

### Preliminary communication

## PREPARATION OF $(\text{PMe}_3)_3\text{HRu}(\mu\text{-CH}_2\text{PMe}_2)_2\text{RuH}(\text{PMe}_3)_3$ AND $\text{Ru}(\eta^1\text{-}\overline{\text{C}}=\text{CH}(\text{CH}_2)_3)(\text{PMe}_3)_4\text{H}$

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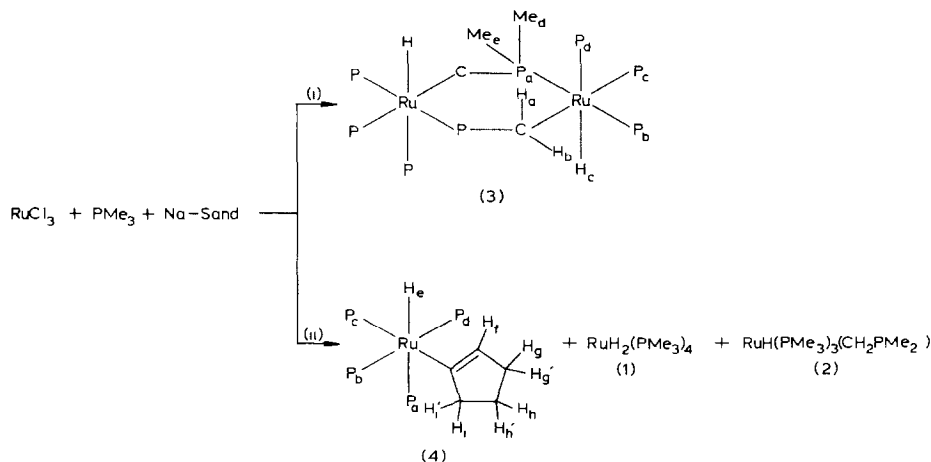
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### Summary

Reduction of anhydrous ruthenium trichloride with sodium sand in pure trimethylphosphine and in a trimethylphosphine/cyclopentene mixture gives the compounds  $(\text{PMe}_3)_3\text{HRu}(\mu\text{-CH}_2\text{PMe}_2)_2\text{RuH}(\text{PMe}_3)_3$  and  $\text{Ru}(\eta^1\text{-}\overline{\text{C}}=\text{CH}(\text{CH}_2)_3)(\text{PMe}_3)_4\text{H}$ , respectively.

It has been found that reduction of the transition metal halides  $\text{WCl}_6$ ,  $\text{MoCl}_5$ ,  $\text{TaCl}_5$  and  $\text{ReCl}_5$  with sodium sand in pure trimethylphosphine as a reactive solvent gives the highly reactive compounds  $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ ,  $\text{Mo}(\text{PMe}_3)_5\text{H}_2$ ,  $\text{Ta}(\text{PMe}_3)_3(\eta^2\text{-CHPMe}_2)(\eta^2\text{-CH}_2\text{PMe}_2)$  and  $\text{Re}(\text{PMe}_3)_5\text{H}$ .



SCHEME 1. (i) Stir at room temperature for 3 d, 36%; (ii) trimethylphosphine/cyclopentene ratio  $\text{PMe}_3/\text{C}_5\text{H}_8$ , 1/1, at room temperature for 2 d, 22% ( $\text{P} = \text{PMe}_3$ ). The other possible structure of 3 is with  $\text{H}_c$  and  $\text{P}_d$  interchanged.

respectively [1]. Here we describe the reduction by sodium of ruthenium trichloride both in pure trimethylphosphine and in a trimethylphosphine/cyclopentene mixture.

Commercial anhydrous ruthenium trichloride (2 g) and sodium sand (2 g) in  $\text{PMe}_3$  (50  $\text{cm}^3$ ) were stirred at room temperature for two days to give a deep red solution. The NMR spectrum of the impure solids obtained by extraction with petroleum ether of the initial reaction products showed the presence of the three compounds  $\text{Ru}(\text{PMe}_3)_4\text{H}_2$  (1),  $\text{Ru}(\text{PMe}_3)_3(\eta^2\text{-CH}_2\text{PMe}_2)_2\text{H}$  (2) and the binuclear compound  $(\text{PMe}_3)_3\text{HRu}(\mu\text{-CH}_2\text{PMe}_2)_2\text{RuH}(\text{PMe}_3)_3$  (3). The compounds 1 and 2 have been described previously [2,3]. Pure 3 was obtained by crystallisation of the solid reaction products from pentane at room temperature as air-sensitive, colourless crystals in 36% yield.

Microanalysis\* and detailed NMR studies\*\* show 3 to have one of two binuclear structures (Scheme 1) but does not permit distinction between them. The closely related compounds  $(\text{PMe}_3)_2\text{Rh}(\mu\text{-CH}_2\text{PMe}_2)_2\text{Rh}(\text{PMe}_3)_2$  and  $(\text{PMe}_3)\text{HPt}(\mu\text{-CH}_2\text{PMe}_2)_2\text{PtH}(\text{PMe}_3)_2$  have recently been described [4,5].

Reduction of  $\text{RuCl}_3$  with sodium sand in a  $\text{PMe}_3$ /cyclopentene (1/1) mixture gives a dark solid, from the pentane extract of which air-sensitive colourless crystals separate at room temperature. Microanalysis and especially NMR spectra show the product to be  $\text{Ru}(\eta^1\text{-}\overline{\text{C}}=\overline{\text{CH}}(\overline{\text{CH}_2})_3)(\text{PMe}_3)_4\text{H}$  (4). Double-resonance experiments showed the connectivity of the resonances assigned to the  $\text{C}_5$ -ring hydrogens f,g,g',h,h',i and i' (Scheme 1).

The insertion of the ruthenium into the olefinic C—H of cyclopentene is unusual: we assume that the reaction proceeds via an intermediate  $\eta^2$ -cyclopentene compound in a manner somewhat analogous to the formation of  $\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{-}(\text{PMe}_3)\text{PhH}$  from the intermediate  $\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\eta^2\text{-C}_6\text{H}_6)$  [6].

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\*Analytical data. 3: Found: C, 34.62; H, 8.73.  $\text{C}_{12}\text{H}_{30}\text{P}_4\text{Ru}$  calcd.: C, 34.98; H, 8.81. IR (Nujol mull)  $\nu(\text{Ru-H})$  1795  $\text{cm}^{-1}$ . 4: Found: C, 42.30; H, 9.22.  $\text{C}_6\text{H}_{20}\text{P}_4\text{Ru}$  calcd.: C, 42.53; H, 9.23%. IR (Nujol, mull)  $\nu(\text{Ru-H})$  1850  $\text{cm}^{-1}$ .

\*\*NMR data, in  $\text{C}_6\text{D}_6$ , labelling of atoms are given in Scheme 1: 3,  $^1\text{H}$  NMR:  $\delta$  2.83, 2.59 (2H, dddd, AB-system,  $\Delta\nu$  59.52), 2.59 ( $^2J(\text{H}_{a,b}\text{-P}_a)$  9.12,  $^3J(\text{H}_{a,b}\text{-P}_c)$  1.4,  $^2J(\text{H}_a\text{-H}_b)$  15.87,  $\text{CH}_2$  (a and b)), 1.24 (9H, d,  $^2J(\text{H-P})$  6.43,  $\text{P-Me}_3$  (a or b or c)), 0.21 (3H, d,  $^2J(\text{H-P})$  7.71,  $\text{P-Me}_3$  (d or e)), 1.03 (9H, d,  $^2J(\text{H-P})$  5.77,  $\text{P-Me}_3$  (a or b or c)), 0.94 (3H, d,  $^2J(\text{H-P})$  5.66,  $\text{P-Me}_3$  (d or e)), 0.86 (9H, d,  $^2J(\text{H-P})$  7.84,  $\text{P-Me}_3$  (a or b or c)), -8.18 (1H, d quar,  $^2J(\text{H}_c\text{-P}_{a,b,c,\text{cis}})$  27.20,  $^2J(\text{H}_c\text{-P}_{d,\text{trans}})$  96.90,  $\text{Ru-H}_c$ ) ppm.

$^{31}\text{P}$  NMR:  $\delta$  17.9 (1P, dt,  $^2J(\text{P}_a\text{-P}_d)$  23.20,  $^2J(\text{P}_a\text{-P}_{b,c})$  33.3,  $\text{P}_a$ ), -0.42, -3.79 (2P, dddd, AB-system,  $^2J(\text{P}_b\text{-P}_c)$  258.59,  $^2J(\text{P}_c\text{-P}_d) = ^2J(\text{P}_b\text{-P}_d) = ^2J(\text{P}_a\text{-P}_d)$  23.20,  $^2J(\text{P}_{b,c}\text{-P}_a)$  33.3,  $\Delta\nu$  341.02,  $\text{P}_c, \text{P}_b$ ), -14.06 (1P,  $^2J(\text{P}_d\text{-P}_a) = ^2J(\text{P}_d\text{-P}_{b,c})$  23.20,  $\text{P}_d$ ) ppm.

$^{13}\text{C}$  NMR:  $\delta$  41.79 (1C, d,  $^1J(\text{C-P})$  28.4, additional splitting of 3.2), 26.49 (3C, d,  $^1J(\text{C-P})$  26.5, additional splitting of 2.3), 25.25 (1C, dt,  $^1J(\text{C-P})$  26.4,  $^2J(\text{C-P})$  6.4), 22.25 (3C, dt,  $^1J(\text{C-P})$  19.99,  $^2J(\text{C-P})$  4.20), 21.53 (3C, d,  $^1J(\text{C-P})$  17.60), 19.7 (1C, m) ppm.

4,  $^1\text{H}$  NMR:  $\delta$  5.7 (1H, v br s,  $\text{H}_f$ ), 2.63 (4H, br s,  $\text{H}_{g,g',i,i'}$ ), 2.01 (2H, quin,  $^3J(\text{H}_{h,h'}\text{-H}_{g,g',i,i'})$  7.23,  $\text{H}_{h,h'}$ ), 1.24 (18H, t,  $^3J(\text{H-P})$  2.57,  $\text{P}_b\text{-Me}_3$ ), 1.17 (9H, d,  $^3J(\text{H-P})$  5.63,  $\text{P}_a$  or  $\text{P}_c$ ), 1.15 (9H, d,  $^3J(\text{H-P})$  5.71,  $\text{P}_a$  or  $\text{P}_c$ ), -9.39 (1H, d quar,  $^2J(\text{H}_e\text{-P}_{b,c,d})$  26.15,  $^2J(\text{H}_e\text{-P}_a,\text{trans})$  94.06,  $\text{H}_e$ ) ppm.

$^{31}\text{P}$  NMR: -5.4 (2P, broad<sup>a</sup>,  $\text{P}_b$ ), -15.3 (1P, broad<sup>a</sup>,  $\text{P}_c$  or  $\text{P}_a$ ), -20.6 (1P, broad<sup>a</sup>,  $\text{P}_a$  or  $\text{P}_c$ ) ppm. <sup>a</sup>All resonances showed partially resolved fine structure.

**References**

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