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Preliminary communication

CATALYTIC DEHYDROGENATION OF PRIMARY AND SECONDARY ALCOHOLS BY $Ru(OCOCF_3)_2(CO)(PPh_3)_2$

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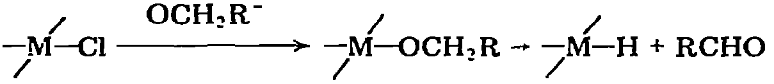
Summary

The complex $Ru(OCOCF_3)_2(CO)(PPh_3)_2$ is an efficient homogeneous catalyst for the dehydrogenation of primary and secondary alcohols to aldehydes and ketones respectively; a mechanism involving a "β-elimination" step is proposed.

The important stoichiometric "β-elimination" reaction 1 extensively employed in the synthesis of platinum group metal hydride complexes [1] has now been developed as an efficient catalytic process for the dehydrogenation of primary and secondary alcohols to aldehydes and ketones respectively*.



$$-M-Cl \xrightarrow{OCH_2R^-} -M-OCH_2R \rightarrow -M-H + RCHO \qquad (1)$$

We find that the ruthenium complex $Ru(OCOCF_3)_2(CO)(PPh_3)_2$ (I)** containing trifluoroacetate *trans* to a relatively strong σ-donor ligand (PPh_3) is solvolysed by boiling primary and secondary alcohols to afford alkoxide complexes which rapidly undergo β-elimination to form the hydride species $RuH(OCOCF_3)(CO)(PPh_3)_2$ (II) and liberate the corresponding aldehydes or ketones. The hydrido complex is, in turn, attacked by trifluoroacetic acid to regenerate the original catalyst and thereby establish a catalytic cycle (scheme 1). The hydrido complex II in the presence of free trifluoroacetic acid displays the catalytic activity implied by the proposed reaction cycle.

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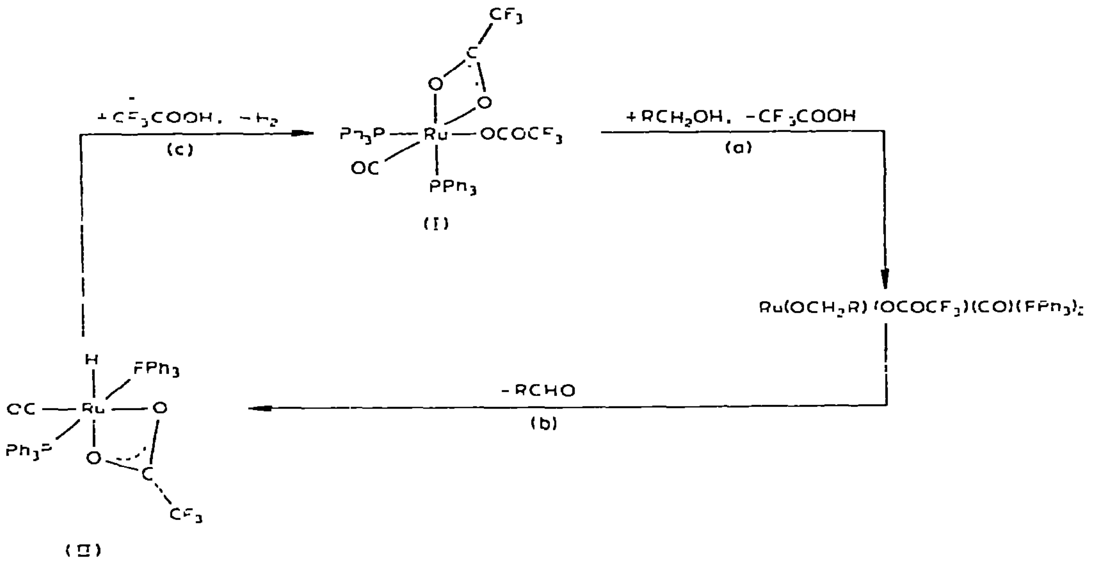
*The only comparable homogeneous catalyst system [5] for alcohol dehydrogenation is based on rhodium—tin species and is ca. 10-60 times less efficient than the one disclosed here.

**The stereochemistry of complexes I and II has been established by ^1H and ^{31}P NMR; I exhibits rapid intramolecular exchange of mono- and bi-dentate trifluoroacetate ligands. The osmium analog of I is a less active catalyst for dehydrogenation; a variety of other trifluoroacetato complexes of the platinum group metals containing trifluoroacetate ligands *trans* to carbonyl or trifluoroacetate groups are not solvolysed by alcohols and do not exhibit catalytic activity.



The catalytic reactions, which were performed using ca. 4.5 × 10^{-3} molar solutions of the catalyst in neat boiling alcohol, were monitored by dihydrogen evolution; organic products were identified by gas chromatography, infrared spectroscopy and formation of 2,4-dinitrophenylhydrazones. Concentrations of free trifluoroacetic acid, up to an optimum of twelve moles per mole of catalyst, promote the dehydrogenation, presumably by aiding regeneration of the catalyst (Fig. 1, reaction c). Acid concentrations > ca. 12 moles/mole of catalyst, and free aldehyde (or ketone) inhibit the catalysis, presumably by suppressing the forward reactions (a) and (b) respectively. The catalyst has been shown to dehydrogenate ethanol, n-propanol, isopropanol, n-butanol, n-pentanol, n-hexanol, cyclohexanol and benzyl alcohol but is inert to methanol (boiling point too low) and tertiary alcohols (t-butanol). Dehydrogenation of allyl alcohol to acrolein is accompanied by formation of some propene presumably due to the occurrence of a hydrogen-transfer reaction [2] similar to that previously observed for allyl alcohol in the presence of other ruthenium-based catalysts [3,4]. Propargyl alcohol decomposes and deactivates the ruthenium catalyst. Initial rates of dehydrogenation, obtained using 4.5 × 10^{-3} molar catalyst solutions, range from 1 × 10^{-3} mol l^{-1} min^{-1} (isopropanol) to 180 × 10^{-3} mol l^{-1} min^{-1} (benzyl alcohol).

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