

**Preliminary communication**

**Activation of arene and alkyne C–H bonds by ruthenium.  
 The synthesis and crystal structure  
 of  $[\text{Ru}(\text{CO})\{\text{C}_6\text{H}_3\text{MeC}(\text{O})\text{C}_6\text{H}_4\text{Me}\}(\text{C}\equiv\text{CPh})(\text{PMe}_2\text{Ph})_2]$**

**Madeleine Helliwell, K. Michelle Stell and Roger J. Mawby \***

*Department of Chemistry, University of York, York YO1 5DD (Great Britain)*

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**Abstract**

An X-ray diffraction study of the product of reaction of  $[\text{Ru}(\text{CO})_2(\text{C}_6\text{H}_4\text{Me}-4)_2(\text{PMe}_2\text{Ph})_2]$  with  $\text{PhC}\equiv\text{CH}$  has shown it to be  $[\text{Ru}(\text{CO})\{\text{C}_6\text{H}_3\text{MeC}(\text{O})\text{C}_6\text{H}_4\text{Me}\}(\text{C}\equiv\text{CPh})(\text{PMe}_2\text{Ph})_2]$ . A possible mechanism for the reaction involves intramolecular ketone formation, activation of C–H bonds in both ketone and alkyne, and elimination of  $\text{H}_2$ .

Complexes  $[\text{Ru}(\text{CO})_2\text{Me}(\text{R})(\text{PMe}_2\text{Ph})_2]$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ) decompose in  $\text{CHCl}_3$  solution to give ketones  $\text{MeCOR}$  in high yield [1]. In contrast, diaryl complexes  $[\text{Ru}(\text{CO})_2(\text{C}_6\text{H}_4\text{X}-4)_2(\text{PMe}_2\text{Ph})_2]$  ( $\text{X} = \text{Me}$  or  $\text{Cl}$ ) react with  $\text{CHCl}_3$  to yield products  $[\text{Ru}(\text{CO})\{\text{C}_6\text{H}_3\text{XC}(\text{O})\text{C}_6\text{H}_4\text{X}\}\text{Cl}(\text{PMe}_2\text{Ph})_2]$  in which the ketone is retained within the coordination sphere and undergoes activation of a C–H bond. We have suggested that an intermediate ketone complex  $[\text{Ru}(\text{CO})\{\text{OC}(\text{C}_6\text{H}_4\text{X}-4)_2\}(\text{PMe}_2\text{Ph})_2]$  undergoes reversible C–H activation to yield a hydride complex  $[\text{Ru}(\text{CO})\{\text{C}_6\text{H}_3\text{XC}(\text{O})\text{C}_6\text{H}_4\text{X}\}\text{H}(\text{PMe}_2\text{Ph})_2]$ , and that this then reacts with the  $\text{CHCl}_3$  to give  $[\text{Ru}(\text{CO})\{\text{C}_6\text{H}_3\text{XC}(\text{O})\text{C}_6\text{H}_4\text{X}\}\text{Cl}(\text{PMe}_2\text{Ph})_2]$ . In a solvent which does not contain halogen, however, the ketone  $(4\text{-XC}_6\text{H}_4)_2\text{CO}$  is released [2]. We have been unable to isolate or identify the ruthenium species which is the co-product of ketone formation.

In an attempt to trap the ruthenium as a stable ruthenium(0) alkyne complex we carried out the decomposition of  $[\text{Ru}(\text{CO})_2(\text{C}_6\text{H}_4\text{Me}-4)_2(\text{PMe}_2\text{Ph})_2]$  in refluxing propanone in the presence of  $\text{PhC}\equiv\text{CH}$ . From NMR studies, the reaction appeared to yield a single ruthenium-containing product, **1**, in essentially quantitative yield. After removal of the solvent under reduced pressure, the residue was washed with a

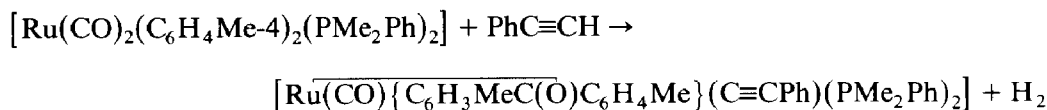
Table 1

Selected bond lengths (Å) and angles (°) for compound **1**

|                  |          |                     |           |
|------------------|----------|---------------------|-----------|
| Ru–P(1)          | 2.332(2) | C(151)–C(152)       | 1.413(6)  |
| Ru–P(2)          | 2.347(2) | O(14)–C(14)         | 1.236(5)  |
| Ru–C(152)        | 2.071(5) | C(14)–C(151)        | 1.443(10) |
| Ru–O(14)         | 2.142(3) | O(162)–C(161)       | 1.166(7)  |
| Ru–C(161)        | 1.812(5) | C(17)–C(18)         | 1.192(7)  |
| Ru–C(17)         | 2.120(5) | C(18)–C(181)        | 1.432(7)  |
| P(2)–Ru–P(1)     | 178.1(1) | C(17)–Ru–C(152)     | 168.4(2)  |
| C(152)–Ru–P(1)   | 92.4(1)  | C(17)–Ru–O(14)      | 91.9(2)   |
| C(152)–Ru–P(2)   | 89.5(1)  | C(17)–Ru–C(161)     | 94.5(2)   |
| O(14)–Ru–P(1)    | 89.2(1)  | O(14)–Ru–C(161)     | 173.5(3)  |
| O(14)–Ru–P(2)    | 91.3(1)  | C(151)–C(152)–Ru    | 114.2(3)  |
| O(14)–Ru–C(152)  | 76.8(2)  | C(14)–C(151)–C(152) | 113.8(4)  |
| C(161)–Ru–P(1)   | 89.4(2)  | O(14)–C(14)–C(151)  | 118.8(4)  |
| C(161)–Ru–P(2)   | 90.3(2)  | C(14)–O(14)–Ru      | 116.0(3)  |
| C(161)–Ru–C(152) | 96.9(2)  | O(162)–C(161)–Ru    | 178.2(5)  |
| C(17)–Ru–P(1)    | 90.3(2)  | C(18)–C(17)–Ru      | 176.2(5)  |
| C(17)–Ru–P(2)    | 87.9(2)  | C(181)–C(18)–C(17)  | 178.9(6)  |

little propanone. Crystals of **1** suitable for X-ray work were obtained by recrystallization from a mixture of ethanol, propanone, and light petroleum (b.p. 40–60 °C) \*.

The structure of **1** consists of discrete molecules, the shortest intermolecular contact being 3.181 Å. Important bond lengths and angles are listed in Table 1. As shown in Fig. 1, **1** is an alkynyl complex of ruthenium(II) rather than the expected alkyne complex of ruthenium(0). As in the case of the decomposition of  $[\text{Ru}(\text{CO})_2(\text{C}_6\text{H}_4\text{Me-4})_2(\text{PMe}_2\text{Ph})_2]$  in  $\text{CHCl}_3$ , the ketone has been retained in the complex, but here both ketone and alkyne have undergone C–H activation:



The ligand arrangement in **1** is similar to that in  $[\text{Ru}(\overline{\text{CO}})\{\text{C}_6\text{H}_3\text{MeC}(\text{O})\text{C}_6\text{H}_4\text{Me}\}\text{Cl}(\text{PMe}_2\text{Ph})_2]$  [2], with the largest deviation from regular octahedral geometry being the angle O(14)–Ru–C(152) (76.8(2)°). The Ru–C≡C–C group is almost linear, with angles of 176.2(5) and 178.9(6)° at the C≡C carbon atoms.

\* *Crystal data:*  $\text{C}_{40}\text{H}_{40}\text{O}_2\text{P}_2\text{Ru}$ ,  $M = 715.7$ , triclinic, space group  $P\bar{1}$ ,  $a$  14.519,  $b$  13.389,  $c$  9.570 Å,  $\alpha$  98.718,  $\beta$  104.890,  $\gamma$  82.398°,  $U$  1768.61 Å<sup>3</sup>,  $Z = 2$ ,  $D_c$  1.34 g cm<sup>-3</sup>,  $F(000) = 740$ ,  $\mu$  (Mo- $K_\alpha$ ) 4.95 cm<sup>-1</sup>, crystal size ca. 1.0 × 0.4 × 0.2 mm. Data were collected on a Hilger and Watts four-circle diffractometer, using filtered Mo- $K_\alpha$  radiation. Absorption corrections were applied using the empirical method of North, Phillips and Mathews [3], and corrections for Lorentz and polarization factors were also applied. The structure was solved by MULTAN86 [4] and refined by SHELX76 [5] using 5544 independent reflections ( $I > 2\sigma(I)$ ). Measurement of four standard reflections every 200 reflections provided no evidence of decay.

The final version of the structure was obtained using conventional least squares refinement in SHELX76 [5], with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement with constraints on bond lengths, angles and thermal parameters. The final  $R$  and  $R_w$  were 0.0569 and 0.0604 respectively;  $w = 2.2250/[\sigma^2(F_o) + 0.001616|F_o|^2]$ .

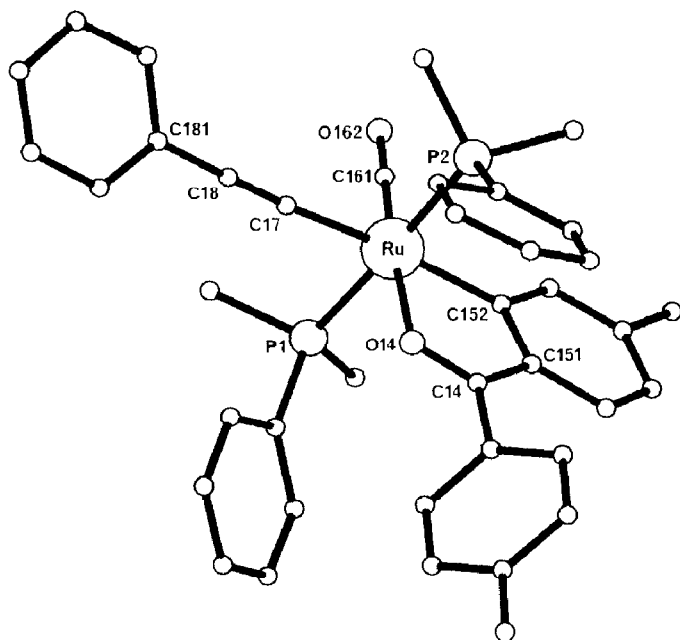


Fig. 1. The crystal structure of complex **1**.

The route to **1** may involve a reaction between the postulated hydride complex  $[\text{Ru}(\text{CO})\{\text{C}_6\text{H}_3\text{MeC}(\text{O})\text{C}_6\text{H}_4\text{Me}\}\text{H}(\text{PMe}_2\text{Ph})_2]$  (see above) [2] and  $\text{PhC}\equiv\text{CH}$ . If this occurs by successive oxidative addition of alkyne and elimination of  $\text{H}_2$ , the ruthenium(IV) intermediate would be expected to be seven- rather than eight-coordinate, and it is possible that the Ru–O bond to the ketone oxygen breaks and then reforms after elimination of  $\text{H}_2$  from the intermediate  $[\text{Ru}(\text{CO})\{\text{C}_6\text{H}_3\text{MeC}(\text{O})\text{C}_6\text{H}_4\text{Me}\}(\text{C}\equiv\text{CPh})\text{H}_2(\text{PMe}_2\text{Ph})_2]$ .

A complete list of bond lengths and angles and a table of atom coordinates are available from the Cambridge Crystallographic Data Centre.

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