Pergamon

Polyhedron Vol. 16, No. 12, pp. 2141–2143, 1997

0277–5387/97 $17.00+0.00

PII: S0277–5387(96)00603–1

COMMUNICATION

The first fullerene tungsten complex containing a dppb ligand *fac/mer*-W(CO)$_3$(dppb)(η^2-C$_{60}$) *via* displacement reaction of *fac*-W(CO)$_3$(MeCN)(dppb)

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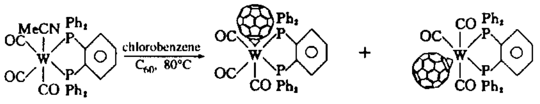
(Received 27 November 1996; accepted 10 December 1996)

Abstract—An isomeric fullerene tungsten complex *fac/mer*-[W(CO)$_3$(dppb)(η^2-C$_{60}$)][dppb = 1,2-bis(diphenylphosphino)benzene] was synthesized by reaction of C$_{60}$ with *fac*-[W(CO)$_3$(MeCN)(dppb)], and has been fully characterized by elemental analysis and spectroscopic techniques. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: fullerene C$_{60}$; tungsten; acetonitrile; carbonyl; synthesis; characterization.

Since the first preparation of organotransition-metal fullerene derivatives [1(a)], many such organometallic complexes have been synthesized and structurally characterized: for example M(η^2-C$_{60}$)(PPh$_3$)$_2$(M = Pt, Pd) [1], (η^2-C$_{60}$)Co(H)(CO)(PPh$_3$)$_2$ [2], (η^2-C$_{60}$)Rh(H)(PPh$_3$)$_2$(CO) [3], Ir(CO)(PPh$_3$)(Cl)(η^2-C$_{60}$)·5C$_6$H$_6$ [4], Fe(CO)$_4$(η^2-C$_{60}$) [5], (η^2-C$_{60}$)Ru(CO)$_4$ [6], (η^2-C$_{60}$)Os$_3$(CO)$_{11}$ [7], and C$_{60}$[Re(CO)$_5$]$_2$ [8]. However, among all the known organotransition-metal fullerene derivatives prepared so far, those of group 6 metals are very rare [9]. We now report the synthesis and characterization of a new isomeric fullerene tungsten complex *fac/mer*-[W(CO)$_3$(dppb)(η^2-C$_{60}$)] formed *via* thermal displacement reaction between C$_{60}$ and *fac*-[W(CO)$_3$(MeCN)(dppb)].

An equivalent of fullerene C$_{60}$ (36 mg, 0.05 mmol) was added to a solution of *fac*-[W(CO)$_3$(MeCN)(dppb)] (**1**) (38 mg, 0.05 mmol) in 80 cm^3 of chlorobenzene. The mixture was stirred for 6 h at about 80°C with subsequent purification by TLC (1 : 1 toluene/petroleum ether, silica gel G) to afford *fac/mer*-[W(CO)$_3$(dppb)(η^2-C$_{60}$)] (**2**), as shown in Scheme 1. The new complexes (**1**) and (**2**) were fully characterized by elemental analysis and spectroscopic methods.†



fac-isomer

1

fac-isomer

2

mer-isomer

Scheme 1.

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†Characterization data for *fac*-[W(CO)$_3$(MeCN)(dppb)] (**1**): Yield 54%. pale yellow crystal. M.p. 210–212°C (decomp.). IR (KBr disk): $\nu_{C\equiv O}$, 1922.2 (vs), 1850.1 (vs), 1804.5 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS, δ, ppm): 1.86(s,3H,CH$_3$), 6.88–7.82 (m, 24H, 4C$_6$H$_5$, C$_6$H$_4$). UV-vis (chlorobenzene, 2×10^{-4} M): 288.5 nm. ^{31}P NMR (CDCl$_3$, H$_3$PO$_4$, δ, ppm): 53.997 (s). Found: C, 55.3; H, 4.0; N, 1.8. Calc. for C$_{35}$H$_{27}$ NO$_3$P$_2$W: C, 55.6; H, 3.6; N, 1.8%. *fac/mer*-[W(CO)$_3$(dppb)(η^2-C$_{60}$)] (**2**): Yield 63%. dark-green solid. M.p. 230–233°C (decomp.). IR (KBr disk): $\nu_{C\equiv O}$, 2005.6(s), 1935.8(s), 1883.4 (vs), 1839.4(m), 1813.5(m); ν_{C60}, 1432.5 (m), 1185.3(w), 582.8 (w), 524.4 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS, δ, ppm): 7.04–7.66 (m, 24H, 4C$_6$H$_5$, C$_6$H$_4$). ^{31}P NMR (CDCl$_3$, H$_3$PO$_4$, δ, ppm): 45.984 (s), 44.726(s), 38.948(s). UV-vis (chlorobenzene, 2×10^{-4} M), 288.3, 334.3, 434.9, 605.5 nm. FD-MS *m/z*: 1432–1438 (M$^+$), 720(C$_{60}^+$). Found: C, 74.9; H, 2.0. Calc. for C$_{93}$H$_{24}$O$_3$P$_2$W: C, 77.8; H, 1.7%.

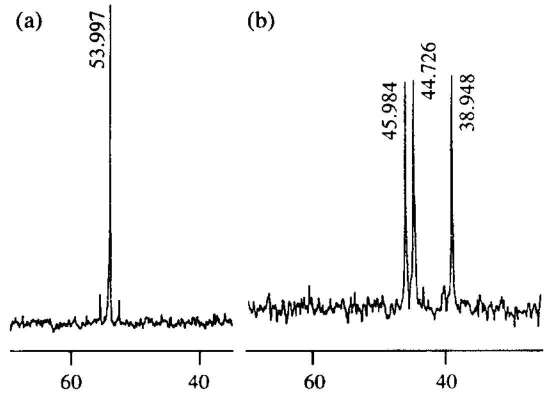

Fig. 1. (a) ^{31}P NMR spectrum of complex **1**; (b) ^{31}P NMR spectrum of complex **2**.

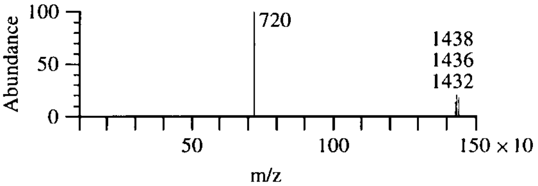

Fig. 3. FD-MS of complex **2**.

Fullerene C_{60} derivative **2** is easily soluble in common organic solvents, for example, toluene, chloroform, diethyl ether and carbon disulfide, but is not soluble in non-polar solvents such as petroleum ether. Furthermore, **2** is remarkably air-stable, for instance, its CH_2Cl_2 solution, upon the exposure to air, does not change at all during one week.

In principle, complex **2** and its precursor **1** may have two geometric isomers, namely *fac*-isomer and *mer*-isomer. For precursor **1**, its ^{31}P NMR spectrum (Fig. 1(a)) has only one signal at 53.997 ppm. This indicates two identical P atoms present in **1** and thus it is presumably the *fac*-isomer. However for complex **2**, since its ^{31}P NMR spectrum (Fig. 1(b)) has three signals, it would contain both *fac*- and *mer*-isomers. The *fac*-isomer exhibits one signal at 44.726 ppm caused by two identical P atoms, whereas the *mer*-isomer shows two signals, one at 45.984 ppm assigned to the P atom *cis* to the C_{60} ligand and the other at 38.948 ppm attributed to the P atom *trans* to the C_{60} ligand. This implies that an inversion of the *fac*-configuration of starting material **1** occurred partially during the course of the displacement reaction. In the ^1H NMR spectrum of **2** there is a multiplet assigned to the dppb ligand, whereas in that of **1** besides the multiplet, there is a singlet at 1.86 ppm assigned to the MeCN ligand. The singlet for MeCN coincides very well with the deduction from the ^{31}P NMR that **1** exists as the *fac*-isomer. In addition, the IR spectrum of **1** (Fig. 2(a)) has three bands within the terminal CO region, whereas that of **2** has five bands (Fig. 2(b)). This is also in good agreement with the conclusions that **1** has one isomer and **2** is a mixture of two isomers, since the number of IR active bands cannot exceed but may be less than the number of CO ligands in the complex [10].

Although the elemental analysis data for **2** is not so well in agreement with its formulation (this is often the case for C_{60} organometallic derivatives [11]), the FD-MS of **2** shows a C_{60} ion peak and a group of molecular ion peaks having the tungsten isotopic distribution (Fig. 3). The UV–vis spectrum of complexes **1**, **2** and free C_{60} are shown in Fig. 4. As seen from Fig. 4, the spectrum of **2** is very similar to that of free C_{60}; However in contrast to free C_{60}, the first band of **2** at 288.3 nm is stronger than the second band of **2** at 334.3 nm. This is probably due to the overlap of two bands generated from the C_{60} ligand of **2** and $W(CO)_3$(dppb) moiety. In addition, the spectrum of

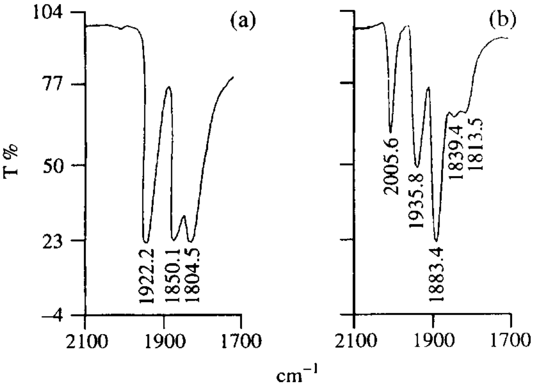

Fig. 2. (a) IR spectrum of complex **1**; (b) IR spectrum of complex **2**.

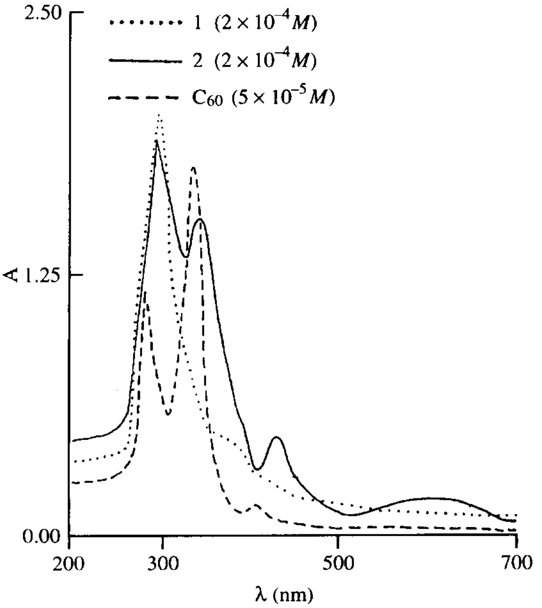

Fig. 4. UV-vis spectra of **1**, **2** and C_{60} in C_6H_5Cl.

2 shifts slightly towards a higher wavelength when compared to that of free C_{60}. This phenomenon might be caused by π-electron back-bonding from the tungsten atom to the C_{60} ligand.

The kinetics of the displacement reaction for formation of **2** has been studied by means of a conventional HPLC method. However, the detailed results will be reported later in a full paper.

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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