Pergamon

PII: S0277-5387(97)00370-7

Polyhedron Vol. 17, No. 4, pp. 469–473, 1998
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0277-5387/98 \$19.00+0.00

The chemical reactivity of fullerene C_{60} towards *fac*-$Mo(CO)_3$ (MeCN)(dppe) and $Mo(CO)_4$(dppe). Synthesis, characterization and reactions of the novel fullerene molybdenum derivative *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$

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(Received 15 July 1997; accepted 20 August 1997)

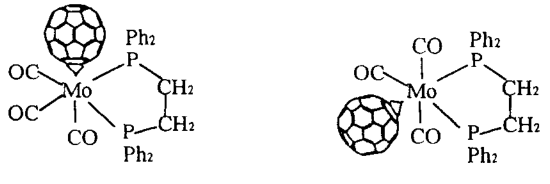
Abstract—The acetonitrile ligand of *fac*-$Mo(CO)_3(MeCN)(dppe)$[dppe = bis-(1,2-diphenylphosphino)ethane] can be easily replaced by fullerene C_{60} in chlorobenzene at about 80°C to give exclusively *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$, whereas fullerene C_{60} reacted with $Mo(CO)_4(dppe)$ in refluxing chlorobenzene to afford an isomeric mixture of *fac*- and *mer*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$. These organomolybdenum C_{60} derivatives were characterized by elemental analysis and spectroscopic techniques. In addition, the $\eta^2\text{-}C_{60}$ ligand in *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ was also found to be easily displaced by MeCN, PPh_3 or pyridine to give corresponding *fac*-organomolybdenum complexes. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: fullerene C_{60}; $Mo(CO)_3(MeCN)(dppe)$; $Mo(CO)_4(dppe)$; ligand substitution; synthesis; characterization.

Although C_{60} derivatives of group 8 to group 10 transition metals have been extensively studied [1–8], little is known about those of group 6 metals [9–11]. So far, structurally characterized organotransition metal C_{60} derivatives may fall into two categories: (1) fullerene core directly bonded to transition metals, such as $(\eta^2\text{-}C_{60})M(PPh_3)_2$(M = Pd, Pt) [1], $(C_{60})\{Pt(PEt_3)_2\}_6$ [2], $(\eta^2\text{-}C_{60})Ni(PEt_3)_2$ [3], $(\eta^2\text{-}C_{60})IrCl(CO)(PPh_3)_2$ [4], $(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2$ [5], $(\eta^2\text{-}C_{60})Os_3(CO)_{10}(PPh_3)$ [6], $(C_{60})Ru_2(\mu\text{-}Cl)_2Cp^*_2$ [7], $(\eta^2\text{-}C_{60})Fe(CO)_4$ [8], $(C_{60})[W(CO)_3(dppe)]_n(n = 1,2)$ [9a], $[Mo(CO)_3(DDH)]_2C_{60}\cdot 2.5C_6H_6$ (DDH = diacetyldihydrazone, $H_2NN = C(Me)\ C(Me) = NNH_2$) [10]; and *fac*/*mer*-$W(CO)_3(dppb)(\eta^2\text{-}C_{60})$ [11]; (2) fullerene core indirectly bonded to transition metals, such as $(\eta^2\text{-}C_{60})[S_2Fe_2(CO)_6]$ [12] and $(\eta^2\text{-}C_{60})[o\text{-}(CH_2)_2C_5H_3\text{-}\eta^5]Co(\eta^4\text{-}C_4Ph_4)$ [13]. In order to further develop the organometallic chemistry of group 6 metals' fullerene derivatives, we undertook this study. Herein we report the synthesis and structural characterization of fullerene molybdenum derivatives *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ and *fac*/*mer*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$, as well as $\eta^2\text{-}C_{60}$ substitution reactions of *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ with MeCN, Ph_3P and pyridine.

RESULTS AND DISCUSSION

We found that an equimolar amount of C_{60} reacted with *fac*-$Mo(CO)_3(MeCN)(dppe)$ in chlorobenzene at about 80°C to give 84% of the product *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (Scheme 1).



fac-isomer

mer-isomer

Scheme 1.

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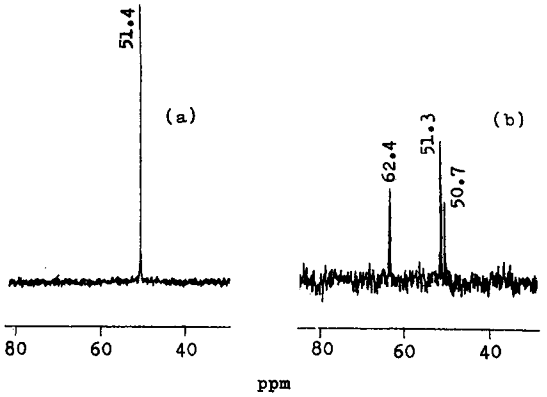

Fig. 1. (a) ^{31}P NMR spectrum of *fac*-Mo(CO)$_3$(dppe)(η^3-C$_{60}$), (b) ^{31}P NMR spectrum of *fac*- and *mer*-Mo(CO)$_3$(dppe) (η^2-C$_{60}$).

In principle, the product might exist as another isomer, i.e. *mer*-isomer or as a mixture of *fac*- and *mer*-isomers (Scheme 1). However, since its ^{31}P NMR spectrum (Fig. 1(a)) shows only one singlet at 51.4 ppm, the product should exist only as *fac*-isomer. This is because the *fac*-isomer has two P atoms in the same chemical environment and *mer*-isomer does not. The formation of only one isomer implies that the displacement of MeCN by C$_{60}$ took place completely with *fac*-configuration retention of the starting material.

The ^{1}H NMR spectrum of its ethylene group is also consistent with the *fac*-configuration of the product. It shows two kinds of resonances in an equal intensity, which were caused by two groups of hydrogen atoms: one at 2.60 ppm is on the same side of the equatorial plane (consisting of two equatorial CO, two P and two C of the ethylene group) as the C$_{60}$ cage, whereas the other at 2.40 ppm is on the opposite side of the plane as the C$_{60}$ cage. This assignment was made basically according to the electron-withdrawing effect of C$_{60}$ ligand.

In the ^{13}C NMR spectrum of the product, we observed 28 resonances in the fullerene sp^2-C area (133–152 ppm). This is actually in agreement with its Cs symmetry, although 32 peaks are theoretically expected for Cs symmetry. This is because the four carbon resonance peaks at 145.88, 142.85, 133.82 and 133.62 ppm each and have the intensity equivalent to two sp^2-C resonances [14].

In the IR spectrum of the product there are three absorption bands in the region 1880–1930 cm^{-1}, characteristic of the terminal carbonyls. The IR spectra of the product and its precursor determined in CH$_2$Cl$_2$ are shown in Fig. 2. In comparison with its precursor, the lowest ν_{CO} of the product shifts towards higher energy by about 72 cm^{-1}. Such an IR difference between them is obviously related to the stronger electron-withdrawing effect of C$_{60}$ ligand than MeCN ligand.

The UV spectrum of the product with that of free C$_{60}$ is shown in Fig. 3. As seen from Fig. 3 the first band at 280.7 nm for the product is much stronger than its second band at 350.5 nm, whereas the first band at 286.5 nm for free C$_{60}$ is smaller than its second band at 335.3 nm. This is probably due to the overlap of those two bands at around 280 nm, generated from C$_{60}$ ligand and the phenyl groups attached to P atoms in the product [15].

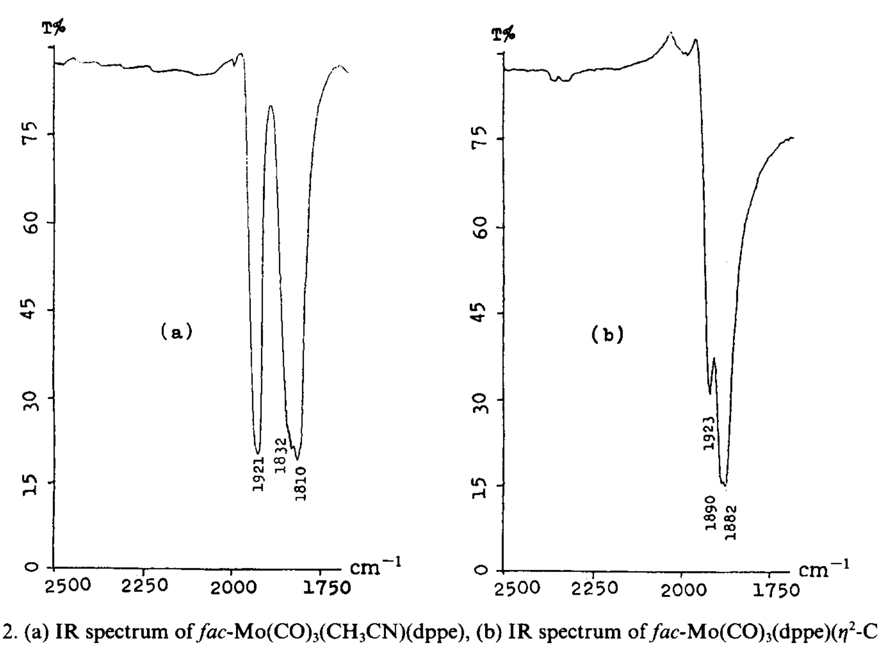

Fig. 2. (a) IR spectrum of *fac*-Mo(CO)$_3$(CH$_3$CN)(dppe), (b) IR spectrum of *fac*-Mo(CO)$_3$(dppe)(η^2-C$_{60}$).

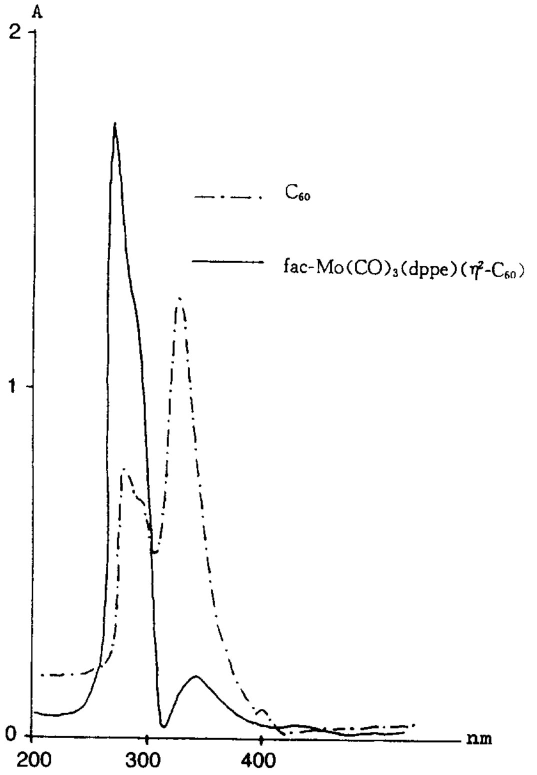

Fig. 3. UV-*vis* spectra of *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ and C_{60} in toluene (1.85×10^{-5} M)

In addition, the C/H analysis for the product is satisfactory and its FD–MS spectrum displays a molecular ion peak at m/z 1296.

The product is somewhat air-sensitive, whose half-life of decomposition in CH_2Cl_2 is approximately 2.5 days. It is readily soluble in common organic solvents, for example, chlorobenzene, toluene, benzene, chloroform, dichloromethane and carbon disulphide, but it is hardly soluble in petroleum ether. Interestingly, the product *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ can also take part in ligand displacement reactions. For example, addition of acetonitrile to a chlorobenzene solution of the product, followed by stirring the refluxing mixture for 6 h afforded 84% of *fac*-$Mo(CO)_3(MeCN)(dppe)$ [16]; Similarly, the product reacted with pyridine or with PPh_3 in chlorobenzene to yield 91% of *fac*-Mo $(CO)_3(dppe)(C_5H_5N)$ [17], and 85% of *fac*-$Mo(CO)_3$ $(PPh_3)(dppe)$ [17], respectively.

It is noteworthy that the thermal reaction of a slightly excessive $Mo(CO)_4(dppe)$ with C_{60}, in contrast to that of $Mo(CO)_3(MeCN)(dppe)$ with C_{60} mentioned above, gave a mixture of *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ and *mer*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ in 43% yield. The two isomers are very close in polarity and thus could not be separated by conventional chromatography and recrystallization methods. Although the isomer mixture was claimed to be prepared by a photolytic procedure [9b], the thermal reaction procedure used here is much more convenient and produces the isomer mixture in higher yield. In addition, no detailed characterization data for the isomer mixture were given in the published paper [9b]. The ^{31}P NMR spectrum for this mixture (Fig. 1(b)) shows three signals, one at 51.3 ppm assigned to two identical P atoms of *fac*-isomer and two signals at 62.4 and 50.7 ppm in an equal intensity assigned to one P atom *cis* to C_{60} and the other P atom *trans* to C_{60} in *mer*-isomer respectively. The ^1H NMR spectrum for this mixture is similar to that of pure *fac*-isomer. However, the upfield broad singlet at 2.47 ppm is caused by *trans*-two hydrogens of CHCH in *fac*-isomer and two hydrogens of CH_2 attached to the *trans* P atom in *mer*-isomer, whereas the downfield singlet at 2.60 ppm is caused by *cis*- two hydrogens of CHCH in the *fac*-isomer and two hydrogens of CH_2 attached to the *cis* P atom in the *mer*-isomer due to the electron-withdrawing effect of the C_{60} ligand. While the IR spectrum of *fac*-isomer displays three terminal CO bands, that of this isomer mixture exhibits four bands within the terminal CO region. This is consistent with the observations that the number of IR active bands cannot exceed but may be less than the number of CO ligands in the complexes [18].

It follows that we have found a simple and convenient synthetic method for obtaining the single isomer *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ in high yield. This method involves a ligand displacement reaction between C_{60} and *fac*-$Mo(CO)_3(MeCN)(dppe)$ with *fac*-configuration retention of the starting material. We have also found that the thermal reaction between C_{60} and $Mo(CO)_4(dppe)$ affords an isomer mixture of *fac*- and *mer*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ with more convenient manipulations and higher yield than the reported photolysis method [9b]. Finally, we have demonstrated that the $\eta^2\text{-}C_{60}$ ligand in *fac*-Mo $(CO)_3(dppe)(\eta^2\text{-}C_{60})$ can also be displaced by MeCN, PPh_3 and C_5H_5N to give corresponding *fac*-organomolybdenum complexes in high yields.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere using standard Schlenk or vacuum-line techniques. Silica gel (10–40 μm) on TLC plates ($24 \times 16 \times 0.3$ cm) was activated for 3 h at 110°C, whereas silica gel (300–400 mesh) for column chromatography (15×2 cm) was activated for 1 h at 120°C. Toluene, THF, petroleum ether were dried and deoxygenated by distillation from sodium-/benzophenone ketyl. Chlorobenzene, MeCN and $CHCl_3$ were dried by distillation from P_2O_5. Pyridine and PPh_3 were chemical reagents used without further purification. Fullerene C_{60} was purchased from Yin-Han Fullerene High-Tech. Co. Ltd. *fac*-$Mo(CO)_3$ $(MeCN)(dppe)$ [16], dppe [19] and $Mo(CO)_4(dppe)$ [20] were prepared according to the literature. 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 qoQ or a Bruker AC-P 200 spectrometer. Elemental analysis and MS determinations were performed using a Yanaco CHN Corder MT-3 analyzer and a Zabspec spectrometer, respectively. Melting points were determined on a Yanaco MP-500 apparatus.

Reaction of fac-$Mo(CO)_3(MeCN)(dppe)$ *with* C_{60} *and preparation of fac-*$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$

A 100 cm^3 two-necked flask equipped with a magnetic stir-bar, a serum cap and a reflux condenser, was charged with 35 mg (0.056 mmol) of *fac*-$Mo(CO)_3$ (MeCN)(dppe) and 40 cm^3 of chlorobenzene. To this solution was added 40 mg (0.056 mmol) of C_{60} in 40 cm^3 of chlorobenzene during about 2 h at room temperature. The reaction mixture was heated to about 80°C and then kept at this temperature for 6 h. After removal of the solvent under reduced pressure, the residue was purified by TLC (1 : 1 toluene : petroleum ether as eluent) to give 61 mg (84%) of *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ as a dark green solid. m.p. 125–127°C. Found : C, 82.43 ; H, 2.21. Calc. for $C_{89}H_{24}MoO_3P_2$: C, 82.29; H, 1.85%, IR(CH_2Cl_2): $\nu_{C\equiv O}$, 1923 (s), 1890 (vs), 1882 (vs) cm^{-1}; ν_{C60} 1432 (m), 1182 (w), 588 (m), 518 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 90 MHz): 2.40 (br. s, *trans*-CHCH), 2.60 (br.s, *cis*-CHCH), 7.20–7.60 (m, 4C_6H_5) ppm. ^{31}P NMR ($CDCl_3$, H_3PO_4, 80.9 MHz): 51.4 ppm. ^{13}C NMR ($CDCl_3$, TMS, 50.3 MHz) : 217.99, 210.63 (s, s, CO) ; 151.82, 151.59, 150.84, 150.76, 148.06, 147.94, 147.65, 147.29, 146.76, 146.59, 146.24, 146.04, 145.88 (2C), 145.18, 144.71, 144.67, 144.35, 143.47, 143.24, 142.85 (2C), 141.60, 135.70, 134.90, 134.63, 134.09, 133.82 (2C), 133.62 (2C), 133.38 (s, 28 resonances for C_{60}) ; 138.00, 137.39, 132.45, 132.20 (4 resonances for C_6H_5) ; 132.20, 130.51, 129.49, 129.30 (4 resonances for C_6H_5) ppm ; 29.22, 28.14 (s, s, 2CH_2) ppm. UV-*vis*(toluene, 1.85×10^{-5} M) : λ_{max}(log ε) 280.7 (5.13), 350.5 (4.17), 433.3 (3.43), 537.7 (3.21) nm. FD–MS *m*/*z* (^{94}Mo, ^{31}P) : 1296 (M$^+$).

Reaction of fac-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ *with* MeCN *and preparation of fac-*$Mo(CO)_3(MeCN)(dppe)$

The same flask was charged with 3 mg (2.31×10^{-3} mmol) of *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$, 10 cm^3 of chlorobenzene and 10 cm^3 of MeCN. The dark green solution was refluxed for 6 h to give a light green solution. The same workup as above gave 1.20 mg (84%) of *fac*-$Mo(CO)_3(MeCN)(dppe)$ as a pale yellow solid, which was identified by comparison of its m.p. and ^{1}H NMR spectrum with an authentic sample [16].

Reaction of fac-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ *with pyridine and preparation fac-*$Mo(CO)_3(dppe)(C_5H_5N)$

Similarly, from 6 mg (4.62×10^{-3} mmol) of *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$, 10 cm^3 of chlorobenzene and 0.38 cm^3 of pyridine, 2.8 mg (92%) of *fac*-Mo $(CO)_3$(dppe) (C_5H_5N) as a light yellow solid was obtained and identified by comparison of its m.p. and IR spectrum with an authentic sample [17].

Reaction of fac-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ *with* PPh_3 *and preparation of fac-Mo(CO)*$_3(PPh_3)(dppe)$

Similarly, from 6 mg (4.62×10^{-3} mmol) of *fac*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$, 10 cm^3 of chlorobenzene and 1.3 mg (4.96×10^{-3} mmol) of PPh_3, 3.3 mg (85%) of *fac*-$Mo(CO)_3$ (dppe)PPh_3 as a light yellow solid was obtained and identified by comparison of its m.p. and IR spectrum with those of an authentic sample [17].

Reaction of $Mo(CO)_4(dppe)$ *with* C_{60} *and preparation of a mixture of fac- and mer-*$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$

The same flask charged with 40 mg (0.066 mmol) of $Mo(CO)_4$(dppe), 36 mg (0.05 mmol) of C_{60} and 50 cm^3 of chlorobenzene. The reaction mixture was refluxed for 12 h. Removal of the solvent gave a residue which was subjected to column chromatography using toluene as eluent. The green band was collected to give 28 mg (43%) of an isomer mixture of *fac*- and *mer*-$Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ as a dark green solid. m.p. 120–128°C. Found : C, 82.30 ; H, 2.20. Calc. for $C_{89}H_{24}MoO_3P_2$: C, 82.29; H, 1.85% IR(CH_2Cl_2): $\nu_{C\equiv O}$, 1923 (s), 1891 (vs), 1880 (vs), 1856 (m) cm^{-1}; ν_{C60} 1429 (m), 1188 (w), 589 (m), 518 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 90 MHz): 2.47 (br.s, *trans*-CHCH of *fac*-isomer and *trans*-CH_2 of *mer*-isomer, 2.60 (br.s, *cis*-CHCH of *fac*-isomer and *cis*-CH_2 of *mer*-isomer), 7.24–7.56 (m, 4C_6H_5) ppm. ^{31}P NMR ($CDCl_3$, H_3PO_4 80.9 MHz) : 62.4, 51.3, 50.7 ppm.

Acknowledgements—We are grateful to the National Natural Science Foundation of China and the Special Foundation of State Education Committee of China for financial support of this project.

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