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Synthesis and characterization of Group 6 transition-metal [70]fullerene derivatives containing dppb ligands. Crystal structure of *fac*-$Mo(CO)_3(dppb)(CH_3CN)$

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Abstract

The thermal reaction of an equimolar quantity of *fac*-$Mo(CO)_3(dppb)(CH_3CN)$ [dppb = 1,2-bis(diphenylphosphino)benzene] (**1**) with C_{70} in chlorobenzene at 80–85 °C gave an isomeric mixture of *fac*/*mer*-$Mo(CO)_3(dppb)(\eta^2\text{-}C_{70})$ (**2**) in 46% yield, whereas the photochemical reaction of an equimolar amount of $Mo(CO)_6$, dppb and C_{70} in chlorobenzene at room temperature afforded the isomeric mixture **2** in 48% yield and a single isomer *mer*-$[Mo(CO)_3\ (dppb)]_2(\eta^2,\eta^2\text{-}C_{70})$ (**3**) in 19% yield. Similarly, while the thermal reaction of *fac*-$W(CO)_3$ $(dppb)(CH_3CN)$ (**4**) with C_{70} produced a single isomer *mer*-$W(CO)_3(dppb)\ (\eta^2\text{-}C_{70})$ (**5**) in 42% yield, the photochemical 'one pot' reaction of $Cr(CO)_6$, dppb and C_{70} gave rise to a single isomer *mer*-$Cr(CO)_3(dppb)(\eta^2\text{-}C_{70})$ (**6**) in 62% yield and a single isomer [*mer*-$Cr(CO)_3(dppb)]_2(\eta^2,\eta^2\text{-}C_{70})$ (**7**) in 25% yield, respectively. All the new [70]fullerene mono- and dinuclear organometallic derivatives **2**, **3** and **5**–**7** have been characterized by elemental analysis, and IR, ^1H-, ^{31}P-, ^{13}C-NMR (partly), UV–vis and FAB-MS spectroscopic methods, as well as the crystal structure of one of their starting materials *fac*-$Mo(CO)_3(dppb)(CH_3CN)$ (**1**) has been determined by X-ray diffraction analysis.

Keywords: Chromium; Molybdenum; Tungsten; [70]Fullerene; dppb Ligand; Crystal structures

1. Introduction

The organometallic chemistry of [60]- and [70]fullerenes, primarily including the synthesis, structural characterization and properties of transition-metal [60]- and [70]fullerenes is of great interest and has become one of the most active research areas in chemistry [1]. Theoretically, [60]- and [70]fullerenes can form organometallic compounds with single, double, triple or multiple metal centers in a variety of coordination patterns from η^1 to η^6. In fact, some of these types of transition-metal fullerene derivatives have been already prepared and structurally characterized [2–5]. However, among such known fullerene metal complexes an overwhelming majority belongs to [60]fullerene derivatives, which actually involve nearly all of the transition-metals in the Periodic Table [2–5]. In contrast to this, the known [70]fullerene transition-metal complexes are rare and only limited to few metals, which is apparently due to less abundant of [70]fullerene and the complexes of [70]fullerene being more difficult to be isolated and characterized than those of [60]fullerene [2a–c,2n,3b,5c,5f]. In order to develop the organometallic chemistry of [70]fullerene, we recently carried out the thermal reaction of *fac*-$M(CO)_3(dppb)(CH_3CN)$ (M = Mo, W) with C_{70}, and the photochemical reaction of $M(CO)_6$ (M = Cr, Mo), dppb and C_{70}. Herein we describe the synthesis, characterization and properties of five new mono- and dinuclear [70]fullerene complexes obtained from the reactions mentioned above, namely, *fac*/*mer*-$Mo(CO)_3(dppb)(\eta^2\text{-}C_{70})$, [*mer*-$Mo(CO)_3$-$(dppb)]_2(\eta^2,\eta^2\text{-}C_{70})$, *mer*-$W(CO)_3(dppb)(\eta^2\text{-}C_{70})$, *mer*-$Cr(CO)_3(dppb)(\eta^2\text{-}C_{70})$ and [*mer*-$Cr(CO)_3(dppb)]_2(\eta^2,\eta^2\text{-}C_{70})$, as well as the crystal structure of *fac*-$Mo(CO)_3(dppb)(CH_3CN)$, which is the precursor of *fac*/*mer*-$Mo(CO)_3(dppb)(\eta^2\text{-}C_{70})$.

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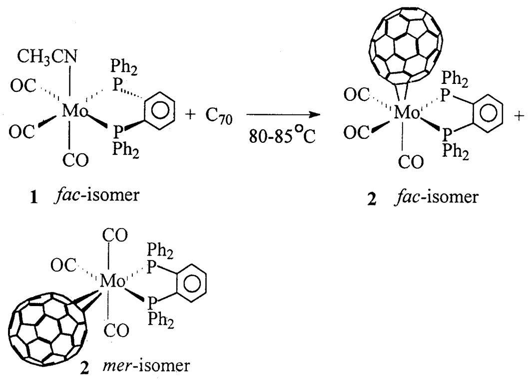
2. Results and discussion

2.1. Synthesis and characterization of *fac*/*mer*-$Mo(CO)_3(dppb)(\eta^2\text{-}C_{70})$ (**2**) and [*mer*-$Mo(CO)_3(dppb)]_2(\eta^2,\eta^2\text{-}C_{70})$ (**3**)

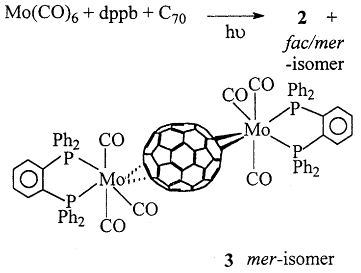
Reaction of an equimolar amount of *fac*-$Mo(CO)_3(dppb)(CH_3CN)$ (**1**) with C_{70} in chlorobenzene at 80–85 °C for 6 h gave an isomeric mixture **2** in 46% yield, as shown in Eq. (1).



(1)

The formation of the *fac*/*mer* isomeric mixture **2** means that the substitution of CH_3CN by C_{70} took place with partial conversion of the *fac* configuration of the starting material **1** under the studied conditions.

More interestingly, when a mixture of an equimolar quantity of $Mo(CO)_6$, dppb and C_{70} in chlorobenzene was irradiated with a UV 450 W photochemical lamp at room temperature for 2 h, the *fac*/*mer*-isomer mixture **2** was produced in 48% yield along with *mer*-isomer **3** in 19% yield, as shown in Eq. (2).



(2)

We previously reported that the [60]fullerene dppf analogue of **2**, i.e. *fac*/*mer*-$Mo(CO)_3(dppf)(\eta^2\text{-}C_{60})$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] can be prepared by CO substitution of $Mo(CO)_4(dppf)$ with C_{60} [3h]. So, the [70]fullerene dppb derivatives **2** and **3** obtained from the one pot reaction described above could be regarded as produced via the substitution of one CO ligand from one molecule of the intermediate $Mo(CO)_4(dppb)$ (generated in situ from $Mo(CO)_6$ and dppb) by C_{70} and the substitution of two CO ligands each from one molecule of the intermediate by C_{70}, respectively.

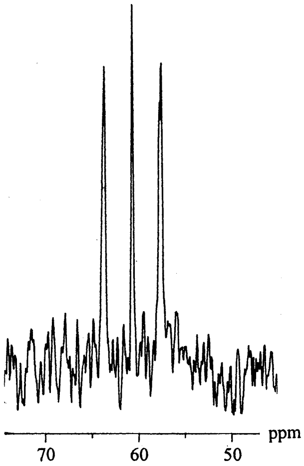


Fig. 1. ^{31}P-NMR spectrum of **2**.

Compounds **2** and **3** are air-stable, brown solids, which dissolve in benzene, toluene, THF, $CHCl_3$, CS_2 and chlorobenzene, but do not dissolve in hexane and petroleum ether. Compounds **2** and **3** have been characterized by elemental analysis and spectroscopic methods.

The ^{31}P-NMR spectrum of **2** (Fig. 1) shows two apparent singlets (the J_{P-P} values are too small to be recognized as two doublets) at 57.56 and 63.70 ppm for the two different P atoms *cis* and *trans* to C_{70}, respectively in the *mer*-isomer and one singlet at 60.68 ppm for the two identical P atoms all *cis* to C_{70} core in the *fac*-isomer, whereas that of **3** (Fig. 2) displays one singlet at 62.48 ppm and one singlet at 70.04 ppm for the two types of P atoms, in which the one type of P atoms including two identical P atoms *cis* to C_{70} and the other type of P atoms including another two identical P atoms *trans* to C_{70} core in the *mer*-isomer [2q,3h]. The IR spectra of **2** and **3** display six absorption bands in the range 1431–525 cm^{-1} for their C_{70} cores [6], and five (for **2**) or three (for **3**) absorption bands in the region 2023–1893 cm^{-1} for their terminal carbonyls [7]. The number of IR bands caused by CO's of **2** and **3** is in

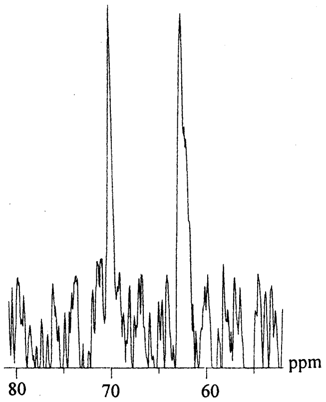


Fig. 2. ^{31}P-NMR spectrum of **3**.

good agreement with **2** being a *fac/mer* isomeric mixture and **3** being a *mer*-isomer, since the number of IR active bands cannot exceed but may be less than the number of CO ligands in transition-metal complexes [7]. In addition, such IR bands of **2** and **3**, when compared to corresponding those of **1**, are shifted toward higher frequency, which is obviously due to C_{70} being a stronger electron-withdrawing ligand than CH_3CN and therefore causing the decrease in the π-back-bonding between Mo–CO in **2** and **3** [3h,7]. The UV–vis spectrum of **2** showing five absorption bands between 200 and 500 nm is very similar to that of free C_{70} [6]. In order to make an accurate comparion, we determined the UV–vis spectrum of free C_{70} in its saturated THF solution (λ_{max} (log ε): 240.5 (5.14), 331.1 (4.53), 359.5 (4.43), 378.5 (4.57), 470.1 (4.32) nm). The blue-shift of the fifth band of **2** relative to that of free C_{70} might be ascribed to the [70]fullerene being coordinated to the metals in an η^2-fashion [2i,2q,8].

In addition, the ^{13}C-NMR spectrum of **2** shows the presence of its terminal carbonyls (three signals from 217.98 to 209.89 ppm) and the C_{70} core (six signals from 150.36 to 145.08 ppm along with the others overlapped with those of benzene rings).

It is known [1d,2a,2k,3b] that the C_{70} molecule has five types of carbon atoms (labeled a–e in Fig. 3) that form nine layers and display five ^{13}C-NMR signals (150.07, 147.52, 146.82, 144.77 and 130.28 ppm). Connecting these carbon atoms are eight types of C–C bonds. Of these bonds four (Ca–Cb, Cc–Cc, Cd–Ce, Ce–Ce) occurs between 6:6 ring junctions, and four (Ca–Ca, Cb–Cc, Cc–Cd, Cd–Cd) involve 6:5 ring junctions. The C–C bond lengths at the 6:6 ring junctions are shorter than the C–C bond lengths at the 6:5 ring junctions. The most reactive bonds are expected to be the Ca–Cb bonds at the poles of the molecule since they have the highest π bond orders and the greatest cuvature [1d,2a,2k,3b]. In fact, that C_{70} is bound to a metal in an η^2-fashion with Ca–Cb bond has been confirmed by X-ray diffraction analysis for the known C_{70} metal complexes, such as Ir(CO)(Cl)-$(PPh_3)_2(\eta^2\text{-}C_{70})$ [2a] and *mer*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{70})$ [2k]. So, in product **2** the C_{70} is most likely bonded to Mo atom through one Ca–Cb bond at the pole of C_{70} ligand. It is also known [1d,2a,2k,3b] that when a second metal is bonded to C_{70} core the metal is also attached to the Ca–Cb bond which is located at opposite pole of the C_{70} core, presumably due to the electronic and steric effects between the two transition-metal moieties. In fact, at the opposite pole of C_{70} core there are three distinct Ca–Cb bonds (Fig. 3), of which the Ca–Cb at site A is closest to the first metal, the Ca–Cb at site **B** is intermediate and the Ca–Cb at site C is farthest. It appears that in compound **3** the second metal moiety $Mo(CO)_3(dppb)$ is most likely to be bonded at the Ca–Cb bond of site B, although the addition of $Mo(CO)_3(dppb)$ to Ca–Cb bonds at sites A and C cannot be completely ruled out. This is because that the X-ray diffraction has revealed that in $(C_{70})[Ir(CO)Cl(PPhMe_2)_2]_2\cdot 3C_6H_6$ the second Ir-containing fragment is added to the Ca–Cb of site B [3b]. However, the exact structure of **3** remains to be solved in the future by X-ray diffraction analysis.

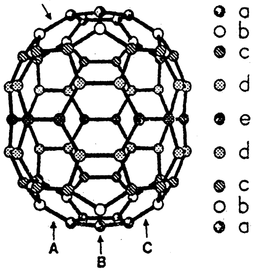


Fig. 3. The idealized structure of C_{70} and sites for the first and second metal moieties added to C_{70} [1d].

Additionally, it should be pointed out that the elemental analysis and the FAB-MS data are also consistent with the mononuclear and dinuclear structures of **2** and **3** discussed above. For instance, the FAB-MS spectra show the molecular ion [M$^+$] peaks at $m/z = 1468$ for **2** and $m/z = 2096$ for **3**, respectively.

2.2. Crystal structure of fac-$M(CO)_3(dppb)(CH_3CN)$ (1)

Although the crystal structures of the [70]fullerene derivatives **2** and **3** failed to be determined due to lack of the single crystals suitable for X-ray diffraction, we have successfully determined the crystal structure of their parent complex **1** by means of X-ray diffraction techniques. The single crystals were obtained through slow cooling the hot CH_3CN solution of **1**. It should be noted [2q] that although the structure of **1** was previously characterized by combustion analysis and spectroscopic methods, it could not be confirmed by X-ray diffraction analysis due to lack of suitable single

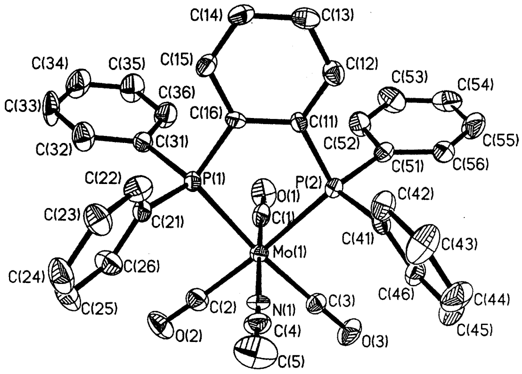


Fig. 4. ORTEP drawing of **1** with ellipsoids drawn at 30% probability.

Table 1
Selected bond lengths (Å) and angles (°) for *fac*-Mo(CO)$_3$(dppb)(CH$_3$CN) (**1**)

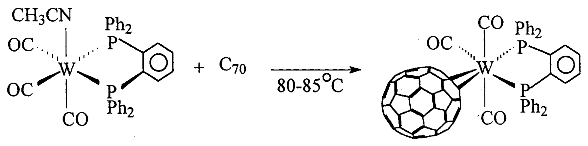
Bond lengths			
Mo(1)–C(1)	1.933(8)	Mo(1)–P(1)	2.497(2)
Mo(1)–C(2)	1.970(9)	P(1)–C(16)	1.826(7)
Mo(1)–N(1)	2.217(7)	P(1)–C(31)	1.819(7)
Mo(1)–P(2)	2.4902(19)	P(2)–C(41)	1.813(7)
C(11)–P(2)	1.836(7)	N(1)–C(4)	1.125(8)
Bond angles			
C(1)–Mo(1)–N(1)	179.0(3)	C(1)–Mo(1)–P(2)	94.5(2)
P(1)–Mo(1)–C(1)	96.0(2)	N(1)–Mo(1)–P(2)	84.64(16)
N(1)–Mo(1)–P(1)	84.43(16)	P(2)–Mo(1)–P(1)	79.73(6)
C(41)–P(2)–Mo(1)	113.8(2)	C(11)–P(2)–Mo(1)	110.8(2)
C(31)–P(1)–Mo(1)	121.0(2)	C(21)–P(1)–Mo(1)	114.8(2)
C(4)–N(1)–Mo(1)	172.8(6)	N(1)–C(4)–C(5)	177.2(9)

crystals during that time. The molecular ORTEP diagram of **1** is shown in Fig. 4, whereas Table 1 lists its selected bond lengths and angles.

Fig. 4 shows that **1** contains one CH$_3$CN ligand bonded to Mo via its N atom and *cis* to both of the phosphorous atoms P(1) and P(2) of the dppb ligand. That is, the X-ray diffraction analysis confirmed that **1** adopts the *fac* configuration, indeed. This molecule is symmetrical with respect to the plane passing through N(1), Mo(1) and C(1) atoms, and the midpoints of C(11)–C(16) and C(13)–C(14) bonds. The chelated dppb ligand has a bite angle of P(1)–Mo(1)–P(2) (79.73(6)°), which is greater than corresponding that of *fac*-W(CO)$_3$(dppm)(CH$_3$CN) (67.5(1)°) [9], but less than corresponding those of *fac*-Mo(CO)$_3$(dppf)(CH$_3$CN) (97.80(19)°) [3h], *fac*-W(CO)$_3$(dppf)(CH$_3$CN) (98.05(6)°) [10], Mo(CO)$_4$(dppf) (95.28(2)°) [11], W(CO)$_4$(dppf) (95.24(5)°) [3h]. The two Mo–P, and one Mo–N bond lengths of **1** are 2.497(2) (Mo(1)–P(1)), 2.4902(19) (Mo(1)–P(2)) and 2.217(7) (Mo(1)–N(1)) Å, whereas the three Mo–C(carbonyl) bond lengths in **1** are 1.933(8) (Mo(1)–C(1)), 1.970(9) (Mo(1)–C(2)) and 1.965(8) (Mo(1)–C(3)) Å, respectively. That the Mo(1)–C(1) bond is the shortest among the three Mo–C(carbonyl) bonds implies that acetonitrile possesses a weaker *trans* effect than dppb and this is consistent with CH$_3$CN being a weaker ligand and being more easily replaced by C$_{70}$ to give fullerene derivative **2**.

2.3. Synthesis and characterization of mer-W(CO)$_3$(dppb)(η^2-C$_{70}$) (5)

Interestingly, an equimolar quantity of *fac*-W(CO)$_3$(dppb)(CH$_3$CN) (**4**) reacted with C$_{70}$ in chlorobenzene at 80–85 °C for 6 h to give **5** in 42% yield, as shown in Eq. (3).



4 *fac*-isomer **5** *mer*-isomer

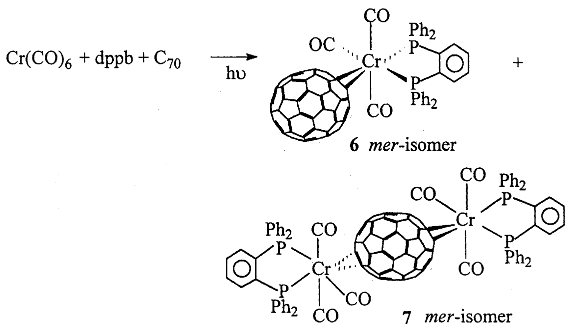
(3)

So, in contrast to reaction of **1** with C$_{70}$, this reaction did not afford the corresponding *fac*/*mer* isomeric mixture, but instead it produced only the *mer*-isomer **5**, which means that the substitution of CH$_3$CN by C$_{70}$ occurred in this case with complete conversion of the *fac* configuration of starting material **4**.

Compound **5** is an air-stable, black solid, which is soluble in benzene, toluene, THF, CHCl$_3$, CS$_2$ and chlorobenzene, but is insoluble in hexane and petroleum ether. Compound **5** has been characterized by elemental analysis IR, UV–vis, ^{1}H-, ^{31}P-NMR and FAB-MS techniques. For example, the FAB-MS spectrum shows its molecular ion peak at $m/z = 1556$ and C_{70}^{+} ion peak. The UV–vis spectrum of **5** is similar to that of free C$_{70}$, in which the fifth band at 460.9 nm, characteristic of an η^2-coordinating fashion of C$_{70}$ with the metal, is blue-shifted by ca. 9 nm relative to that of free C$_{70}$ [2i,2q,8]. The IR spectrum of **5** displays four bands in the region 1430–525 cm^{-1} for its C$_{70}$ core [6] and three bands in the range 2009–1886 cm^{-1} for its terminal carbonyls [7]. In addition, the ^{31}P-NMR spectrum of **5** shows two broader singlets centered at 43.40 and 38.90 ppm, each singlet being surrounded by satellite peaks due to coupling between P atoms and tungsten isotopes, such as isotope ^{183}W. This indicates that it has two different P atoms, and thus **5** is a single *mer*-isomer [2q,3h]. According to the above discussion regarding the metal position bonded to C$_{70}$ core, we might suggest that in the *mer*-isomer **5** the metal tungsten is just like the Mo atoms in *mer*-isomers **2** and **3** to be bonded to C$_{70}$ core through its Ca–Cb bond [1d,2a,2k,3b].

2.4. Synthesis and characterization of mer-Cr(CO)$_3$(dppb)(η^2-C$_{70}$) (6) and [mer-Cr(CO)$_3$(dppb)]$_2$(η^2,η^2-C$_{70}$) (7)

Although the Mo and W organometallics of [70]fullerene are known [2k,3h] none of the corresponding Cr derivatives has appeared in literature until now. So, the efforts were made to synthesize the Cr analogues of **2**, **3** and **5**. Fortunately, while the Cr analogue **6** could not be prepared by reaction of *fac*-Cr(CO)$_3$(dppb)(CH$_3$CN) with C$_{70}$ under the above-mentioned thermal reaction conditions, the Cr analogues **6** and **7** were obtained, respectively in 62 and 25% yields through photochemical reaction of a mixture of Cr(CO)$_6$, dppb and C$_{70}$, as shown in Eq. (4).



6 *mer*-isomer

7 *mer*-isomer

(4)

Compounds **6** and **7** are air-sensitive, brown solids, which are, similar to **2**, **3** and **5**, soluble in benzene, toluene, THF, $CHCl_3$, CS_2 and chlorobenzene, but are insoluble in hexane and petroleum ether. The structures of **6** and **7** shown in Eq. (4) have been characterized by elmental analysis, IR, UV–vis, $^1H(^{13}C, ^{31}P)$-NMR, and FAB-MS methods.

The FAB-MS spectrum of **6** exhibits its molecular ion $[M^+]$ at $m/z = 1424$ and fragment ions $[M^+ - 3CO]$ and C_{70}^+, whereas that of **7** displays the peaks corresponding to its $[M^+ - 3H]$ at $m/z = 2005$, $[M^+ - 3CO]$, $[M^+ - 6CO]$ and C_{70}^+. The IR spectra of **6** and **7** each show three absorption bands in the range 2008–1884 cm^{-1} for their terminal carbonyls [7], and three to four absorption bands in the region 1434–527 cm^{-1} for its C_{70} core [6], whereas the ^1H-NMR spectra of **6** and **7** display all of their corresponding organic groups. The ^{13}C-NMR spectrum of **6**, similar to that of **2**, also shows its terminal carbonyls (three signals from 226.54 to 225.89 ppm) and the C_{70} core (six signals from 150.79 to 136.49 ppm along with the others overlapped with those from C_6H_5 and C_6H_4 groups). It is worthy of note that the ^{31}P-NMR spectrum of **6** displays two singlets at 93.66 and 82.45 ppm for its two different P atoms, whereas that of **7** shows two doublets at 95.23 and 82.94 ppm for its two sets of two different P atoms [2q,3h]. So, it seems that the structures of **6** and **7** are very similar to **5** and **3** resepctively, i.e. they all belong to *mer*-isomers in which the first $Cr(CO)_3(dppb)$ moiety is presumably bonded via Cr atom to the Ca–Cb bond of C_{70} core and the second $Cr(CO)_3(dppb)$ moiety is bound to the Ca–Cb bond at the opposite pole of the C_{70} core [1d,2a,2k,3b].

In summary, we have synthesized a series of new organometallic [70]fullerene compounds by use of thermal reaction of *fac*-$M(CO)_3(dppb)(CH_3CN)$ ($M = Mo$, W) with C_{70}, and photochemical reaction of $M(CO)_6$ ($M = Cr$, Mo), dppb and C_{70}. Interestingly, while the thermal reaction gives mononuclear [70]fullerene complexes **2** and **5**, the photochemical reaction affords both mononuclear and dinuclear [70]fullerene complexes **2/3** and **6/7**. So far, the photochemical 'one pot' reaction, which was first carried out in our laboratory, is probably the most simple and straightforward reaction for preparation of such types of organometallic fullerene complexes and it would be very useful in preparation of other novel fullerene organometallic compounds. Finally, it is worth pointing out that although the [70]fullerene transition-metal complexes are known (but very few), the complexes **6** and **7** reported in this paper, to our best knowledge, are the first examples of the [70]fullerene organometallic complexes in which the [70]fullerene is coordinated to transition-metal chromium.

3. Experimental

All reactions were carried out under an atmosphere of highly purified nitrogen using standard Schlenk or vacuum-line techniques. Acetonitrile and chlorobenzene were dried by distillation from P_2O_5 and CaH_2 under nitrogen. $M(CO)_6$ ($M = Cr$, Mo), 1,2-bis(diphenylphosphino)benzene (dppb) and [70]fullerene (98%) were of commercial origin. $M(CO)_3(dppb)(CH_3CN)$ ($M =$ Mo,W) [2n] were prepared according to literature procedures. Products were separated by thin-layer chromatography (TLC glass plates of $20 \times 25 \times 0.25$ cm coated with silica gel 60H). M.p. were determined on a Yanaco MP-500 apparatus. Elemental analysis and FAB-MS spectrometry were performed on a Yanaco CHN Corder MT-3 analyzer and a Zebspec spectrometer. IR and UV–vis spectra were recorded on a Bio-Rad FTS 135 and a Shimadzu UV-2401/PC spectrometers. ^1H-, ^{31}P- and ^{13}C-NMR spectra were obtained on a Bruker AC-P200 or a UNITY Plus-400 spectrometer.

3.1. Synthesis of *fac/mer*-$Mo(CO)_3(dppb)(\eta^2\text{-}C_{70})$ (**2**)

A 100-ml three-necked flask equipped with a stir-bar, a serum cap and a reflux condenser topped with a N_2 inlet tube was charged with 0.042 g (0.05 mmol) of C_{70} and 50 ml of chlorobenzene. The mixture was stirred at room temperature (r.t.) until all C_{70} was dissolved. To the brown solution was added 0.033 g (0.05 mmol) of $Mo(CO)_3(dppb)(CH_3CN)$, and the reaction mixture was heated to about 80 °C and stirred at 80–85 °C for 6 h, during which time the solution turned dark brown. The resulting solution was evaporated at reduced pressure, and the residue was separated by TLC using 1:1 (v/v) $C_6H_5CH_3$–light petroleum ether as eluent. From the yellow–green band 0.034 g (46%) of **2** as a brown solid was obtained. m.p. > 300 °C. Anal. Found: C, 84.68; H, 1.51. Calc. for $C_{103}H_{24}MoO_3P_2$: C, 84.32; H, 1.65%. IR (KBr disc): $\nu_{C\equiv O}$, 2023m, 2021s, 1951s, 1924s, 1896vs; ν_{C70} 1431s, 795w, 673w, 641w, 579w, 525m cm^{-1}. UV–vis (THF, 8.36×10^{-6} M): λ_{max} (log ε): 239.9 (5.30), 329.3 (4.57), 357.7 (4.57), 378.3 (4.55), 464.1 (4.43) nm. ^1H-NMR (200 MHz, $CDCl_3$, Me_4Si): 7.24–7.45 (m, 24H, $4C_6H_5$, C_6H_4) ppm. ^{13}C-NMR

(100.6 MHz, *o*-$C_6D_4Cl_2$, Me_4Si, 25 °C): 3 multiplets centered at 217.98, 210.81 and 209.89 (CO), 6 singlets at 150.36, 148.09, 147.83, 147.37, 147.12 and 145.08 (C_{70}), 15 singlets at 134.24, 133.56, 133.31, 132.76, 132.51, 131.07, 130.85, 130.61, 129.62, 129.37, 128.42, 127.74, 127.49, 127.24 and 126.99 (C_{70}+Ph+C_6H_4+*o*-$C_6D_4Cl_2$) ppm. ^{31}P-NMR (81 MHz, *o*-$C_6D_4Cl_2$, H_3PO_4): 63.70 (s, 1P), 57.56 (s, 1P), 60.68 (s, 2P) ppm. FAB-MS: *m*/*z* 1468 ($Mo(CO)_3$(dppb) (η^2-C_{70})$^+$, ^{98}Mo); *m*/*z* 840 (C_{70}^+).

3.2. Synthesis of **2** and [*mer*-$Mo(CO)_3$(dppb)]$_2$(η^2,η^2-C_{70}) (**3**)

A 100-ml photoreactor equipped with a N_2 inlet tube and a serum cap was charged with 0.042 g (0.05 mmol) of C_{70}, 0.014 g (0.05 mmol) of $Mo(CO)_6$, 0.023 g (0.05 mmol) of dppb and 50 ml of chlorobenzene. The photoreactor containing the resulting brown solution was evacuated to a pressure of ca. 0.1 mmHg and then the solution was irradiated by a water-cooled UV 450 W mercury vapor lamp for 2 h, with periodic evacuation of CO to give a dark brown solution. The same work-up was used as that in preparation of **2** by thermal reaction. From the yellow–green band 0.035 g (48%) of **2** was obtained. From the red–brown band 0.010 g (19%) of **3** as a brown solid was obtained. m.p. > 300 °C. Anal. Found: C, 78.08; H, 2.29. Calc. for $C_{136}H_{48}Mo_2O_6P_4$: C, 78.02; H, 2.31%. IR (KBr disc): $\nu_{C\equiv O}$, 2006s, 1940s, 1893vs; ν_{C70} 1431s, 792w, 670w, 640w, 595w, 525m cm^{-1}. ^{1}H-NMR (200 MHz, CS_2–C_3H_6O-d_6, Me_4Si): 7.02–7.62 (m, 48H, 8C_6H_5, 2C_6H_4) ppm. ^{31}P-NMR (81 MHz, CS_2, H_3PO_4): 70.04 (s, 2P), 62.48 (br.s, 2P) ppm. FAB-MS: *m*/*z* 2096 ([$Mo(CO)_3$(dppb)]$_2$ (η^2,η^2-C_{70})$^+$, ^{98}Mo); *m*/*z* 840 (C_{70}^+).

3.3. Synthesis of *mer*-$W(CO)_3$(dppb)(η^2-C_{70}) (**5**)

The same procedure as that for preparation of **2** by thermal reaction was followed, but 0.038 g (0.05 mmol) of *fac*-$W(CO)_3$(dppb)(CH_3CN) was used instead of *fac*-$Mo(CO)_3$(dppb)(CH_3CN). From the yellow–green band 0.037 g (42%) of **5** as a black solid was obtained. m.p. > 300 °C. Anal. Found: C, 79.56; H, 1.51. Calc. for $C_{103}H_{24}O_3P_2W$: C, 79.55; H, 1.56%. IR (KBr disc): $\nu_{C\equiv O}$, 2009s, 1943s, 1886vs; ν_{C70} 1430s, 671w, 536m, 525m cm^{-1}. UV–vis (THF, 1.50×10^{-5} M): λ_{max} (log ε): 241.1 (5.17), 329.3 (4.46), 357.5 (4.41), 377.9 (4.45), 460.9 (4.35) nm. ^{1}H-NMR (200 MHz, $CDCl_3$, Me_4Si): 7.10–7.66 (m, 24H, 4C_6H_5, C_6H_4) ppm. ^{31}P-NMR (81 MHz, *o*-$C_6D_4Cl_2$, H_3PO_4): 43.40 (s, 1P), 38.90 (s, 1P) ppm. FAB-MS: *m*/*z* 1556 ($W(CO)_3$(dppb) (η^2-C_{70})$^+$, ^{186}W); *m*/*z* 840 (C_{70}^+).

3.4. Synthesis of *mer*-$Cr(CO)_3$(dppb)(η^2-C_{70}) (**6**) and [*mer*-$Cr(CO)_3$(dppb)]$_2$(η^2,η^2-C_{70}) (**7**)

The same procedure as that for preparation of **2** and **3** by photochemical reaction was followed, but 0.042 g (0.05 mmol) of C_{70}, 0.016 g (0.075 mmol) of $Cr(CO)_6$ and 0.034 g (0.075 mmol) of dppb were employed. From the yellow–green band 0.044 g (62%) of **6** as a brown solid was obtained. m.p. > 300 °C. Anal. Found: C, 87.02; H, 1.66. Calc. for $C_{103}H_{24}CrO_3P_2$: C, 86.92; H, 1.70%. IR (KBr disc): $\nu_{C\equiv O}$, 2008s, 1917vs, 1890vs; ν_{C70} 1432s, 793w, 675m, 528s cm^{-1}. UV–vis (THF, 9.56×10^{-6} M) λ_{max} (log ε): 239.3 (5.18), 378.0 (4.40), 469.1 (4.41) nm. ^{1}H-NMR (200 MHz, CS_2–C_3H_6O-d_6, Me_4Si): 7.10–7.70 (m, 48H, 8C_6H_5, 2C_6H_4) ppm. ^{13}C-NMR (100.6 MHz, $CDCl_3$, Me_4Si, 25 °C): 3 broad singlets centered at 226.54, 226.23 and 225.89 (CO), 6 singlets at 150.79, 148.23, 147.53, 145.48, 143.33 and 136.49 (C_{70}), 8 singlets at 132.32, 131.02, 130.43, 129.86, 129.25, 128.58, 123.93 and 120.55 (C_{70}+Ph+C_6H_4) ppm. ^{31}P-NMR (81 MHz, CS_2, H_3PO_4): 93.66 (s, 1P), 82.45 (s, 1P) ppm. FAB-MS: *m*/*z* 1424 ($Cr(CO)_3$(dppb) (η^2-C_{70})$^+$, ^{54}Cr); *m*/*z* 1340 ($Cr(CO)_3$(dppb)(η^2-C_{70})$^+$ − 3CO, ^{54}Cr); *m*/*z* 840 (C_{70}^+). From the red–brown band 0.019 g (25%) of **7** was obtained as a brown solid. m.p. > 300 °C. Anal. Found: C, 81.70; H, 2.42. Calc. for $C_{136}H_{48}Cr_2O_6P_4$: C, 81.44; H, 2.41%. IR (KBr disc): $\nu_{C\equiv O}$, 1992s, 1921s, 1884vs; ν_{C70} 1434s, 670w, 527s cm^{-1}. UV–vis (THF, 8.97×10^{-6} M) λ_{max} (log ε):

Table 2
Crystal data and structure refinements for *fac*-$Mo(CO)_3$(dppb)(CH_3CN)(**1**)

Empirical formula	$C_{35}H_{27}MoNO_3P_2$
Formula weight	667.46
Temperature (K)	293
Crystal system	$P2_1$/c
Space group	Monoclinic
a (Å)	8.4759(16)
b (Å)	16.792(3)
c (Å)	22.110(4)
α (°)	90
β (°)	98.864(4)
γ (°)	90
V (Å^3)	3109.3(10)
Z	4
D_{calc} (g cm^{-3})	1.426
μ(Mo–K$_\alpha$) (mm^{-1})	0.560
F(000)	1360
θ Range for data collection (°)	2.43–25.03
Observed reflections	11715
Independent reflections	5063
R_{int}	0.1001
Completeness to $\theta = 25.03°$	88.9%
Data/restraints/parameters	5063/03/380
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0749$, $wR_2 = 0.1448$
R indices (all data)	$R_1 = 0.1404$, $wR_2 = 0.1714$
Goodness-of-fit on F^2	0.990
Largest difference peak and hole (e Å^{-3})	0.976 and −0.429

239.5 (5.25), 377.5 (4.56), 470.3 (4.59) nm. ^{1}H-NMR (200 MHz, CS_2–C_3H_6O-d_6, Me_4Si): 7.10–7.60 (m, 48H, $8C_6H_5$, $2C_6H_4$) ppm. ^{31}P-NMR (81 MHz, CS_2, H_3PO_4): 95.23 (d, $J = 26.4$ Hz, 2P), 82.94 (d, $J = 21.6$ Hz, 2P) ppm. FAB-MS: *m/z* 2005 ($[Cr(CO)_3(dppb)]_2$ (η^2,η^2-C_{70})$^+$ −3H, ^{54}Cr); *m/z* 1921 ($[Cr(CO)_3(dppb)]_2(\eta^2,\eta^2$-$C_{70})^+$ −3H−3CO, ^{54}Cr); *m/z* 1837 [$\{Cr(CO)_3(dppb)\}_2(\eta^2,\eta^2$-$C_{70})^+$ −3H−6CO, ^{54}Cr]; *m/z* 840 (C_{70}^+).

3.5. X-ray crystallography

Single crystals of *fac*-$Mo(CO)_3(dppb)(CH_3CN)$ (**1**) suitable for X-ray diffraction analysis were obtained by slow cooling the hot MeCN solution of **1**. The single crystal of **1** (0.20 × 0.20 × 0.15 mm) was glued to a glass fiber and mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at r.t., using Mo–K_α graphite monochromator radiation ($\lambda = 0.71073$ Å) in the ω scanning mode. Absorption corrections were performed using SADABS for all of them. The structure was solved by direct methods using SHELXTL-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on F^2. Hydrogen atoms were located by using geometric method. The crystal data and structural refinements details are listed in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 185862 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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