

## Preliminary Communication

### The first ruthenium carbonyl derivative of fullerene: $(\eta^2\text{-C}_{60})\text{Ru}(\text{CO})_4$

Merja Rasinkangas, Tuula T. Pakkanen  
and Tapani A. Pakkanen

Department of Chemistry, University of Joensuu, PO Box 111,  
FIN-80101 Joensuu (Finland)

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#### Abstract

Buckminsterfullerene,  $\text{C}_{60}$ , reacts with  $\text{Ru}(\text{CO})_5$  to give a 1:1 adduct  $(\eta^2\text{-C}_{60})\text{Ru}(\text{CO})_4$ . The synthesis and spectroscopic (IR and  $^{13}\text{C}$  NMR) characterization of this compound are described.

**Key words:** Fullerene; Ruthenium; Carbonyl

Although fullerenes have been intensively studied, few organometallic fullerene derivatives have been described. Structurally characterized organometallic fullerene compounds include both monoadducts, for example  $(\eta^2\text{-C}_{60})\text{Pt}(\text{PPh}_3)_2$  [1],  $(\eta^2\text{-C}_{60})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  [2], and  $(\eta^2\text{-C}_{60})\text{RhH}(\text{CO})(\text{PPh}_3)_2$  [3], and multiple adducts, for example  $(\eta^2\text{-C}_{60})\{\text{Pt}(\text{PEt}_3)_2\}_6$  [4], and  $\text{C}_{60}\{\text{Ir}_2\text{Cl}_2(1,5\text{-COD})_2\}_2$  [5]. Two examples of transition metal carbonyl derivatives of fullerenes have been reported,  $\text{C}_{60}\{\text{Re}(\text{CO})_5\}_2$  [6] and  $(\eta^2\text{-C}_{60})\text{Fe}(\text{CO})_4$  [7].

It has been shown previously that  $\text{Ru}_3(\text{CO})_{12}$  reacts with an electron-poor alkene ethene ( $\text{C}_2\text{H}_4$ ) when irradiated with Pyrex-filtered sun-light or light from fluorescent tubes under a  $\text{C}_2\text{H}_4$  atmosphere [8]. Since Buckminsterfullerene is known to react like an electron-poor alkene or arene, a similar reaction between  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{C}_{60}$  was to be expected. In this communication we describe the synthesis, spectroscopic characterization and some preliminary reactivity studies of the compound  $(\eta^2\text{-C}_{60})\text{Ru}(\text{CO})_4$ .

The  $\text{Ru}(\text{CO})_5$  complex used as a starting material was prepared as described previously [9];  $\text{Ru}_3(\text{CO})_{12}$  in cyclohexane was irradiated with a 450 W Xe lamp under CO, and the formation of  $\text{Ru}(\text{CO})_5$  was con-

firmed by IR spectroscopy (CO bands at 2040 and 2002  $\text{cm}^{-1}$ ).

The  $\text{Ru}(\text{CO})_5$  solution was added in a mole ratio 1:1 to a toluene solution of  $\text{C}_{60}$  under nitrogen. The solution was stirred at room temperature overnight, during which time it turned dark red. The formation of the fullerene derivative was confirmed by IR spectroscopy. The solvents were removed in vacuum and the reddish brown powder was redissolved in  $\text{CH}_2\text{Cl}_2$ . Figures 1(a) and 1(b) show the FTIR spectra of

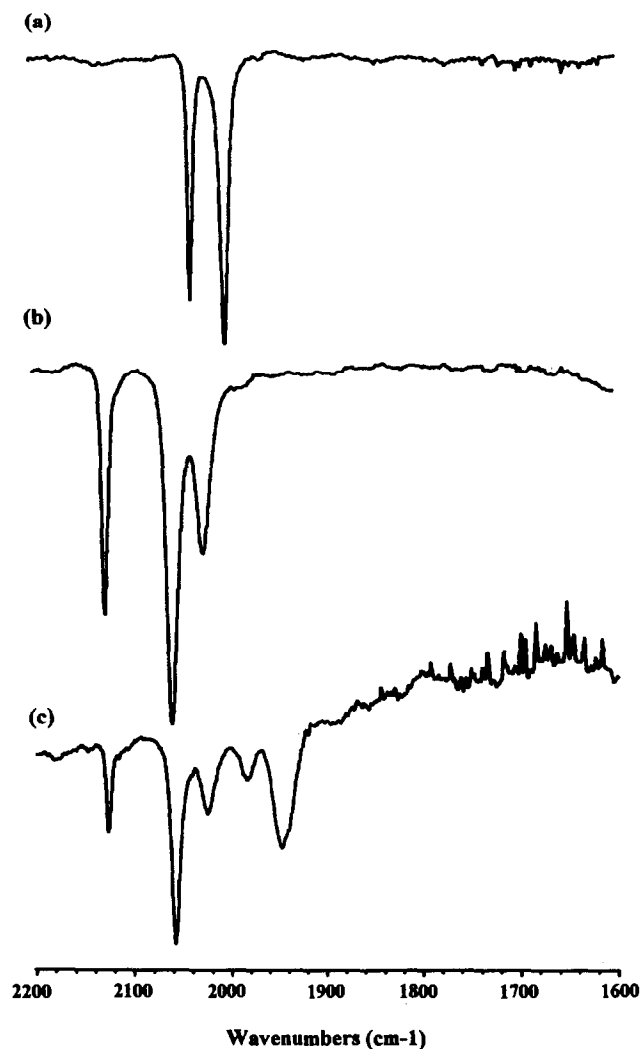


Fig. 1. FTIR spectra of (a)  $\text{Ru}(\text{CO})_5$ , (b)  $\text{C}_{60}\text{Ru}(\text{CO})_4$ , and (c) mixture of  $\text{Ru}(\text{CO})_4(\text{PPh}_3)_3$  and  $\text{C}_{60}\text{Ru}(\text{CO})_4$ .

Correspondence to: Professor T. Pakkanen.

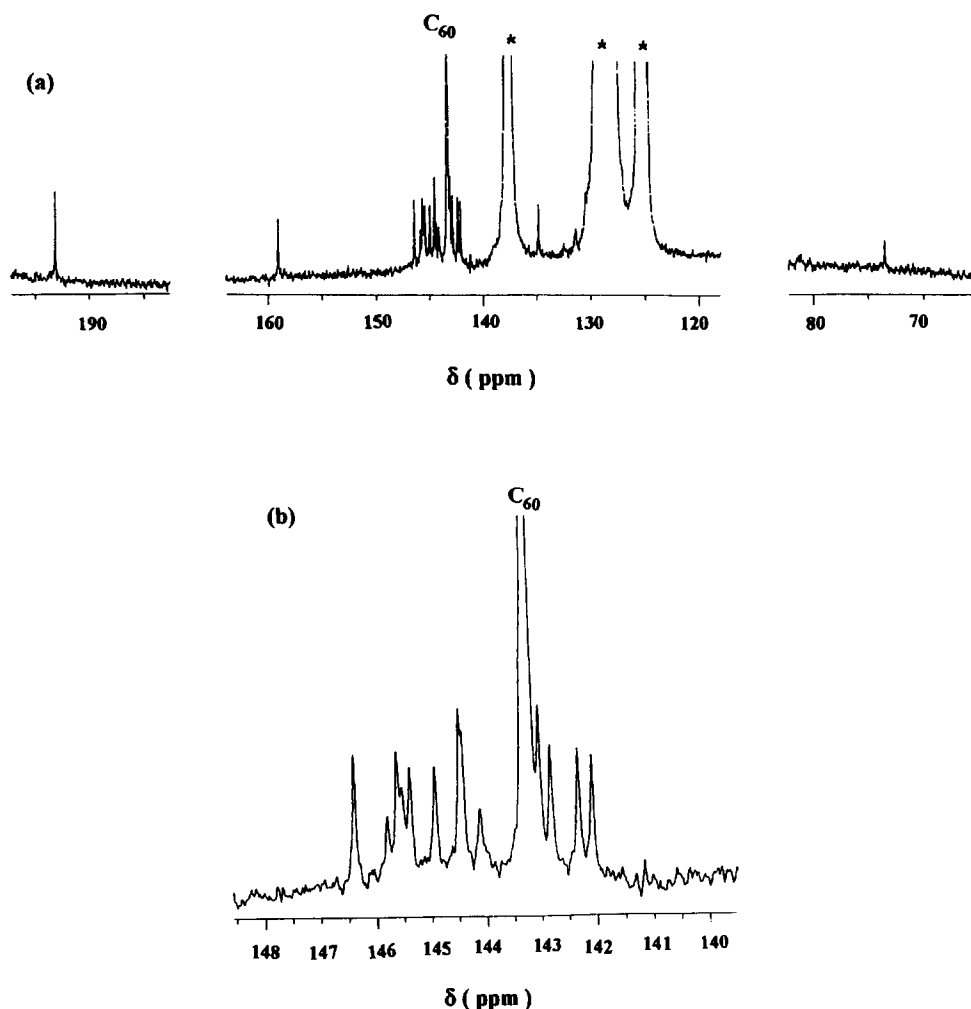


Fig. 2. (a) Quantitative 100.62 MHz <sup>13</sup>C NMR spectrum of C<sub>60</sub>Ru(CO)<sub>4</sub> in toluene-d<sub>8</sub> (\* peaks due to solvent); (b) expansion in the region 149–140 ppm.

Ru(CO)<sub>5</sub> and ( $\eta^2$ -C<sub>60</sub>)Ru(CO)<sub>4</sub> [10 \*]. The corresponding ethene compound Ru(CO)<sub>4</sub>C<sub>2</sub>H<sub>4</sub> has CO bands at 2104, 2021 and 1995 cm<sup>-1</sup> [8].

The moderately air-sensitive product is soluble in common organic solvents, for example, hexane, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and toluene. In the <sup>13</sup>C NMR spectrum [11 \*] of the reddish residue in toluene-d<sub>8</sub> (Fig. 2), 17 resonances can be assigned to the fullerene core, which confirms the proposed C<sub>2v</sub> symmetry for the molecule. One of the 17 resonances has a chemical shift close to that of free C<sub>60</sub>. A carbonyl signal at 193.1 ppm can be assigned to ( $\eta^2$ -C<sub>60</sub>)Ru(CO)<sub>4</sub>. The metal is bound to the fullerene core in  $\eta^2$ -fashion. The signal due to the carbon atoms binding to the metal is

at 73.5 ppm.

The formation of ( $\eta^2$ -C<sub>60</sub>)Ru(CO)<sub>4</sub> is reversible. Addition of PPh<sub>3</sub> to a dichloromethane solution of the fullerene compound produces Ru(CO)<sub>4</sub>(PPh<sub>3</sub>) in the course of a few hours (IR spectrum, CO bands at 2061, 1986, and 1950 cm<sup>-1</sup>, Fig. 1(c)). Furthermore, when the complex is dissolved in cyclohexane and CO is bubbled through for several hours, the IR spectrum shows the formation of Ru(CO)<sub>5</sub>.

The structure of the compound ( $\eta^2$ -C<sub>60</sub>)Ru(CO)<sub>4</sub> is similar to that of ( $\eta^2$ -C<sub>60</sub>)Fe(CO)<sub>4</sub> [7]. They have very similar IR and <sup>13</sup>C NMR spectra. For ( $\eta^2$ -C<sub>60</sub>)Fe(CO)<sub>4</sub> the CO bands appear at 2096, 2033, 2005 and 1974 cm<sup>-1</sup> [7].

The binding of ruthenium to fullerene in ( $\eta^2$ -C<sub>60</sub>)Ru(CO)<sub>4</sub> seems to be stronger than that to iron. In the IR spectrum the CO bands appear at higher wavenumbers and in the <sup>13</sup>C NMR spectrum, the carbon atoms bound to the metal have lower chemical shifts in the

\* Reference number with asterisk indicates a note in the list of references.

ruthenium compound than in the iron compound. On the basis of these observations ( $\eta^2$ -C<sub>60</sub>)Ru(CO)<sub>4</sub> seems to be more stable than ( $\eta^2$ -C<sub>60</sub>)Fe(CO)<sub>4</sub>.

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- 10 ( $\eta^2$ -C<sub>60</sub>)Ru(CO)<sub>4</sub>: IR  $\nu$ (CO) 2128, 2060, 2026 (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>;  $\nu$ (CO) 2123, 2053, 2021,  $\nu$ (C<sub>60</sub>) 1425, 1187, 585, 529 (KBr) cm<sup>-1</sup>.
- 11 ( $\eta^2$ -C<sub>60</sub>)Ru(CO)<sub>4</sub>: <sup>13</sup>C NMR  $\delta$ (CO) 193.1  $\delta$ (C<sub>60</sub>) 159.0, 146.4, 145.8, 145.60, 145.57, 145.4, 144.9, 144.5, 144.4, 144.1, 143.8, 143.0, 142.8, 142.3, 142.0, 134.9, 73.5 (toluene-d<sub>8</sub>) ppm.