

## 152. Preparation of Ru(CO)(diene)<sub>2</sub> Complexes by Electron-Beam Evaporation of Ruthenium

Preliminary Communication

by David N. Cox and Raymond Roulet\*

Institut de chimie minérale et analytique de l'Université de Lausanne,  
3, place du Château, CH-1005 Lausanne

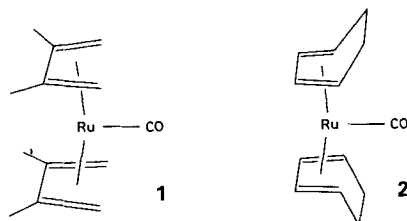
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### Summary

Ru-atoms (0.5–1.5 g) have been generated by electron bombardment and, in separate experiments, were co-condensed at 77 K with excess of 2,3-dimethylbutadiene or 1,3- or 1,4-cyclohexadiene. The complexes Ru(CO)( $\eta^4$ -C<sub>6</sub>H<sub>10</sub>)<sub>2</sub> (**1**) and Ru(CO)( $\eta^4$ -C<sub>6</sub>H<sub>8</sub>)<sub>2</sub> (**2**), respectively, have been isolated in 25–30% yields on warming the condensate under CO.

**Introduction.** – The rational development of the organometallic chemistry of ruthenium has, in part, been retarded by the limitations of the available starting materials (RuCl<sub>3</sub> and Ru<sub>3</sub>(CO)<sub>12</sub>). Hence, although complexes of the type Fe(CO)(diene)<sub>2</sub> have been prepared by a variety of routes [1], little progress has been made in synthesizing analogous Ru-complexes. The first example of a Ru(CO)(diene)<sub>2</sub>-species was, however, very recently isolated from the thermal reaction of Ru<sub>3</sub>(CO)<sub>12</sub> and a novel tetraene, and has been structurally characterized as Ru(CO)[( $\mu$ -CH<sub>2</sub>)<sub>3</sub>( $\eta^4$ -C<sub>5</sub>H<sub>7</sub>)<sub>2</sub>] [2].

It was hoped that the use of Ru-atoms might provide a convenient synthesis of other complexes of this family. Indeed, *Minniti & Timms* [3] reported that Ru(CO)( $\eta^4$ -C<sub>4</sub>H<sub>6</sub>)<sub>2</sub> is produced on condensation of Ru-atoms with excess 1,3-butadiene at 77 K, followed by warming to r.t. under CO. In their experiments, Ru-atoms (from resistively heated filaments) could only be generated on a small scale (50–100 mg), and consequently product isolation and characterization proved problematic.



In this communication, we report the isolation of the new complexes  $\text{Ru}(\text{CO})(\eta^4\text{-C}_6\text{H}_{10})_2$  (**1**) and  $\text{Ru}(\text{CO})(\eta^4\text{-C}_6\text{H}_8)_2$  (**2**) prepared in synthetically viable quantities by electron-beam evaporation of Ru.

**Results.** – Following the method of *Cloke* and *Green* [4] [5], we have evaporated Ru-atoms on a 0.5–1.5 g scale using a positive hearth electron-beam furnace. A commercially available vapour-synthesis plant (*G. V. Planar Ltd.*, Sunbury-on-Thames, England (Series *VSP/500*)) was used for the experiments, and the design is similar to that previously described by *Cloke* and *Green* (see for example *Fig. 3–5* in [5]).

The evaporation apparatus includes: *i*) 20-l capacity stainless steel reaction vessel equipped with a glass viewing port, external cooling jacket, solvent entry and a product collection gutter and outlet; *ii*) 160-mm diameter oil diffusion pump (speed  $700 \text{ l s}^{-1}$ ) backed by a two-stage rotary pump and protected from the reaction vessel by a cold trap; *iii*) an electrostatically focussed, water-cooled, positive hearth electron-beam furnace of capacity  $1.0 \text{ cm}^3$  (*Planar Type B*); *iv*) separate vacuum gauges for the rotary backing pressure and the pressure inside the reactor; *v*) a 220-mm diameter heated ligand vapour-inlet ring.

An ampoule containing the degassed ligand (50 ml) stirred at boiling point served as a ligand reservoir, and a *Teflon* needle valve (*Young NV2*) was sufficient to maintain a steady vapour pressure of  $1.5\text{--}2.0 \cdot 10^{-5}$  mbar in the reactor. A satisfactory ligand bleed of  $10\text{--}15 \text{ ml h}^{-1}$  was thereby achieved without adverse effect on the electron-beam furnace. Suitable ingots (*ca.* 8 g) were first obtained from arc fusion of pressed pellets of Ru-powder. A subsequent brief melting in the electron-beam furnace ensured complete ‘outgassing’ of the ingots, and it was possible to evaporate Ru-atoms at a rate of  $0.3\text{--}0.5 \text{ g h}^{-1}$  for a power input of  $1.4\text{--}1.6 \text{ kW}$  at 5 kV.

In a typical experiment, 0.7 g of Ru-atoms (7 mmol) were co-condensed over 2 h with 30 ml of ligand (*ca.* 300 mmol) at 77 K. Entry of CO was commenced at this temperature and the condensate allowed to warm to r.t. under one atm. of CO. In each case, the orange-brown condensate was extracted from the reactor with dry THF ( $3 \times 100 \text{ ml}$ ) under Ar and immediately filtered through dry *Florisil*. Solvent removal gave an intensely coloured oil which was reextracted with pentane (200 ml), and stirred over *ca.* 2 g of activated charcoal (to remove polymeric products) and then filtered. Concentration of the yellow-orange filtrate and cooling to  $-78^\circ\text{C}$  resulted in pale orange microcrystalline plates of  $\text{Ru}(\text{CO})(\text{diene})_2$ : 500 mg of **1** (25%) or 600 mg of **2** (30%) for 2,3-dimethyl-1,3-butadiene or 1,3- or 1,4-cyclohexadiene, respectively. These complexes are moderately air-stable and have been characterized by mass, IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopies and by satisfactory elemental analyses. [*Carbonylbis*( $\eta$ -(*s-cis*-2,3-dimethyl-1,3-butadiene))ruthenium (**1**): m.p.  $65^\circ$  (dec). IR (pentane): 1993 (CO).  $^1\text{H}$ -NMR (360 MHz,  $\text{CDCl}_3$ ): 1.82 (*d*,  $^2J(\text{H,H}) = 1.3 \text{ 4H}$ ); 1.71 (*s*, 12H); 0.23 (*d*, 4H). MS (70 eV,  $^{102}\text{Ru}$ ): 294 (23,  $M^+$ ), 266 (84,  $M^+ - \text{CO}$ ), 260 (100), 182 (68), 102 (22). Anal. calc. for  $\text{C}_{13}\text{H}_{20}\text{ORu}$  (293.37): C 53.22, H 6.87; found: C 53.37, H 6.79. *Carbonylbis*( $\eta$ -(1,3-cyclohexadiene))ruthenium (**2**): m.p.  $99^\circ$  (dec). IR: 1981 (CO).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 4.65 (*m*, 4H); 3.41 (*m*, 4H), 1.85 (*dm*, 4H); 1.54 (*d*,  $J_{\text{gem}} = 10$ , 4H). MS: 290 (24,  $M^+$ ), 262 (48), 260 (100), 182 (56), 180 (82), 102 (15), 78 (79). Anal. calc. for  $\text{C}_{13}\text{H}_{16}\text{ORu}$  (289.34): C 53.96, H 5.57; found: C 54.08, H. 5.54].

1,3- and 1,4-cyclohexadiene react in a similar manner, but in neither case do we believe that **2** is the primary product. Rather, the species  $\text{Ru}(\text{CO})(\eta^5\text{-C}_6\text{H}_7)(\eta^3\text{-C}_6\text{H}_9)$  (stable at  $-20^\circ\text{C}$ ) is initially formed but rearranges to **2** at r.t. Detailed evidence in

support of this will be given in a subsequent publication where some interesting features of the chemistry of **1** and **2** will also be discussed.

Similar reactions with benzene and 1,5-cyclooctadiene have not as yet led to the isolation of new carbonyl complexes. In the former reaction no stable carbonyl complex has been detected, whereas in the latter a complex mixture of carbonyls was generated.

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