

Preliminary communication

CHEMISTRY OF $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}$: PREPARATION OF CATIONIC RUTHENIUM OLEFIN COMPLEXES

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Summary

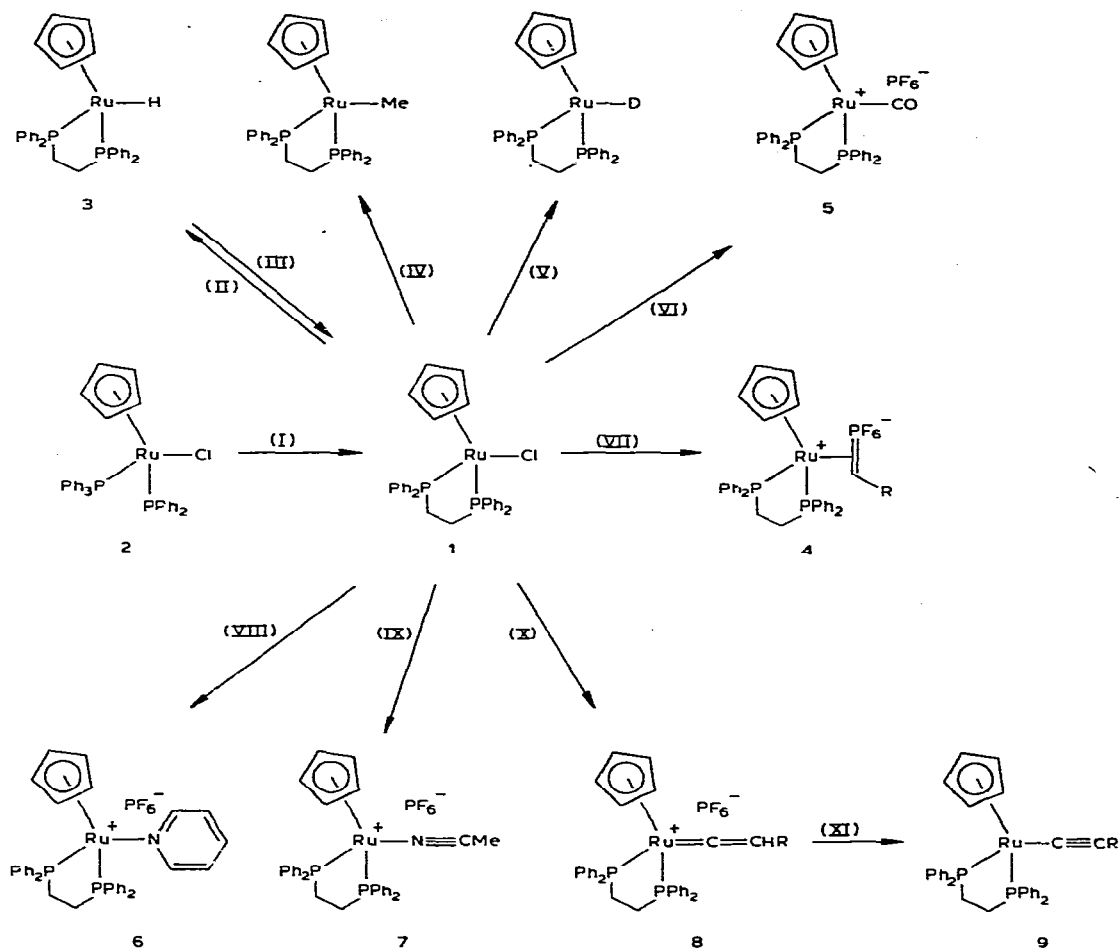
The cationic ruthenium complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{L}]\text{PF}_6$ ($\text{L} =$ olefin, CO, pyridine or acetonitrile) have been prepared by treatment of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}$ with L and NH_4PF_6 in methanol at 20°C .

The preparation of electron-poor 18-electron organometallic cations with olefins as ligands has been extensively studied whereas the corresponding electron-rich cations have received little attention [1]. The activation of olefins by transition metals towards nucleophilic attack is one of the most important applications of organometallic chemistry to organic synthesis. Here we report some reactions of the chloride **1** which allow the preparation of electron-rich cationic ruthenium olefin complexes under remarkably mild conditions.

Treatment of **2** [2] with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ in refluxing benzene results in phosphine exchange to give **1**. Reduction of **1** with LiAlH_4 or activated magnesium [3] in tetrahydrofuran gave the hydride **3**. The chloride **1** may be regenerated from **3** on treatment with CCl_4 . Other nucleophilic displacement reactions on the chloride **1** are summarised in Scheme 1.

The chloride **1** showed considerable ionic character in methanol. Thus treatment of a methanolic solution of **1** in the presence of NH_4PF_6 at 20°C with an excess of olefin (ethylene, propene, styrene, butadiene or methylacrylate) led to the precipitation of the cations **4**. The cations **5**, **6** and **7** could be prepared in the same manner. The preparation of the olefinic cations **4** is in marked contrast to the analogous iron system $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{I}$ where it proved impossible to prepare olefinic cations even in the presence of TlPF_6 [4]. Complex **1** was unreactive towards internal olefins (2-octene, cyclopentene, cyclohexene and 1,4-benzoquinone) presumably for steric reasons. Reaction of **1** with the terminal acetylene 1-hexyne gave the cationic carbene complex **8** rather than an η^2 -acetylene complex. Treatment of **8** with basic alumina gave the η^1 -acetylide **9**.

Satisfactory elemental analyses were obtained for all new compounds.



SCHEME 1. (I) $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, C_6H_6 , 80°C . (II) LiAlH_4 or Mg . (III) CCl_4 . (IV) MeLi . (V) LiAlD_4 . (VI) CO , NH_4PF_6 . (VII) CH_2CHR ($\text{R} = \text{H}$, 72%; Me , 82%; Ph , 83%; CHCH_2 , 85%; CO_2Me , 89%); MeOH , NH_4PF_6 . (VIII) $\text{C}_5\text{H}_5\text{N}$, NH_4PF_6 . (IX) MeCN , NH_4PF_6 . (X) $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{C}_4\text{H}_7$), NH_4PF_6 . (XI) Al_2O_3 .

References

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