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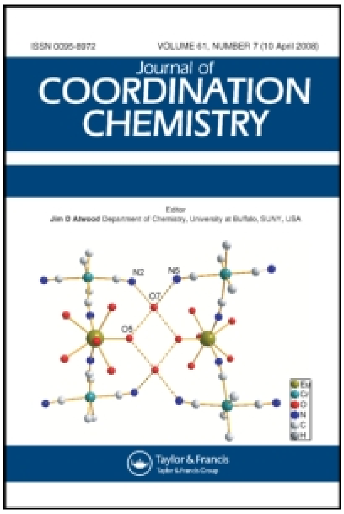

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PHOTOSYNTHESIS OF (DIHAPTO-BUCKMINSTERFULLERENE) PENTACARBONYL TUNGSTEN (O)

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$(\eta^2-C_{60})W(CO)_5$ was synthesized *via* the photoreaction of $W(CO)_6$ with C_{60} in n-hexane using a mercury vapor lamp. The complex was characterized by elemental analysis, infrared spectroscopy in the stretching carbonyl region, and ^{13}C-NMR spectroscopy. Three bands observed in the stretching carbonyl region at 2085 cm^{-1}, 1996 cm^{-1} and 1976 cm^{-1} are consistent with three bands expected for the $W(CO)_5$ fragment of the complex having C_{4v} symmetry. A previous report that the sunlight photo-induced reaction of $W(CO)_6$ with C_{60} in benzene produced $(\eta^6-C_{60})W(CO)_3$ prompted a reinvestigation of the sunlight photo-induced reaction.

Keywords: Fullerene; Buckminsterfullerene; Metal carbonyl complexes; Tungsten

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INTRODUCTION

The electronic surface structure of fullerene, C_{60}, consists of 30 electron-filled and 30 empty π-orbitals [1]. The highest occupied molecular orbitals (HOMOs, the five-fold degenerate h_u orbitals) are occupied with 10 electrons. Since the lowest unoccupied molecular orbitals (LUMOs, the triply degenerate t_{1g} orbitals) are relatively low in energy, C_{60} has the tendency to accept electrons, and it is easily electrochemically reduced [2]. Six reversible reduction potentials ranging from -0.98 to -3.26 V (*vs.* ferrocene/ferrocinium) have been reported, consistent with six stepwise electron gain processes to fill the three low-lying LUMOs [2]. Because of this high electron gain tendency, the

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*Corresponding author. e-mail: jose.cortes.figueroa@usa.net formation of exohedral coordination complexes of C_{60} should be determined by its ability to participate in backbonding with a transition metal.

Fullerene has sixty identical carbons, which are bonded to each other in a truncated icosahedron (soccer-ball) shape containing twenty hexagonal faces and twelve pentagonal faces. A carbon atom occupies each vertex. Two distinct types of carbon–carbon bonds are observed: The C—C bonds separating two hexagons (6:6 ring junction), and the C—C bonds separating a hexagon from a pentagon (6:5 ring junction) [3]. Since the C—C bonds at the 6:6 ring junctions behave as olefinic units, the hapticity (η) of the fullerene-metal complexes may vary from $\eta = 2$ to $\eta = 6$ [3]. However, fullerene has the tendency to form complexes with hapticity two, $\eta = 2$ [4]. The olefinic C—C bonds at the 6:6 ring-junctions on the curved surface of the C_{60} molecule are expected to be strained [5]. The release of the strain energy upon complex formation may explain the tendency to form complexes with $\eta = 2$ hapticity. Higher orders of hapticity are rare, due probably to decreased overlap of the frontier orbitals of the transition metal complex fragment with the "splayed out" LUMOs on the rigid and curved surface of C_{60} [6]. To our knowledge only two metal complexes of highly curved ligands (fullerene-like) with hapticity higher than four have been reported: one is a ruthenium-corannulene complex (corannulene is a polyaromatic ligand less curved than C_{60}) [7] and the other is the complex $(\eta^6-C_{60})W(CO)_3$, both with hapticity of six ($\eta = 6$) [8]. The complex $(\eta^6-C_{60})W(CO)_3$ was sunlight photo-produced from $W(CO)_6$ and C_{60}. We undertook and report here a systematic study to identify other complexes (such as $(\eta^x-C_{60})W(CO)_{(6-(x/2))}$, $x = 2, 4$) that may be photo-produced during the stepwise photo formation of $(\eta^6-C_{60})W(CO)_3$.

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EXPERIMENTAL

General

Infrared spectra were obtained on a Bruker Vector 22 Fourier transform infrared spectrophotometer, UV-visible spectra on a Beckman DU 650 spectrophotometer, and ^{13}C-NMR spectra on a Varian Gemini-300 300 MHz spectrometer. All reactions were carried out under nitrogen. Atlantic Microlab, Norcross, GA, performed elemental analyses.

Preparation and Purification of Materials

Carbon disulfide (Fisher) was used as purchased. n-Hexane (Aldrich) was refluxed over sodium for 24 h followed by fractional distillation.

Triphenylphosphine (PPh_3) (Aldrich) was recrystallized from absolute ethanol (Florida Distillers Company) and the recovered crystals were dried under a stream of nitrogen. C_{60} (Aldrich) and $W(CO)_6$ (Aldrich) were used as purchased without further purification.

Preparation of $(\eta^2-C_{60})W(CO)_5$

The complex $(\eta^2-C_{60})W(CO)_5$ was prepared from $W(CO)_6$ and C_{60}. In a 25 mL round bottom flask equipped with a magnetic stirr bar, a condenser, and a nitrogen inlet, 0.0200 g (5.68 mmol) of $W(CO)_6$ and 0.0354 g (4.91 mmol) of C_{60} were dissolved in 15 mL of nitrogen-purged and dried n-hexane. The resulting reddish purple solution was irradiated with a medium pressure mercury lamp (Hanovia). The progress of the reaction was monitored by observing and recording the increase of the ν_{CO} bands intensities at 2085 cm^{-1}, 1996 cm^{-1} and 1973 cm^{-1} and the decrease of the band intensity at 1983 cm^{-1}, corresponding to $(\eta^2-C_{60})W(CO)_5$ and $W(CO)_6$ complexes, respectively [9]. Upon irradiation, a reddish brown solid precipitated out of solution. After the reaction was complete, judging by the infrared spectrum, the reaction mixture volume was reduced by bubbling nitrogen directly into the mixture to induce more precipitation. The reddish brown solid was heated at 35°C under reduced pressure for 24 h to eliminate traces of unreacted $W(CO)_6$ and solvent; 38.5 mg of product was recovered. The UV-visible spectrum of the complex showed a set of very intense bands in the vicinity of 200–300 nm and another set of weak bands *ca.* 550–600 nm. The ν_{CO} of the complex in carbon disulfide solution showed three bands: (ν_{CO}, cm^{-1}): 2082(s), 1991(s), 1967(vs). Anal. Calcd. for $C_{65}O_5W^{10}$: C, 74.75; Found: C, 75.56. ^{13}C-NMR: 180 ppm, 143 ppm.

RESULTS AND DISCUSSION

The photoreaction of $W(CO)_6$ with C_{60} in n-hexane was monitored using infrared spectroscopy in the stretching carbonyl region (ν_{CO}) from 2100 cm^{-1} to 1800 cm^{-1}. The color of the solution of C_{60} and $W(CO)_6$ in n-hexane is deep purple. This color results from a set of spin forbidden singlet–singlet transitions in the 400–600 nm region [11]. The ν_{CO} spectrum of the solution (Fig. 1a) shows a band at 1983 cm^{-1}, corresponding to the ν_{CO} active vibration of $W(CO)_6$. The parent C_{60} compound absorbs at 1400 cm^{-1}, 1180 cm^{-1}, 580 cm^{-1} and 510 cm^{-1} [12]. These bands correspond to four t_{1u} infrared active vibrations. After forty minutes of irradiation the reaction mixture turned reddish brown due to the formation

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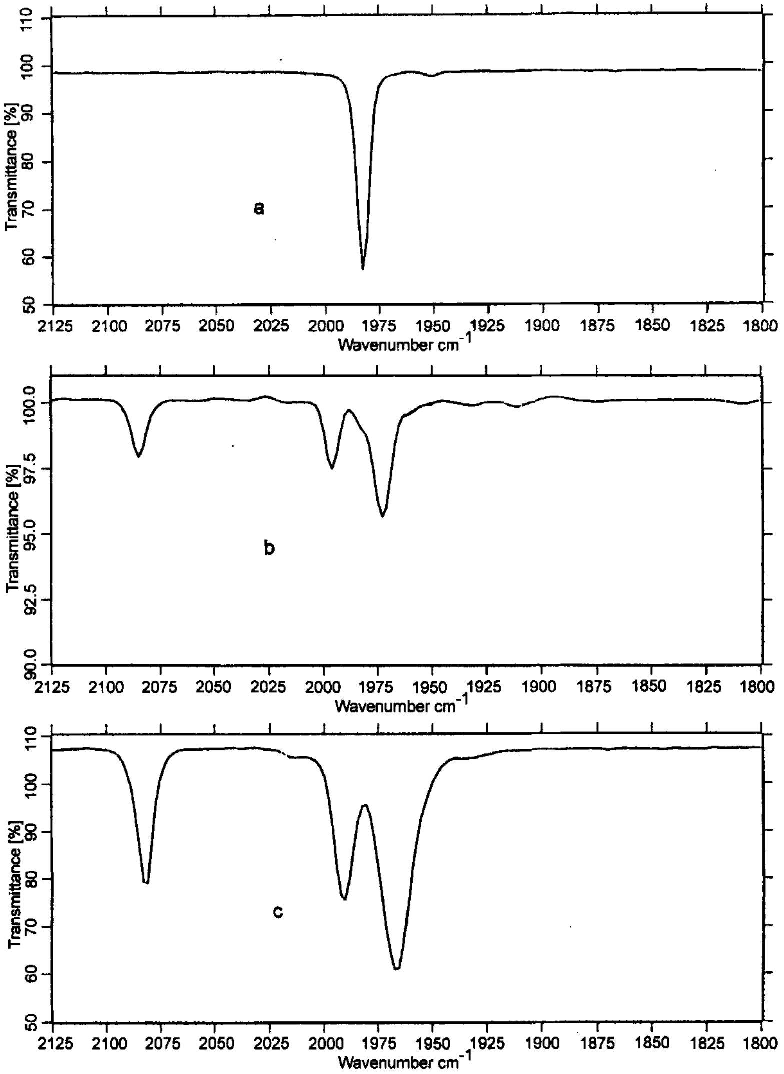

FIGURE 1 Infrared spectrum in the stretching carbonyl region of: (a) reaction mixture of $W(CO)_6$ and C_{60} in n-hexane before irradiation; (b) reaction mixture of $W(CO)_6$ and C_{60} in n-hexane after 40 minutes of irradiation; (c) $(\eta^2-C_{60})W(CO)_5$ in carbon disulfide.

of a reddish brown solid. Three new bands appear at 2085 cm^{-1}, 1996 cm^{-1} and 1973 cm^{-1} (Fig. 1b) in the ν_{CO} spectrum of the reaction mixture. These bands are assigned to the four C—O stretching (two of them degenerate) infrared active vibrations (a_1, a_1, e) of $(\eta^2-C_{60})W(CO)_5$. The spectrum in

Figure 1b corresponds to a dilute solution because most $(\eta^2-C_{60})W(CO)_5$ precipitates out of solution as soon as it is produced from $W(CO)_6$ and C_{60}. Figure 1c shows the ν_{CO} spectrum of $(\eta^2-C_{60})W(CO)_5$ in carbon disulfide. In carbon disulfide the bands are shifted 2 to 5 cm^{-1} to lower wavenumbers relative to the bands when the complex is dissolved in n-hexane.

The sunlight photo-induced reaction of $W(CO)_6$ with C_{60} in benzene to produce the complex $(\eta^6-C_{60})W(CO)_3$ has been reported elsewhere [8]. The ν_{CO} spectrum of the photoproduct showed three bands at 2083 cm^{-1}, 1996 cm^{-1} and 1957 cm^{-1}. The authors of the work suggested that three bands are observed, instead of the expected two (a_1 and e) for the $W(CO)_3$ moiety, because the degenerate bands (e) split due to distortion of the complex's C_{3v} geometry. Our group reinvestigated the sunlight photo-induced reaction of $W(CO)_6$ with C_{60} (in n-hexane). The ν_{CO} spectrum of the reaction mixture after 20 minutes and 70 minutes of sun exposure (Figs. 2a and b, respectively) indicates a mixture of the pentacarbonyl

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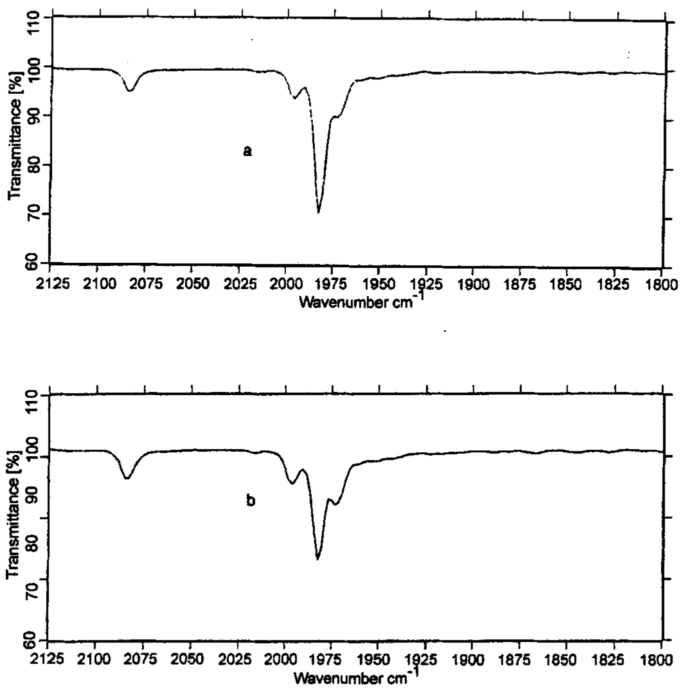

FIGURE 2 Infrared spectrum in the stretching carbonyl region of: (a) reaction mixture of $W(CO)_6$ and C_{60} in n-hexane after 20 minutes of sunlight exposure; (b) reaction mixture of $W(CO)_6$ and C_{60} in n-hexane after 70 minutes of sunlight exposure.

complex ($\eta^2 - C_{60}$)W(CO)$_5$ (2085 cm^{-1}, 1996 cm^{-1}, 1973 cm^{-1}) and W(CO)$_6$ (1985 cm^{-1}). After *ca.* 3 h of sun exposure the band characteristic of W(CO)$_6$ (1983 cm^{-1}) is not present in the ν_{CO} spectrum. The ν_{CO} spectrum of the reaction product in carbon disulfide is similar to the spectrum in Figure 2b.

Figures (3a–c) shows the ^{13}C-NMR spectra of W(CO)$_6$, ($\eta^2 - C_{60}$)W(CO)$_5$, and C_{60}, respectively. The signal at $\delta = 190$ ppm (Fig. 3a) corresponding to the six chemically equivalent CO groups of W(CO)$_6$ is shifted to $\delta = 180$ ppm in the spectrum of the complex (Fig. 3b). It is interesting that only one signal is observed for the W(CO)$_5$ fragment. The signal of the

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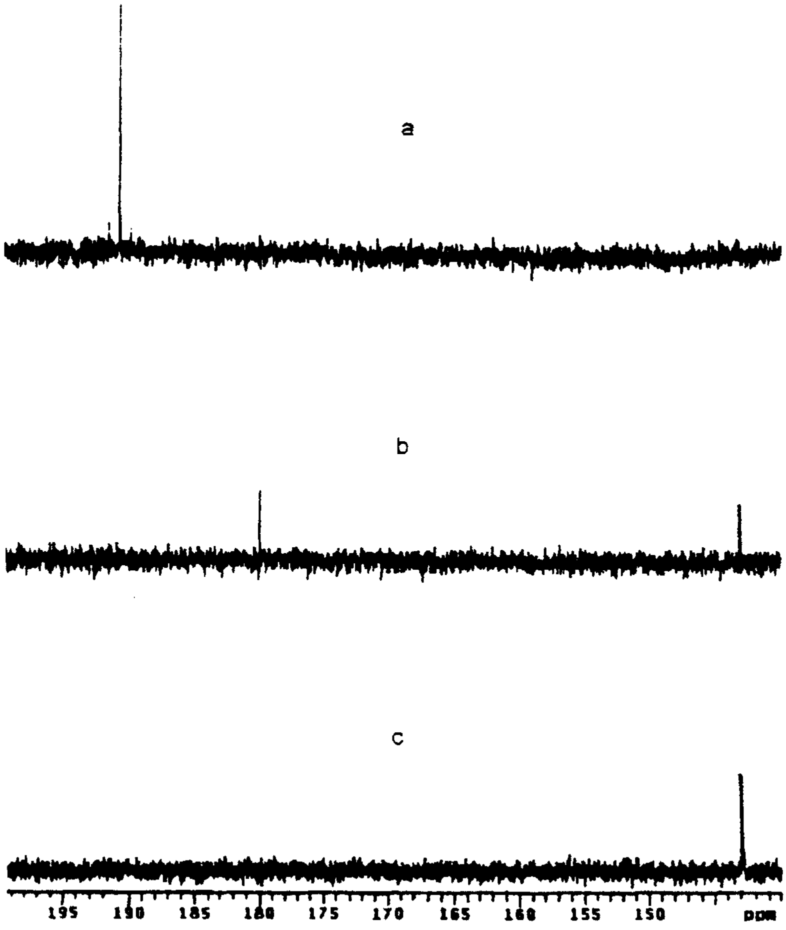

FIGURE 3 ^{13}C-NMR spectrum in toluence-d$_6$ of: (a) W(CO)$_6$; (b) ($\eta^2 - C_{60}$)W(CO)$_5$; (c) C_{60}.

parent C_{60} at $\delta = 142.9$ ppm (3c) is not significantly shifted upon coordination to W [13]. The presence of only one carbon signal for C_{60} is consistent with the fluxional nature of organotransition-metal fullerene complexes [14].

Figure 4a shows the ν_{CO} spectrum of a mixture of the photoproduct and a 100-fold excess of PPh_3 after heating the mixture for 24 h under nitrogen. Two new bands appear at 2075 cm^{-1} and at 1941 cm^{-1} characteristic of the C—O stretching vibrational active modes (a_1, a_1, and e) of $(\eta^1-PPh_3)W(CO)_5$. The spectrum of an actual sample of $(\eta^1-PPh_3)W(CO)_5$ is shown in Figure 4b for comparison. The observation that the a_1 band of $(\eta^2-C_{60})W(CO)_5$ is 10 cm^{-1} (2085 cm^{-1} *vs.* 2075 cm^{-1}) higher in energy than the corresponding band for $(\eta^1-PPh_3)W(CO)_5$ suggests that C_{60} is a better π-acceptor than PPh_3 [15]. This observation is not surprising in view of the low-lying LUMOs of C_{60} with a tendency to accept electron density from W.

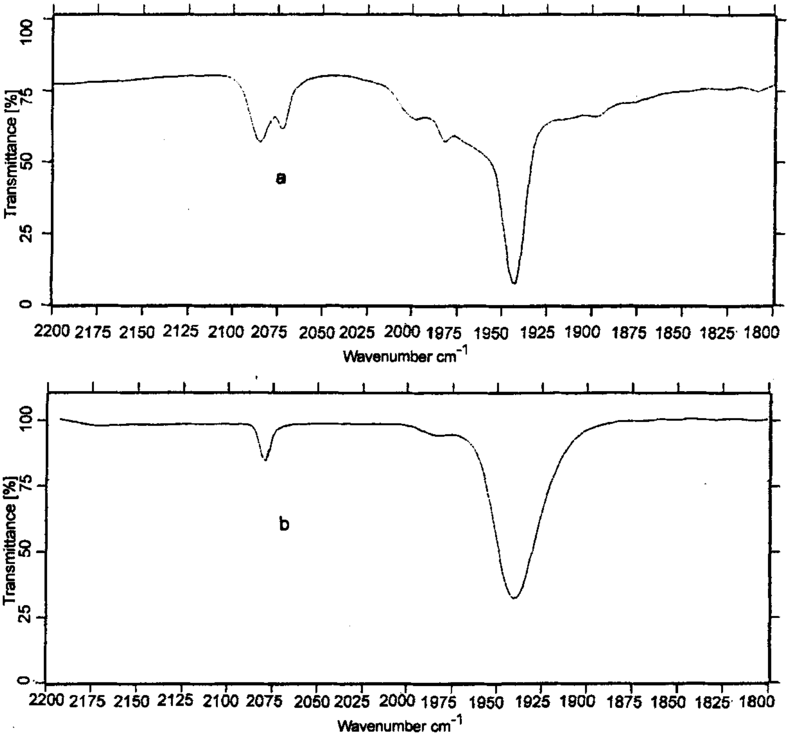

FIGURE 4 Infrared spectrum in the stretching carbonyl region of: (a) reaction mixture of $(\eta^2-C_{60})W(CO)_5$ and PPh_3 in n-hexane; (b) $(\eta^1-PPh_3)W(CO)_5$ in n-hexane.

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CONCLUSION

Photoreaction of $W(CO)_6$ with C_{60} in n-hexane produces the pentacarbonyl complex $(\eta^2-C_{60})W(CO)_5$. C_{60} is a good π-acceptor.

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