2)–C(1)	120.8(4)

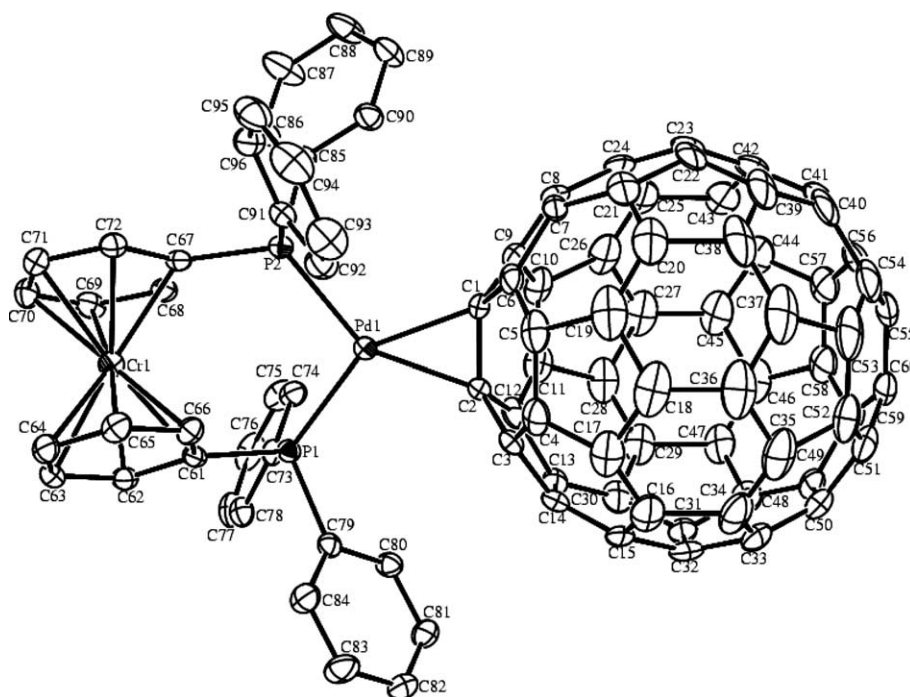
Table 2  
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths (Å)			
Mo(1)–C(1)	2.018(7)	Mo(1)–P(2)	2.552(3)
Mo(1)–C(2)	2.006(8)	Cr(1)–C(5)	2.125(4)
Mo(1)–C(3)	2.031(8)	Cr(1)–C(8)	2.143(4)
Mo(1)–C(4)	1.986(8)	P(1)–C(11)	1.875(4)
Mo(1)–P(1)	2.558(3)	P(2)–C(5)	1.864(4)
Bond angles (°)			
P(2)–Mo(1)–P(1)	100.21(11)	C(2)–Mo(1)–P(2)	88.3(2)
C(4)–Mo(1)–C(2)	86.5(3)	C(1)–Mo(1)–P(2)	91.4(2)
C(4)–Mo(1)–C(1)	87.5(3)	C(3)–Mo(1)–P(1)	91.5(2)
C(2)–Mo(1)–C(1)	93.3(3)	C(4)–Mo(1)–P(1)	85.1(3)
C(1)–Mo(1)–C(3)	178.8(3)	C(2)–Mo(1)–P(1)	170.9(2)
C(2)–Mo(1)–C(3)	85.6(3)	C(1)–Mo(1)–P(1)	89.6(2)

other, the distances from Cr(1) atom to the two centroids of two benzene rings are equal (1.611 Å) and the two Ph<sub>2</sub>P substituents are trans to each other with respect to the central Cr(1) atom.

Interestingly, as shown in Fig. 3, the diphosphine ligand **3** in complex **1** is chelated via its two P atoms to the Mo atom of the Mo(CO)<sub>4</sub> moiety, thus completing a *cis* octahedral coordination geometry for the Mo atom. However, the configuration at the Mo atom is distorted from a normal octahedral geometry, with the P(1)–Mo(1)–P(2) angle of 100.21(11)° increased from the ideal value of 90° and larger than that of Mo(CO)<sub>4</sub>(dppf) (95.28(2)°) [19]. The chelated ligand **3** has two parallel benzene rings (with a dihedral angle of only 0.5°), which are staggered to each other. In addition, the two distances between Cr(1) atom and the centroids of the two benzene rings are equal to 1.612(7) Å.

Particularly interesting is that product **4** is the first synthesized and crystallographically characterized transition-metal fullerene complex containing a bis(η<sup>6</sup>-benzene)metal moiety. As can be seen in Fig. 4, product **4** has a C<sub>60</sub> ligand bonded to Pd(1) atom in an η<sup>2</sup>-fashion with the C(1)–C(2) bond between two six-membered rings (see Table 3). The C(1)–C(2) bond length (1.466(5) Å) is actually the same as the corresponding that in (η<sup>2</sup>-C<sub>60</sub>)Pd(dppf) (1.466(11) Å), but considerably longer than the 6:6 bond length in free C<sub>60</sub> (1.38 Å) [20], obviously due to metal-to-C<sub>60</sub> π-back-donation. In addition, the Ph<sub>2</sub>P-disubstituted bis(η<sup>6</sup>-benzene)chromium ligand **3** is chelated via its two P atoms to Pd(1) atom. The zerovalent Pd(1) is at the center of a tetragon constituted by C(1), C(2), P(1) and P(2) atoms, and all the five atoms are almost coplanar with a mean deviation of 0.0493 Å. The two bond angles P(1)–Pd(1)–P(2) (106.50(3)°) and C(1)–Pd(1)–C(2) (40.39(12)°) are very close to the corresponding those in (η<sup>2</sup>-C<sub>60</sub>)Pd(dppf) (103.30(9) and 40.8(3), respectively) [9]. While the distances from Cr(1) atom to the two centroids of the two benzene rings are 1.632(3) Å, the two benzene rings are parallel and arranged in a staggered manner. The distance between Pd(1) and Cr(1) is 4.396(1) Å, which is far greater than the sum of their van der Waals radii and thus no metal–metal interactions between these two metal

Fig. 4. ORTEP plot of **4** with the atom labeling scheme.Table 3  
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths (Å)			
Pd(1)–C(2)	2.116(3)	P(1)–C(61)	1.817(3)
Pd(1)–C(1)	2.129(3)	P(2)–C(67)	1.824(3)
Pd(1)–P(1)	2.3341(10)	Pd(1)–P(2)	2.3410(11)
Cr(1)–C(62)	2.133(3)	C(1)–C(2)	1.466(5)
Cr(1)–C(67)	2.136(3)	Cr(1)–C(61)	2.138(3)
Bond angles (°)			
C(2)–Pd(1)–C(1)	40.39(12)	P(1)–Pd(1)–P(2)	106.50(3)
C(2)–Pd(1)–P(1)	106.46(9)	C(61)–P(1)–C(73)	106.76(15)
C(62)–Cr(1)–C(61)	38.71(12)	C(61)–P(1)–Pd(1)	114.36(10)
C(1)–Pd(1)–P(2)	70.27(19)	C(79)–P(1)–Pd(1)	115.32(10)
C(1)–Pd(1)–P(1)	106.76(10)	C(67)–P(2)–C(91)	104.84(16)
C(62)–Cr(1)–C(67)	135.19(13)	C(2)–C(1)–Pd(1)	69.34(18)

centers. Similar cases were seen in its bis( $\eta^5$ -cyclopentadienyl)metal analogues, such as ( $\eta^2$ -C<sub>60</sub>)Pd(dppf) (Pd··Fe = 4.196 Å) [9], ( $\eta^2$ -C<sub>60</sub>)Pd(dppr) (Pd··Ru = 4.276 Å) [10] and [( $\eta^2$ -C<sub>60</sub>)Pd(dppc)]<sup>+</sup>(PF<sub>6</sub>)<sup>−</sup> (Pd··Co = 4.113 Å) [10].

### 3. Experimental

All reactions were carried out under 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 15 min before use. ( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr [17], Mo(CO)<sub>4</sub>[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] [18], Pd(dba)<sub>2</sub> [21], and Pt(dba)<sub>2</sub> [22] were prepared according to the literature methods. C<sub>60</sub> (99.9%) was available commercially. <sup>1</sup>H NMR and <sup>31</sup>P NMR were recorded on a Bruker AC-P200 spectrometer. UV–Vis on a Shimadzu TU 1901 spec-

trophotometer and IR spectra on a Bio-Rad FTS 135 spectrophotometer. Elemental analysis was performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

#### 3.1. Preparation of fac[mer-( $\eta^2$ -C<sub>60</sub>)Mo(CO)<sub>3</sub>[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**2**)

A 100-ml photoreactor equipped with a N<sub>2</sub> inlet tube and a serum cap was charged with 0.044 g (0.06 mmol) of C<sub>60</sub>, 0.039 g (0.05 mmol) of Mo(CO)<sub>4</sub>[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr], and 30 ml of toluene. The photoreactor containing the resulting purple solution was irradiated under N<sub>2</sub> by a water-cooled UV 450 W mercury vapor lamp for 2 h to give a dark green solution. Solvent was removed at reduced pressure, leaving a solid which was washed with 20 ml of toluene and 10 ml of hexane successively, and finally dried in vacuo to give 0.064 g (87%) of **2** as a dark green solid. m.p. > 300 °C. Anal. Found: C, 80.39; H, 2.04%. C<sub>99</sub>H<sub>30</sub>CrMoO<sub>3</sub>P<sub>2</sub> Calc.: C, 80.50; H, 2.05. IR (KBr disk):  $\nu_{\text{C=O}}$  2043s, 1997s, 1980m, 1920s, 1889m;  $\nu_{\text{C60}}$  1433m, 1182m, 576m, 526s cm<sup>−1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  3.69 (s, 2H,  $\gamma$ -CH), 3.97(s, 4H,  $\beta$ -CH), 4.23(s, 4H,  $\alpha$ -CH), 7.26–7.42 (m, 20H, 4C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P NMR (81.0 MHz, CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>):  $\delta$  29.84 (d, 1P,  $J_{\text{P-P}} = 31.7$  Hz), 33.49 (s, 2P), 39.18 (d, 1P,  $J_{\text{P-P}} = 31.7$  Hz). UV–Vis (C<sub>6</sub>H<sub>5</sub>Me):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 284.2 (4.62), 285.8 (4.61), 334.2 (4.44), 435.0 (3.90) nm.

#### 3.2. Preparation of ( $\eta^2$ -C<sub>60</sub>)Pd[( $\eta^6$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cr] (**4**)

A 100-ml three-necked flask equipped with a magnetic stir-bar, a rubber septum and a nitrogen inlet tube was

charged with 0.036 g (0.05 mmol) of  $C_{60}$ , 0.030 g (0.05 mmol) of  $(\eta^6\text{-Ph}_2\text{PC}_6\text{H}_5)_2\text{Cr}$  and 20 ml of toluene. To the purple toluene solution was added 0.029 g (0.05 mmol) of  $\text{Pd}(\text{dba})_2$ . The mixture was stirred at room temperature for 0.5 h to give a deep green suspension, and then the suspension was carefully layered with 40 ml of hexane overnight to give a precipitate. The precipitate was filtered, washed with 40 ml of hexane and dried in vacuo to afford 0.062 g (88%) of **4** as a green solid. m.p. > 300 °C. Anal. Found: C, 81.99; H, 2.15%.  $C_{96}H_{30}CrP_2Pd$  Calc.: C, 82.15; H, 2.15. IR (KBr disk):  $\nu_{C60}$  1435m, 1184m, 575m, 523s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.73 (s, 2H,  $\gamma$ -CH), 3.97 (s, 4H,  $\beta$ -CH), 4.23 (s, 4H,  $\alpha$ -CH), 7.26–7.32 (m, 20H,  $4C_6H_5$ ).  $^{31}\text{P}$  NMR (81.0 MHz, benzene- $d_6$ ,  $H_3PO_4$ ):  $\delta$  29.62 (s, 2P). UV–Vis ( $C_6H_5Me$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 281.7 (4.73), 284.2 (4.74), 331.7 (4.96), 440.8 (3.48) nm.

### 3.3. Preparation of $(\eta^2\text{-}C_{60})\text{Pt}[(\eta^6\text{-Ph}_2\text{PC}_6\text{H}_5)_2\text{Cr}]$ (**5**)

Similarly, when using 0.033 g (0.05 mmol) of  $\text{Pt}(\text{dba})_2$ , 0.069 g (92%) of **5** as a green solid was prepared. m.p. > 300 °C. Anal. Found: C, 77.33; H, 2.05%.  $C_{96}H_{30}CrP_2Pt$  Calc.: C, 77.27; H, 2.03. IR (KBr disk):  $\nu_{C60}$  1434m, 1183m, 575m, 526s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.69 (s, 2H,  $\gamma$ -CH), 3.97 (s, 4H,  $\beta$ -CH), 4.23 (s, 4H,  $\alpha$ -CH), 7.26–7.28 (m, 20H,  $4C_6H_5$ ). UV–Vis ( $C_6H_5Me$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 281.7 (4.75), 284.2 (4.75), 332.5 (4.89), 436.7 (3.64) nm.

### 3.4. X-ray crystal structure determinations of **3** and **1**

Single-crystals of **3** and **1** suitable for X-ray diffraction analyses were obtained by slow diffusion of hexane into their toluene solutions at room temperature. The single-crystal of **3** or **1** was glued to a glass fiber and mounted on a Bruker SMART 1000 automated diffractometer. Data were collected using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature in the  $\omega$ – $2\theta$  scanning mode. Absorption correction was performed with SADABS [23]. The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on  $F^2$  [24]. Hydrogen atoms were located by using the geometric method. All calculations were performed on a Bruker Smart computer. Details of the crystals, data collections, and structure refinements are summarized in Table 4.

### 3.5. X-ray crystal structure determination of **4**

The X-ray qualified single-crystals of **4** were obtained by slow diffusion of hexane into its toluene solution at room temperature. Data were collected using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at  $-20 \text{ }^\circ\text{C}$  on a MAR diffractometer with a 300-mm image plate detector. Data collection was made with  $2^\circ$  oscillation step of  $\varphi$ , 120 s exposure time and scanner distance at 120 mm. 90 images were collected. The structure was solved by direct methods employing SHELXS-97 program [25a] and

Table 4  
Crystal data and structural refinements details for **3**, **1** and **4**

	<b>3</b>	<b>1</b>	<b>4</b>
Formula	$C_{36}H_{30}CrP_2$	$C_{47}H_{38}CrMoO_4P_2$	$C_{109}H_{52}CrP_2Pd$
Formula weight	576.54	876.65	1581.85
Temperature (K)	293(2)	293(2)	253(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P2_1/c$
$a$ (Å)	8.721 (3)	11.357(16)	14.122(3)
$b$ (Å)	18.732(6)	12.572(18)	24.509(5)
$c$ (Å)	9.025(3)	14.37(2)	20.023(4)
$\alpha$ (°)	90	93.55(3)	90
$\beta$ (°)	101.694(6)	95.87(2)	99.22(3)
$\gamma$ (°)	90	93.50(3)	90
$V$ (Å <sup>3</sup> )	1443.7(8)	2033(5)	6841(2)
$Z$	2	2	4
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.326	1.432	1.536
$\mu$ (Mo $K\alpha$ ) ( $\text{mm}^{-1}$ )	0.531	0.698	0.529
Crystal size (mm)	0.40 × 0.30 × 0.10	0.20 × 0.20 × 0.10	0.35 × 0.25 × 0.15
$F(000)$	600	896	3224
$2\theta_{\text{max}}$ (°)	50.06	50.06	51.24
No. of observations	5902	8101	40534
No. of independent observations	2552	6828	11708
Index ranges	$-10 \leq h \leq 9,$ $-21 \leq k \leq 22, -10 \leq l \leq 9$	$-13 \leq h \leq 13,$ $-14 \leq k \leq 9, -16 \leq l \leq 17$	$-16 \leq h \leq 16,$ $-29 \leq k \leq 29, -24 \leq l \leq 24$
Goodness-of-fit	0.956	0.999	0.988
$R$	0.0473	0.0640	0.0432
$R_w$	0.1042	0.1496	0.1212
Largest difference peak and hole ( $e \text{ \AA}^{-3}$ )	0.591 and $-0.290$	0.900 and $-1.001$	0.791 and $-0.823$

refined by full-matrix least-squares on  $F^2$  employing SHELXS-97 program [25b] on PC. In the least-squares refinements, all non-hydrogen atoms were refined anisotropically, and the H atoms at calculated positions were not refined. Details of the crystal, data collection, and structure refinement are summarized in Table 4.

#### 4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 271997 for **3**, 271998 for **1** and 273171 for **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

#### Acknowledgments

We are grateful to the National Natural Science Foundation of China, the Research Fund for the Doctoral Program of Higher Education of China, and the Hong Kong Research Grants Council (HKU 7026/04P) for financial support of this work.

#### References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* 318 (1985) 162.
- [2] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, *Nature* 347 (1990) 354.
- [3] For monometallic fullerene complexes, see for example: (a) A.L. Balch, V.J. Catalano, J.W. Lee, M.M. Olmstead, *J. Am. Chem. Soc.* 114 (1992) 5455; (b) M. Sawamura, H. Iikura, E. Nakamura, *J. Am. Chem. Soc.* 118 (1996) 12850; (c) H.-F. Hsu, Y. Du, T.E. Albrecht-Schmitt, S.R. Wilson, J.R. Shapley, *Organometallics* 17 (1998) 1756; (d) M.N. Bengough, D.M. Thompson, M.C. Baird, G.D. Enright, *Organometallics* 18 (1999) 2950; (e) L.-C. Song, J.-T. Liu, Q.-M. Hu, L.-H. Weng, *Organometallics* 19 (2000) 1643; (f) L.-C. Song, P.-C. Liu, J.-T. Liu, F.-H. Su, G.-F. Wang, Q.-M. Hu, P. Zanello, F. Laschi, M. Fontani, *Eur. J. Inorg. Chem.* (2003) 3201; (g) L.-C. Song, G.-A. Yu, H.-T. Wang, F.-H. Su, Q.-M. Hu, Y.-L. Song, Y.-C. Gao, *Eur. J. Inorg. Chem.* (2004) 866; (h) L.-C. Song, P.-C. Liu, Q.-M. Hu, G.-L. Lu, G.-F. Wang, *J. Organomet. Chem.* 681 (2003) 264.
- [4] For bimetallic fullerene complexes, see for example: (a) A.L. Balch, J.W. Lee, B. Noll, M.M. Olmstead, *J. Am. Chem. Soc.* 114 (1992) 10984; (b) A.L. Balch, J.W. Lee, M.M. Olmstead, *Angew. Chem., Int. Ed. Engl.* 31 (1992) 1356; (c) S. Zhang, T.L. Brown, Y. Du, J.R. Shapley, *J. Am. Chem. Soc.* 115 (1993) 6705; (d) I.J. Mavunkal, Y. Chi, S.-M. Peng, G.-H. Lee, *Organometallics* 14 (1995) 4454; (e) Y.-H. Zhu, L.-C. Song, Q.-M. Hu, C.-M. Li, *Org. Lett.* 1 (1999) 1693.
- [5] For trimetallic fullerene complexes, see for example: (a) H.-F. Hsu, J.R. Shapley, *J. Am. Chem. Soc.* 118 (1996) 9192; (b) J.T. Park, H. Song, J.-J. Cho, M.-K. Chung, J.-H. Lee, I.-H. Suh, *Organometallics* 17 (1998) 227; (c) H. Song, K. Lee, J.T. Park, M.-G. Chio, *Organometallics* 17 (1998) 4477.
- [6] For multimetallic fullerene complexes, see for example: (a) A.L. Balch, L. Hao, M.M. Olmstead, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 188; (b) K. Lee, F.-F. Hsu, J.R. Shapley, *Organometallics* 16 (1997) 3876; (c) K. Lee, J.R. Shapley, *Organometallics* 17 (1998) 3020; (d) K. Lee, Z.-H. Choe, Y.-J. Cho, H. Song, J.T. Park, *Organometallics* 20 (2001) 5564; (e) G. Lee, Y.-J. Cho, B.K. Park, K. Lee, J.T. Park, *J. Am. Chem. Soc.* 125 (2003) 13920.
- [7] For reviews, see for example: (a) K. Lee, H. Song, J.T. Park, *Acc. Chem. Res.* 36 (2003) 78; (b) W. Sliwa, *Transition Met. Chem.* 21 (1996) 583; (c) A.L. Balch, M.M. Olmstead, *Chem. Rev.* 98 (1998) 2123; (d) J.R. Bowser, *Adv. Organomet. Chem.* 36 (1994) 57.
- [8] L.-C. Song, J.-T. Liu, Q.-M. Hu, G.-F. Wang, P. Zanello, M. Fontani, *Organometallics* 19 (2000) 5342.
- [9] L.-C. Song, G.-F. Wang, P.-C. Liu, Q.-M. Hu, *Organometallics* 22 (2003) 4593.
- [10] L.-C. Song, G.-A. Yu, F.-H. Su, Q.-M. Hu, *Organometallics* 23 (2004) 4192.
- [11] J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor, A.W. Allaf, S. Balm, D.R.M. Walton, *J. Chem. Soc., Chem. Commun.* (1991) 412.
- [12] J.P. Collman, L.S. Hegeudus, J.R. Norton, R.J. Finke, *Principles and Applications of Organotransition Metal Chemistry*, second ed., University Science Books, Mill Valley, CA, 1987.
- [13] (a) R. Taylor, J.P. Hare, A.K. Abdul-Sada, H.W. Kroto, *J. Chem. Soc., Chem. Commun.* (1990) 1423; (b) J.P. Hare, H.W. Kroto, R. Taylor, *Chem. Phys. Lett.* 177 (1991) 394; (c) T. Akasaka, W. Ando, K. Kobagashi, S. Nagase, *J. Am. Chem. Soc.* 115 (1993) 1605.
- [14] A. Hirsch, T. Grösser, A. Skiebe, A. Soi, *Chem. Ber.* 126 (1993) 1061.
- [15] H. Nagashima, A. Nakaoka, Y. Saito, M. Kato, T. Kawanishi, K. Itoh, *J. Chem. Soc., Chem. Commun.* (1992) 377.
- [16] H. Nagashima, Y. Kato, H. Yamaguchi, E. Kimura, T. Kawanishi, M. Kato, Y. Saito, M. Haga, K. Itoh, *Chem. Lett.* (1994) 1207.
- [17] C. Elschenbroich, F. Stohler, *J. Organomet. Chem.* 67 (1974) C51.
- [18] C. Elschenbroich, F. Stohler, *Angew. Chem., Int. Ed. Engl.* 14 (1975) 174.
- [19] I.R. Butter, W.R. Cullen, T.-J. Kim, S.J. Rettig, J. Trotter, *Organometallics* 4 (1985) 972.
- [20] H.B. Bürgi, E. Blanc, D. Schwarzenbach, S. Liu, Y. Lu, M.M. Kappes, J.A. Ibers, *Angew. Chem., Int. Ed. Engl.* 31 (1992) 640.
- [21] Y. Takahashi, T. Ito, S. Sakai, Y. Ishii, *J. Chem. Soc. D* (1970) 1065.
- [22] W.J. Cherwinski, B.F.G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.* (1974) 1405.
- [23] G.M. Sheldrick, *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.
- [24] G.M. Sheldrick, *SHELXTL*, Structure Determination Software Programs, Bruker Analytical X-ray System, Inc., Madison, WI, USA, 1997.
- [25] (a) G.M. Sheldrick, *SHELXS-97*, Programs for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997; (b) G.M. Sheldrick, *SHELXS-97*, Programs for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.