

## New Ruthenium Complexes of Fullerene C<sub>60</sub>&C<sub>70</sub>

Da Dian CHENG, Zhen Rong DONG, Zhen Yi WU, Yong Sheng LIN, Sen Gen YANG  
Meng Xiong ZHAN\*

Department of Chemistry, Xiamen University, Xiamen 361005

**Abstract:** The new complexes [Ru(NO)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^2$ -C<sub>m</sub>)(m=60 **1** or 70 **2**) have been prepared by heating a solution of C<sub>60</sub>(or C<sub>70</sub>) with [Ru(NO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in toluene. They have been characterized by elemental analysis, IR, UV/VIS, XPS, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy. The photovoltaic effect for the new compounds has been studied.

**Keywords:** Fullerene, ruthenium complex, photovoltaic effect.

Since subsequent development of the large-scale synthesis of fullerenes<sup>1</sup>, the fullerene coordination chemistry has played an important role.

In the previous studies<sup>2</sup>, a number of metallo-C<sub>60</sub> derivatives have been synthesized, but it was unsuccessful for A. N. Chernega et al. to attach some fragments to C<sub>60</sub>, after heating a solution containing equimolar amounts of either [RuH(Cl)(PPh<sub>3</sub>)<sub>3</sub>] or [RhCl(PPh<sub>3</sub>)<sub>3</sub>] and C<sub>60</sub> in toluene at 50°C for 1 week, they found no reaction occurred; they also found C<sub>60</sub> was unreactive towards [RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>] and [Ru(NO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], the electron richness of the fragments was considered as a reason of the lack of reactivity.

Recently we found that above mentioned fragments could react with fullerenes in reflux toluene. This paper describes the preparation and characterization of new ruthenium complexes of fullerene C<sub>60</sub>&C<sub>70</sub>, which were synthesized *via* the reactions of [Ru(NO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with the fullerene C<sub>60</sub>&C<sub>70</sub>.

### Experimental

All manipulations were performed under nitrogen atmosphere. The complex [Ru(NO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] was prepared according to the literature<sup>3</sup>.

Elemental analysis was recorded on a Carlo Erba-1110 elemental analyzer. Infrared spectra were recorded on a Nicolet AVATAR FT-IR360 spectrometer using KBr pellets. The UV/VIS electronic spectra were recorded on a UVIKON UV-240 spectrometer. X-ray photoelectron spectroscopy (XPS) were recorded on a VGESCAP MK II spectrometer, <sup>13</sup>C and <sup>31</sup>P NMR spectra were obtained on a Varian UNITY

---

\*E-mail: kanzhu@xmu.edu.cn

plus-500 spectrometer in solution.

*General procedure for synthesis* A solution of  $C_m$  ( $m=60$  or  $70$ ) in toluene (20 mL) was added to a solution of  $[Ru(NO)_2(PPh_3)_2]$  in toluene (5 mL). The mixture was refluxed with stirring for 18 h, then kept at  $\sim 90^\circ C$  and stirred for another 6 h. Volume of the reaction mixture was reduced to 5 mL by evaporation and the product precipitated by addition of *n*-hexane (50 mL). The solid was filtrated and washed with *n*-hexane ( $3 \times 10$  mL), dried *in vacuo*.

$[Ru(NO)(PPh_3)]_2(\eta^2-C_{60})$  **1**. Yield 32 mg, 67%. (Found: C, 76.89; H, 1.45; N, 1.86. Calcd. for  $[Ru(NO)(PPh_3)]_2(\eta^2-C_{60})$ : C, 76.49; H, 1.99; N, 1.86%); IR ( $cm^{-1}$ ): 1828s, 1721vs, 1690vs ( $\nu_{NO}$ ); 1182m, 574m, 522s [ $\nu(C_{60})$ ]. UV/VIS (toluene):  $\lambda_{max}/nm$  435, 599, 650. XPS (Ru):  $E_B/eV$  280.6.  $^{31}P$  NMR (solvent  $CDCl_3$ ,  $\delta ppm$ ): 29.8 (s  $PPh_3$ ).  $^{13}C$  NMR (solvent  $CDCl_3+CS_2$ ,  $\delta ppm$ ): 146.2, 144.7, 144.4, 143.9, 142.9, 142.3(s,  $C_{60}$ ), 133.5(d,  $PPh_3$ ), 131.9, 131.6, 131.0, 128.9, 128.8(s,  $PPh_3$ ), 128.2(d,  $PPh_3$ ).

$[Ru(NO)(PPh_3)]_2(\eta^2-C_{70})$  **2**. Yield 31 mg, 56%. (Found: C, 78.58; H, 1.37; N, 1.69. Calcd. for  $[Ru(NO)(PPh_3)]_2(\eta^2-C_{70})$ : C, 78.24; H, 1.85; N, 1.72%); IR ( $cm^{-1}$ ): 1831m, 1723vs, 1691vs ( $\nu_{NO}$ ); 1430s, 794m, 641m, 575m, 536s [ $\nu(C_{70})$ ]; 419w [ $\nu(Ru-(\eta^2-C=C))$ ]. XPS (Ru):  $E_B/eV$  281.0.  $^{13}C$  NMR (solvent  $CS_2+CDCl_3$ ,  $\delta ppm$ ): 150.2, 147.7, 147.0, 145.0, 130.5( $C_{70}$ ); 131.9, 131.8, 131.6, 128.8, 128.2, 128.1, 128.0, 125.1 ( $PPh_3$ ); 115.0( $sp^3C$ ,  $C_{70}$ ).

## Results and Discussion

The synthesis reaction can be expressed as follows:



The IR spectrum of the compound **1** showed the bands of  $C_{60}$  at 522, 574 and 1182  $cm^{-1}$ , the spectrum of the compound **2** showed the bands of  $C_{70}$  at 536, 575, 641, 794 and 1430  $cm^{-1}$ .  $\nu(NO)$  at 1690, 1721  $cm^{-1}$  and 1691, 1723  $cm^{-1}$  respectively, typical absorption for the linear MNO system. These values of  $\nu(NO)$  were higher than that of  $[Ru(NO)_2(PPh_3)_2]$  (1656 and 1614  $cm^{-1}$ ). It suggested that owing to the hyperconjugation of  $C_m$ -Ru-NO-P-Ph, the electronic consistency on the N=O bond increased, the values of  $\nu(NO)$  turned higher, the electrons moved easily. There is a new band at around 1830  $cm^{-1}$  in both IR spectra of the two compounds. The UV/VIS spectrum of compound **1** showed a band at 435 nm and two weak and broad bands at 599 and 650 nm exhibiting considerably less fine structure than for uncoordinated  $C_{60}$ . These data were typical for fullerene cage which has been modified by complexation<sup>4,5</sup>. The XPS spectra of **1** and **2** showed the peak at 280.6 eV and 281.0 eV, respectively. It is higher than that of  $[Ru(NO)_2(PPh_3)_2]$  (280.2 eV). The result suggested that the d electrons of Ru flowed to fullerenes to form  $\pi$  bonds, as a result, the valence of Ru increased. The  $^{31}P$  NMR spectrum of **1** contained a singlet resonance at  $\delta$  29.8, for comparison, the  $^{31}P$  NMR spectrum of  $[Ru(NO)_2(PPh_3)_2]$  showed a singlet at  $\delta$  54.8. It suggested that the electronic consistency around the P nuclear increased as a result of the hyperconjugation of the new compound. The  $^{13}C$  NMR of compound **1** showed a further 6 peaks

assignable to the C<sub>60</sub> moiety. No more resonance of C<sub>60</sub> was detected because of the low solubility of the compound. The <sup>13</sup>C NMR of compound **2** showed a 6 resonances due to C<sub>70</sub>, the resonance at  $\delta$  115.0 is lower than normal sp<sup>3</sup> C, it suggested that the electrons of the sp<sup>3</sup> C flowed to the metal Ru because of forming  $\sigma$  bond.

The characterization data showed that electrons would transfer easier in the new molecule than in the reagents because of the hyperconjugation effect, so the good photovoltaic effect was expected.

The opening circuit voltage was recorded on a Pz-8 direct current voltage meter. A FL-35 Xenon lamp was used to illuminate the samples. The photovoltaic effect (PVE) of the new complexes was observed in a conventional three-electrode cell. A complex film-GaAs disk was used as the working electrode; a Pt disk (1 cm<sup>2</sup>) was used as the subsidiary electrode and a saturated calomel electrode as the reference electrode.

The complex was deposited on the working electrode with the solvent method. The illumination intensity was 0.050 w/cm<sup>2</sup>. Under the dark and illuminated states, the PVE was measured, the photogenerated voltage ( $\Delta V$ ) was obtained and listed in the **Table 1**.

As expected, PVE of the complexes plated GaAs electrode was increased. The effect became best when the thickness of the complex film was around 1  $\mu$ m, then it decreased with increasing the thickness of the film. The reason was that the electric resistance was increasing with the increasing of the thickness of the film. The solution of I<sub>2</sub>/I<sub>3</sub><sup>-</sup> was the best medium for the test of photovoltaic effect. And the  $\Delta V$  for the complex of C<sub>70</sub> was higher than that of C<sub>60</sub>, because there were more hexahedron webs and more photo quantum effect for C<sub>70</sub> than for C<sub>60</sub>.

**Table 1**  $\Delta V$  of the new compounds

$\Delta V$ (mV)	medium	thickness of the complex film ( $\mu$ m)					
		0	0.5	1.0	2.0	3.0	4.0
O <sub>2</sub> /H <sub>2</sub> O (0.1 mol/L KCl)		310	354 <sup>a</sup>	358 <sup>a</sup>	341 <sup>a</sup>	302 <sup>a</sup>	283 <sup>a</sup>
			385 <sup>b</sup>	430 <sup>b</sup>	392 <sup>b</sup>	354 <sup>b</sup>	303 <sup>b</sup>
	BQ/H <sub>2</sub> Q (0.01 mol/L)	265	280 <sup>a</sup>	285 <sup>a</sup>	306 <sup>a</sup>	293 <sup>a</sup>	257 <sup>a</sup>
Fe(CN) <sub>6</sub> <sup>3-/4-</sup> (0.1 mol/L)		347	402 <sup>a</sup>	408 <sup>a</sup>	413 <sup>a</sup>	397 <sup>a</sup>	366 <sup>a</sup>
			417 <sup>b</sup>	395 <sup>b</sup>	392 <sup>b</sup>	381 <sup>b</sup>	357 <sup>b</sup>
I <sub>2</sub> (0.001mol/L)/I <sub>3</sub> <sup>-</sup> (0.1mol/L)		268	358 <sup>a</sup>	387 <sup>a</sup>	322 <sup>a</sup>	293 <sup>a</sup>	262 <sup>a</sup>
			385 <sup>b</sup>	401 <sup>b</sup>	414 <sup>b</sup>	387 <sup>b</sup>	312 <sup>b</sup>

<sup>a</sup>  $\Delta V$  of C<sub>60</sub>[Ru(NO)(PPh<sub>3</sub>)<sub>2</sub>]. <sup>b</sup>  $\Delta V$  of C<sub>70</sub>[Ru(NO)(PPh<sub>3</sub>)<sub>2</sub>].

### Acknowledgments

We wish to express our gratitude for the financial support of this work by the Doctor program of Higher Education of China (No. 98038410), Natural Science Foundation of Fujian (No. E0110001) and Self-select program of Xiamen University.

**References**

1. (a) H. W. Kroto, J. R. Heath, S. C. O' Brein, R. F. Curl, R. E. Smalley, *Nature*, **1985**, 318, 162.  
(b) W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature*, **1990**, 347, 354.  
(c) W. Krätschmer, K. Fostiropoulos, D. R. Huffman, *Chem. Phys. Lett.*, **1990**, 170, 167.
2. (a) K. Tang, S. Zheng, X. Jin, H. Zeng, Z. Gu, X. Zhou, Y. Tang, *J. Chem. Soc. Dalton Trans.*, **1997**, 3585. (b) A. N. Chernega, M. L. H. Green, J. Haggitt, A. H. H. Stephens, *J. Chem. Soc. Dalton Trans.*, **1998**, 755.
3. Parshall G.W., Translated by W Ma, P. S. Pan, Z. K. Xiong *et al*, *Inorganic Synthesis*, Beijing: Science Press, **1986**, 52.
4. J. P. Hare, H. W. Kroto, R. Taylor, *Chem. Phys. Lett.*, **1991**, 177, 394.
5. T. Akasaka, W. Ando, K. Kobayashi, S. Nagase, *J. Am. Chem. Soc.*, **1993**, 115, 1605.

Received 12 March, 2002