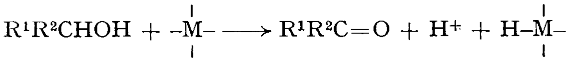
Reactions of $RuCl_2(PPh_3)_3$ with Carbinols: Formation of Ethers, Hydrogen–Deuterium Exchange, and Racemization of Optically Active Alcohols

By YOEL SASSON and JOCHANAN BLUM*

(*Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel*)

Summary $RuCl_2(PPh_3)_3$ catalyses (a) conversion of tertiary and 'positively' substituted secondary carbinols into ethers, (b) H–D exchange in primary and secondary alcohols, and (c) racemization of optically active alcohols; these reactions confirm the intermediacy of ruthenium alkoxides, and β-hydrogen transfer in the formation of ruthenium hydrides from carbinols.

THE formation of hydrido-complexes from carbinols and some platinum–metal compounds in basic media has been summarized in recent reviews.[1,2] The overall reaction is represented by equation (1) and has been assumed to involve an initial step of a ruthenium alkoxide formation, followed by β-hydrogen transfer from the alkoxide ligand to the


(1)

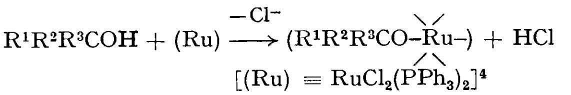
$$R^1R^2CHOH + -\overset{|}{\underset{|}{M}}- \longrightarrow R^1R^2C{=}O + H^+ + H{-}\overset{|}{\underset{|}{M}}- \qquad (1)$$

central metal atom.[3] None of the proposed reaction intermediates has as yet been isolated. The reaction with primary carbinols is somewhat more complicated: the aldehydes formed in the process are decarbonylated by the metal ion to give hydridocarbonyl-complexes instead of metal hydrides.[3,4]

We now report three new reactions of carbinols catalysed by $RuCl_2(PPh_3)_3$, which support strongly the formation and transformation of a metal alkoxide even in non basic solutions.

(a) Formation of ethers. When a solution of 10^{-3}M-$RuCl_2(PPh_3)_3$ in 2-phenylpropan-2-ol is heated at 180° for 15 min, the corresponding ether is obtained in 35% yield. Ethers are formed also from secondary carbinols in the presence of the ruthenium catalyst, under similar conditions. The yields, however, are sensitive to the electronic nature of the carbinol. *E.g.* 1-(4-Methoxyphenyl)ethanol is converted after 15 min at 180° into bis-1-(4-methoxyphenyl)ethyl ether in 40% yield, while 1-(4-tolyl)ethanol gives only 12% of the corresponding ether, and 1-(4-chlorophenyl)ethanol gives no more than traces. Bases strongly inhibit these reactions.

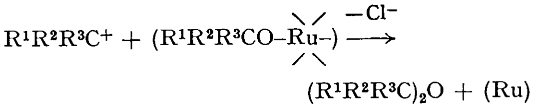
The ether formation can be explained by steps (2)—(4) in which a ruthenium alkoxide is the primary intermediate.


(2)

$$R^1R^2R^3COH + (Ru) \xrightarrow{-Cl^-} (R^1R^2R^3CO{-}\overset{\diagdown\diagup}{\underset{\diagup\diagdown}{Ru}}{-}) + HCl$$

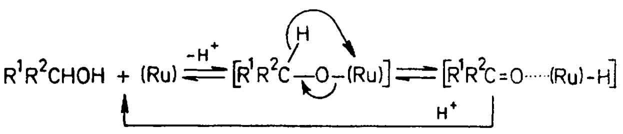
$$[(Ru) \equiv RuCl_2(PPh_3)_2]^4 \qquad (2)$$

$$R^1R^2R^3COH + H^+ \longrightarrow R^1R^2R^3C^+ + H_2O \qquad (3)$$


(4)

$$R^1R^2R^3C^+ + (R^1R^2R^3CO{-}\overset{\diagdown\diagup}{\underset{\diagup\diagdown}{Ru}}{-}) \xrightarrow{-Cl^-} (R^1R^2R^3C)_2O + (Ru) \qquad (4)$$

(b) Racemization of optically active alcohols. (+)-1-Phenylethanol is smoothly racemized when heated with 10^{-3}M-$RuCl_2(PPh_3)_3$ at 180° for 12 h. The reaction is first-order in the active alcohol. Under similar conditions (+)-octan-2-ol is converted into the racemate. The reaction, which is negligible in the absence of the catalyst, can be explained in terms of a reversible β hydrogen transfer from a ruthenium bounded alkoxy-group to the metal atom


(5)

(c) Hydrogen–deuterium exchange in R^1R^2CHOD. At 180° $RuCl_2(PPh_3)_3$ catalyses the H–D exchange in equation (6). When, *e.g.*, 1-phenylethan[^{2}H]ol is heated in the

$$R^1R^2CHOD \longrightarrow R^1R^2CDOH \qquad (6)$$

presence of 3×10^{-3}M of the ruthenium complex, 33% of the deuterium is exchanged during the first 30 min. On further heating, and frequent additions of catalyst, the exchange can be brought to completion and is therefore of synthetic value. The reaction can be applied to a great variety of carbinols, and is especially rapid in benzyl alcohol.

As the reverse reaction, *i.e.*, $R^1R^2CDOH \rightarrow R^1R^2CHOD$ does not take place in a measurable rate, it may be assumed that the intermediate formed in equation (5), $R^1R^2C{=}O\cdots\cdots(Ru){-}H$, exchanges deuterium with the solvent, R^1R^2CHOD. Obviously, the exchange does not occur when the starting carbinol is R_2CDOH and thus prevents the reaction from being reversible.

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