

Preliminary communication

**STEREOCHEMICAL ASPECTS OF THE CONVERSION OF
CYCLOPENTADIENYL RUTHENIUM ALKOXYCARBENE TO THE
CORRESPONDING ACETYLIDE COMPLEXES. CRYSTAL STRUCTURE
OF $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCHMeCHMePPh}_2)(\text{C}\equiv\text{CPh})]$**

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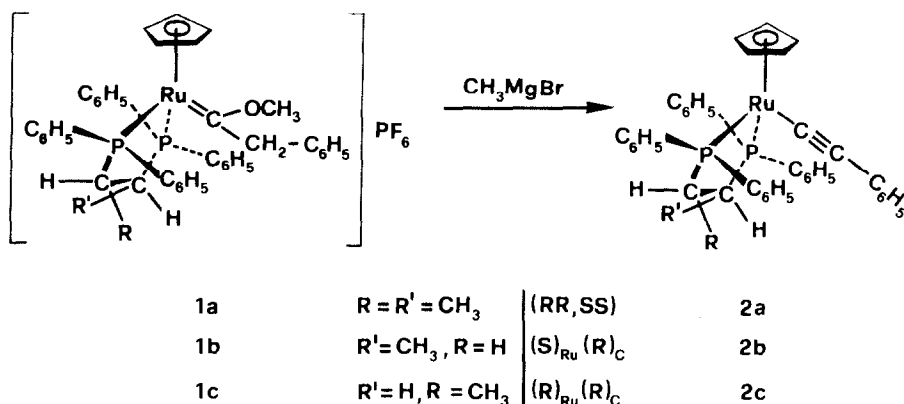
Summary

Reactions of $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{Diphosphine})\{\text{C}(\text{OCH}_3)\text{CH}_2\text{C}_6\text{H}_5\}]\text{PF}_6$ complexes with CH_3MgBr give the corresponding phenylacetylide $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{Diphosphine})\text{C}\equiv\text{CC}_6\text{H}_5]$ complexes. A crystal structure determination has been carried out for the product in which the diphosphine is *rac*-1,2-dimethyl-1,2-ethanediylbis(diphenylphosphine). For the complexes in which the diphosphine is (*R*)-1,2-propanediylbis(diphenylphosphine), the stereochemical outcome of the reaction implies retention of configuration at the metal atom.

We recently reported that the carbene complexes $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{Ph}_2\text{PCHRCHR}'\text{PPh}_2)\{\text{C}(\text{OCH}_3)\text{CH}_2\text{Ph}\}]\text{PF}_6$ (**1**) (*R, R'* = H or CH_3) [**1**] do not undergo the usual reactions with hydride nucleophiles [**2**]. Thus with lithium aluminum hydride in tetrahydrofuran at low temperature they give the corresponding 2-phenylethyl complexes [**3**] $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCHR-CHR}'\text{PPh}_2)\text{CH}_2\text{CH}_2\text{Ph}]$ instead of the expected α -methoxyphenylethyl complexes [**4**].

We have now observed an unexpected reaction of the above complexes with

organomagnesium halides. **1a** was treated in tetrahydrofuran with a large excess of methylmagnesium bromide, the mixture was kept for 48 h at room temperature, and the solvent was replaced by benzene. After treatment with water, the benzene solution was dried over Na_2SO_4 . NMR analysis of the crude reaction mixture revealed formation of two species (^{31}P NMR: 95.8 and 95.4 ppm, $J(\text{PP})$ 33.7 Hz and 90.0 and 79.5 ppm, $J(\text{PP})$ 32.2 Hz) in 22/78 molar ratio (from integration of the $\eta\text{-C}_5\text{H}_5$ signals in the ^1H NMR spectrum). Slow diffusion of n-pentane into the benzene solution caused separation of the major product as yellow crystals.



SCHEME 1

Comparison of the NMR parameters of this major product **2a** with those of previously known derivatives [1,5], enabled us to identify it as the 2-phenylethynyl complex (Scheme 1). Definitive proof of the structure of **2a** was provided by an X-ray diffraction study. Product **2a** crystallized in yellow plates suitable for X-ray diffraction [6]; the crystals belong to a centrosymmetric space group, and contain (*R,R*)- and (*S,S*)- $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2)\text{C}\equiv\text{CPh}]$ molecules in a 1/1 ratio together with a clathrate benzene molecule. A view of the (*R,R*) enantiomer is presented in Fig. 1.

The metallocycle does not have the C_2 symmetry that the 1,2-dimethyl-1,2-ethanediylbis(diphenylphosphine) ligand could allow, but the methyl groups are still roughly in equatorial positions. The $\text{Ru}-\text{C}(5)$ distance of 2.038(7) Å is close to the analogous $\text{Ru}(\text{II})-\text{C}_{\text{sp}}$ distance of 2.016(3) Å found in the $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{C}\equiv\text{CPh}]$ molecule [7], but is ca. 0.13 Å shorter than the value of 2.169(6) Å found in the $(\text{S})_{\text{Ru}}, (\text{R})_{\text{C}}-[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}(\text{CH}_3)\text{-CH}_2\text{PPh}_2)\text{CH}_3]$ molecule [8], in which there is a $\text{Ru}(\text{II})-\text{C}_{\text{sp}^3}$ interaction. This difference is largely due to the different radii of C_{sp} and C_{sp^3} carbon atoms [9].

The analogous reaction of $(\text{S})_{\text{Ru}}, (\text{R})_{\text{C}}\text{-1b}$ and $(\text{R})_{\text{Ru}}, (\text{R})_{\text{C}}-[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2)\{\text{C}(\text{OCH}_3)\text{CH}_2\text{Ph}\}]\text{PF}_6$ (**1c**) was carried out in a 2/1 tetrahydrofuran/diethyl ether mixture for 68 h at room temperature, and is shown to be much more chemoselective (90%) by NMR analysis of the crude reaction product. Thus when **1b** (diastereomeric purity $95 \pm 2\%$) is

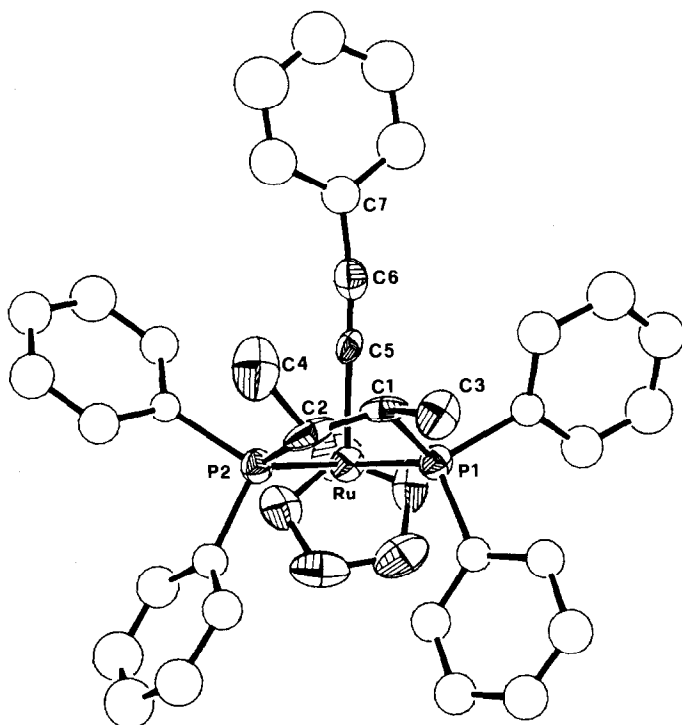


Fig. 1. View of the (*R,R*) enantiomer of **2a**. Selected bond lengths (Å) and bond angles (°): Ru—P(1) 2.241(2); Ru—P(2) 2.255(2); Ru—C(5) 2.038(7); C(5)—C(6) 1.172(9). P(1)—Ru—P(2) 84.16(9); P(1)—Ru—C(5) 83.0(3); P(1)—Ru—Cp* 130.2; P(2)—Ru—C(5) 87.0(2); P(1)—Ru—Cp* 131.0; C(5)—Ru—Cp* 125.4; Ru—C(5)—C(6) 179.4(7); C(5)—C(6)—C(7) 172(1).

used, **2b** (diastereomeric purity $93 \pm 2\%$) is formed. Small amounts (5%) of another product (^{31}P NMR 99.3 and 81.7 ppm, $J(\text{PP})$ 32.1 Hz) are also formed. In the reaction of **1c** (diastereomeric purity $94 \pm 2\%$), in addition to **2c** (diastereomeric purity $91 \pm 2\%$) at least three other products are formed in less than 10% yields (^{31}P NMR: a 98.1 and 81.0 ppm, $J(\text{PP})$ 30.3 Hz; b 82.4 and 73.7 ppm, $J(\text{PP})$ 29.0 Hz; c 92.2 and 83.0 ppm, $J(\text{PP})$ 33.6 Hz). The reaction is thus stereospecific within the limit of the NMR determination; and retention of the configuration at the ruthenium atom is implied by comparison with stereochemically identified samples of **2b** and **2c** [1].

It has been recently reported that alkoxy-carbene complexes of type **1** are deprotonated by bases to give the corresponding vinyl ether derivatives [10]. We are checking whether nucleophiles such as Grignard reagents can then induce β -elimination [11], which would produce the carbon—carbon triple bond, and are trying to identify the other reaction products.

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- 6 *Crystal data*. $C_{47}H_{44}P_2Ru$. $M = 771.9$, orthorhombic, space group $Pcab$, non standard setting of $Pbca$ (No. 61), a 19.538(4) b 18.527(4) c 21.304(4) Å U 7711.6 Å³, $Z = 8$. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 2117 independent significant counter data, up to a current R value of 0.046. The refined positions of the atoms C(1) and C(2) are affected by errors; they have elongated thermal ellipsoids and the distances in which they are involved are systematically shorter or longer than expected (C(1)—C(2) 1.32(1), P(1)—C(1) 1.903(7), P(2)—C(2) 1.914(8), C(1)—C(3) 1.61(1) C(2)—C(4) 1.60(1) Å).
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