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Preliminary communication

THE RUTHENIUM-CATALYSED CONVERSION OF METHANOL INTO METHYL FORMATE

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Summary

Heating of methanol with $[RuCl_2(PPh_3)_3]$ yields methyl formate and hydrogen, together with some dimethoxymethane; at the end of the reaction much of the catalyst is present as the dinuclear cation, $[Ru_2H(Cl)_2(CO)_2(PPh_3)_4]^+$.

We recently reported that transfer of hydrogen from methanol to unsaturated organic compounds, especially ketones, occurs at 150°C in the presence of a number of soluble platinum metal catalysts [1]. Of these the best have so far been the triphenylphosphine—ruthenium halide complexes, for example $[Ru(PPh_3)_3Cl_2]$ (I).

The methanol oxidation product of all these reactions was predominantly methyl formate, the overall reaction thus approximating to equation 1. In some reactions it was observed, however, that the amount of methyl formate produced was greater than the amount of the ketone reduction product expected from equation 1. Experiments were therefore conducted to ascertain if a hydrogen acceptor was in fact required for the formation of methyl formate from methanol. These experiments have proved successful in showing that methanol, when treated with complex I, gives rise to a mixture of hydrogen and methyl formate and dimethoxymethane; the overall process corresponds to a combination of equations 2 and 3.

$$2CH_3OH + 2R_2C{=}O \rightarrow CH_3OOCH + 2R_2CHOH \tag{1}$$

$$2CH_3OH \rightarrow CH_3OOCH + 2H_2 \tag{2}$$

$$3CH_3OH \rightarrow CH_3OCH_2OCH_3 + H_2 + H_2O \tag{3}$$

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Thus, under typical conditions (methanol (0.25 mol), complex I (0.08 mmol), 150°C, 18 h under argon) methyl formate (2.24 mmol, corresponding to a turnover based on I of 28), dimethoxymethane (0.72 mmol, turnover 9), and hydrogen (5.2 mmol, turnover 65) were formed. Only trace amounts of other gases such as methane, carbon dioxide or carbon monoxide were found.

The reaction solution underwent a number of colour changes similar to those already noted for the reactions with cyclohexanone and eventually became a straw-yellow colour. At this point the solution showed the presence of a strong band at 1973 cm^{-1} ; again similar results were obtained in the presence of cyclohexanone. This band can now be identified as due to the cationic μ-hydridodi-μ-chlorodiruthenium complex, $[(Ph_3P)_2Ru(CO)(\mu\text{-}H)(\mu\text{-}Cl)_2Ru(CO)(PPh_3)_2]^+$ (II). This was isolated from the solution on evaporation and characterised as the hexafluorophosphate salt. The structure was most eloquently demonstrated by the NMR spectra. The ^1H spectrum showed the hydride at high field as a triplet of triplets arising from one hydride coupling to two (inequivalent) pairs of (equivalent) phosphines [$CDCl_3$, ^1H NMR; δ +7.3 (m, 60 H, phenyls) and —13.04 (tt, J(P—H) 42.5, 10.8 Hz, 1H,). The ^{31}P NMR spectrum showed multiplets at δ +31.5 and +47.5 ($2 \times PPh_3$), and a septet at δ —142.5 (PF_6^-)]. The same cation II was recently reported to have been made by protonation of $[Ru(PPh_3)_3(H)(CO)Cl]$, using $(CF_3SO_2)_2CHR$ (R = H or Ph) [2] ; we find that it can also be made using HBF_4 [3].

Smaller amounts of other complexes, tentatively identified as $[Ru(PPh_3)_3(H)(CO)Cl]$ and $[Ru(PPh_3)_2(CO)_2Cl_2]$, were precipitated from the reaction solutions at the end.

The roles of I, II and the other species present in the reaction are now under investigation. Heterogeneous reactions of methanol to give methyl formate have been known for a long time, effected, for example by passing methanol vapour over copper metal at 250°C [4], or by passing methanol over the copper exchanged form of fluorotetrasilicic mica [5], or over tungsten carbide [6]. By contrast, homogeneous reactions in the absence of added oxidisers or of added CO, are still rare.

Note added in proof. S. Shinoda, H. Itagoki and Y. Saito have recently found that formaldehyde and hydrogen were formed on refluxing methanol with $[Ru_2(OAc)_4Cl]/R_3P$ (Y. Saito, personal communication, and J. Chem. Soc. Chem. Commun., in press).

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