SHORT PAPER

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Synthesis of σ-bonded [60]fullerene metallacycle compound η^2-σ-$C_{60}[Mo(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2]_2$(dppe) via Reaction of K_2C_{60} and $[\eta 5\text{-}EtO_2CC_5H_4(CO)_2MoI]_2$(dppe)[†]

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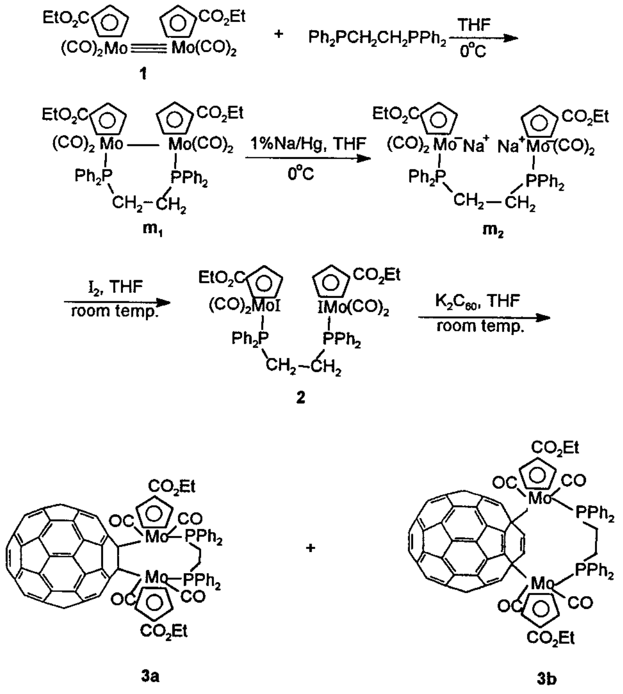
The first σ-bonded [60]fullerene organometallic complex metallacycle η^2-σ-$C_{60}[Mo(\eta^5\text{-}EtO_2CC_5H_4)\ (CO)_2]_2$ (dppe) (dppe=$Ph_2PCH_2CH_2PPh_2$) is synthesized by reaction of K_2C_{60} with a new electrophile η^5-$EtO_2CC_5H_4(CO)_2MoI_2$(dppe), both of which have been characterized by elemental analysis and spectroscopy.

There has been a considerably growing interest in synthesis and characterization of [60]fullerene organometallic derivatives since the platinum derivative, $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$, was first reported by Fagan and coworkers.[1] Up to now, numerous reports concerning such transition metal C_{60} complexes have appeared in literature, which actually involve nearly all of the transition metals across the Periodic Table.[2] However, among all the known C_{60} organotransition metal derivatives the C_{60} ligands are almost π-bonded to transition metals through their one or more double bonds[2] and, to our knowledge, very few isolated σ-bonded derivatives are so far reported.[3] Forturnately, we recently found that the reaction of K_2C_{60} with the electrophile $[(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2\ MoI]_2$(dppe) (dppe=$Ph_2PCH_2CH_2PPh_2$) (**2**), which was prepared from a tandem reaction of $[(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2Mo]_2$ (**1**) with dppe, Na/Hg and I_2, could produce such a kind of σ-bonded transition metal C_{60} derivative, namely η^2-σ-$C_{60}[Mo(\eta^5\text{-}EtO_2CC_5H_4)(CO)_2]_2$(dppe) (**3**), as shown in Scheme 1.



Scheme 1

New transition metal compound **2** and its C_{60} derivative **3** have been characterized by elemental analysis and spectroscopies. For instance, the elemental analyses of **2** and **3** are in agreement with its composition. The FAB-MS spectrum shows the molecular ion peak of **3** at *m/z* 1700 and its fragment ion C_{60}^+ at *m/z* 720. The IR spectrum of **3** exhibits the features similar to its starting materials **2** and C_{60}. For instance, it shows four absorption bands in the range 1846-1967 cm^{-1} for terminal carbonyls, one strong absorption band at 1721 cm^{-1} for ester carbonyls and four absorption bands in the range 1434-523 cm^{-1} for C_{60} sphere. The UV-vis spectra of **3** and free C_{60} in THF are shown in Fig. 1. As seen from Fig. 1, the spectrum of **3** displays one very strong band at 329 nm and one very weak band at 404 nm, whereas that of free C_{60} shows one medium band at 237 nm, one very strong band at 257 nm, one strong band at 330 nm and one very weak band at 404 nm, respectively. The disappearance of the two bands at 237 and 257 nm of free C_{60} in derivative **3** is obviously related to the formation of σ-bonds between C_{60} and Mo atoms in **3**, which creates two sp^3-C in C_{60} sphere and thus disrupts the continuity of the conjugated π-system of free C_{60}. The ^1H NMR spectrum of **3** indicates the presence of all the hydrogen-containing groups in **3**. However, compared to its starting material **2**, the ^1H NMR spectrum of **3** appears to be slightly shifted about 0.05 ppm towards higher field. This may reflect the larger electron-withdrawing effect of the two iodine atoms in **2** than the C_{60} ligand in **3**.

In view of the fact that the similar reaction of C_{60}^{2-} with an organic electrophile MeI gives two isomers 1,2-Me_2C_{60} and 1,4-Me_2C_{60},[4] we might suggest that our metallacycle compound **3** would also have the structures of 1,2-isomer (**3a**) and 1,4-isomer (**3b**), as shown in Scheme 1. Although we could not get the ^{13}C NMR spectrum of **3** due to its very low solubility in ordinary solvents, we obtained the ^{31}P NMR spectrum of **3** along with its precursor **2** as shown in Fig. 2. Fig. 2 shows that

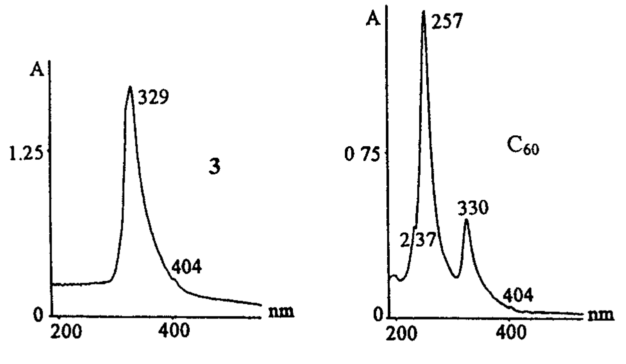


Fig. 1 UV-vis spectra of **3** and C_{60} in THF

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

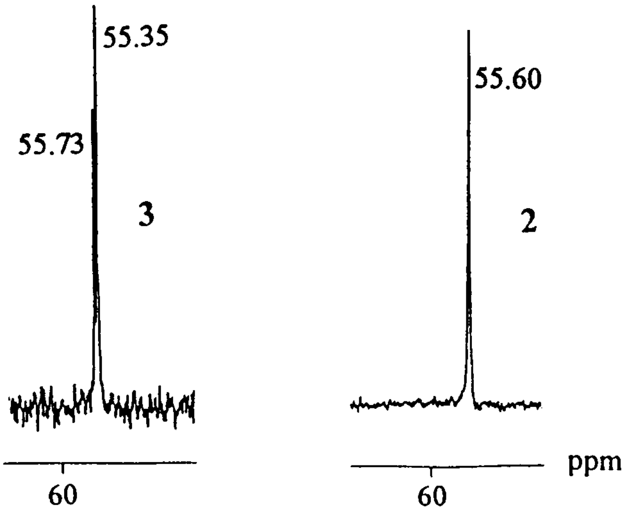

Fig. 2 ^{31}P NMR spectra of **2** and **3**

while **2** displays one singlet at 55.6 ppm for its two identical P atoms, **3** exhibits two singlets at 55.73 and 55.35 ppm, consistent with **3** being a mixture of two isomers described above.

Experimental

All reactions were carried out under an atmosphere of prepurified argon using standard Schlenk and vacuum-line techniques. THF and light petroleum (b.p. 60–90°C) were dried and deoxygenated by distillation from sodium benzophenone ketyl under argon. 1% Na/Hg,[5] $[\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$,[6] dppe[7] and K_2C_{60}[8] were prepared according to literatures. Silica gel (300–400 mesh) for chromatography (15 × 2 cm) was activated for 1 h at 120°C. The IR and UV-vis spectra were recorded on a Nicolet 170 SX FTIR spectrophotometer and a Shimadzu UV-240 spectrometer respectively, whereas the NMR spectra were determined on a Jeol FX 90Q or a Bruker AC-P200 spectrometer. Elemental analysis and MS determinations were performed using a Yanako CHN recorder MT-3 analyser and a Zabspec spectrometer, respectively. Melting points were determined on a Yanaco MP-500 apparatus.

*Preparation of **2**:* A 100 ml two-necked flask equipped with a magnetic stir-bar, a serum cap and an argon inlet tube, was charged with **1** (490 mg, 0.847 mmol), dppe (338 mg, 0.847 mmol) and THF (50 ml). The reaction mixture was stirred at 0°C for 0.5 h to give a purple solution of $\mathbf{m_1}$. To the solution of $\mathbf{m_1}$ was added 1% Na/Hg powder (35 g) and the mixture was stirred at 0°C for an additional 0.5 h. The reaction mixture was filtered under argon to give a yellow filtrate of $\mathbf{m_2}$. To the filtrate of $\mathbf{m_2}$ was added I_2(490 mg, 1.93 mmol) and then the mixture was stirred at room temperature for 6 h. Solvent was removed in vacuo and the residue was subjected to anaerobic column chromatography. After 1:1(v/v) CH_2Cl_2/light petroleum eluted unreacted **1** and other impurities, THF eluted a brown-red band. The volatiles were evaporated in vacuo and the residue was dried in vacuo to afford 200 mg of **2** as a red-brown solid in 19% yield; mp 162-164°C. ν_{max}/cm^{-1} 1713 (C=O); 1893, 1967 (C≡O). δ_H (200 MHz, $CDCl_3$, TMS): 1.36 (t, J = 7.2 Hz, 6 H, 2 CH_3), 2.80 (s, 4 H, 2 PCH_2), 4.30 (q, J = 7.2 Hz, 4 H, 2 CH_2O), 4.80 (s, 4 H, 2 H^3, 2 H^4), 5.32 (s, 4 H, 2 H^2, 2 H^5), 7.30–7.60 (m, 20 H, 4 C_6H_5). $\delta(^{31}P)$ (80.9 MHz, $CDCl_3$, H_3PO_4) 55.60. UV-vis (nm, THF, 1.80×10^{-5}M): λ_{max} (logε) 232 (5.079), 256 (4.665), 263 (4.598), 287 (4.397) (Found: C, 44.42; H, 3.61. $C_{46}H_{42}I_2Mo_2O_8P_2$ requires C, 44.90; H, 3.44%).

*Preparation of **3**:* The above-mentioned flask was charged with C_{60} (40 mg, 0.056 mmol), K (4.4 mg, 0.113 mmol), α-methylnaphthalene (0.5 ml, 3.516 mmol) and THF (20 ml). The reaction mixture was strirred for 4-5 h at room temperature to give a THF solution of K_2C_{60}. To this solution was added **2** (69 mg, 0.056 mmol) and then the mixture was stirred for 10 h at room temperature to produce a flocculent precipitate. The precipitate obtained after centrifugal separation was washed successively with 5% of aqueous HCl (2 × 20 ml) and 1:1(v/v) toluene/light petroleum (2 × 5.0 ml) and dried in vacuo to give 23 mg of **3** as a brown solid in 24% yield; m.p. 110–112°C. ν_{max}/cm^{-1} 1721 (C = O), 1846, 1885, 1891 1967 (C ≡ O); 1434, 1187, 564, 523 (C_{60}). δ_H (200 MHz, $CDCl_3$, TMS): 1.30 (t, *J* = 7.2 Hz, 6H, 2 CH_3), 2.76 (s, 4 H, 2 PCH_2), 4.26(q, J = 7.2Hz, 4 H, 2 CH_2O), 4.75 (s, 4 H, 2 H^3, 2 H^4), 5.26 (s, 4 H, 2 H^2, 2 H^5), 7.24–7.45 (m, 20 H, 4 C_6H_5). δ (^{31}P) (80.9 MHz, $CDCl_3$, H_3PO_4) 55.73, 55.35. UV-vis (nm, THF, 1.80×10^{-6} M): λ_{max}(logε) 329 (6.984), 404 (5.243). FAB-MS *m/z* (^{98}Mo, ^{31}P): 1700 (M^+), 720 ($C_{60}{}^+$). (Found: C, 74.46; H, 2.63. $C_{106}H_{42}Mo_2O_8P_2$ requires C, 75.01; H, 2.49%).

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