Aqueous Catalytic Dimerisation of Ethylene: Characterization of the Reaction Intermediates $[Ru(CH_2{=}CH_2)(H_2O)_5](tos)_2$ and $[Ru(CH_2{=}CH_2)_2(H_2O)_4](tos)_2$ (tos = toluene-*p*-sulfonate)

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It is shown that $[Ru(H_2O)_6]^{2+}$ can efficiently catalyse under mild experimental conditions the dimerisation of ethylene in a fully aqueous solution to form butenes ([*Z*-but-2-ene] : [*E*-but-2-ene] : [but-1-ene] is 1 : 2.2 : 2.2); the reaction intermediates $[Ru(CH_2{=}CH_2)(H_2O)_5](tos)_2$ and $[Ru(CH_2{=}CH_2)_2(H_2O)_4](tos)_2$ have been isolated in solid form.

The recent availability of solid salts of hexaaquaruthenium(II), $[Ru(H_2O)_6](tos)_2$ (tos = toluene-*p*-sulfonate),[1] opens new and efficient synthetic routes to a remarkable variety of new compounds[2] {*e.g.* $[Ru(N_2)(H_2O)_5](tos)_2$[3] or $[Ru(CO)(H_2O)_5](tos)_2$[4]}, including novel routes in aqueous organometallic catalysis.[5] In this context it was decided to try to prepare the first fully aquated mono-and bis-ethylene complex of Ru^{II} according to eqns. (1) and (2). These complexes should be potentially new starting reagents and catalysts, as well as particularly simple model compounds for ethylene bonding in aqueous solution.

$$[Ru(H_2O)_6]^{2+} + CH_2{=}CH_2 \rightarrow [Ru(CH_2{=}CH_2)(H_2O)_5]^{2+} + H_2O \quad (1)$$

$$[Ru(CH_2{=}CH_2)(H_2O)_5]^{2+} + CH_2{=}CH_2 \rightarrow [Ru(CH_2{=}CH_2)_2(H_2O)_4]^{2+} \quad (2)$$

Reactions (1) and (2) were performed in a sapphire NMR tube supporting pressure up to 100 bar,[6] and were followed by ^1H, ^{13}C and ^{17}O NMR.† $[Ru(H_2O)_6](tos)_2$[7] was first enriched by reaction with 3 cm^3 of 10% [^{17}O]water (Yeda, Israel) at ambient temperature and pressure under argon atmosphere. Under these conditions the halflife of the water exchange is less than 1 min ($k_{ex}^{H_2O} = 0.018\ s^{-1}$ at 298 K).[8] The ^{17}O NMR spectrum of this solution shows the free water signal ($SiMe_4$ reference) and the characteristic signal of $[Ru(H_2O)_6]^{2+}$ at δ − 192. The sample was then pressurized with ethylene at 60 bar, and mixed for 6 h. For this 0.1 mol dm^{-3} Ru^{2+} solution the disappearance of the ^{17}O signal of the hexaaquaruthenium(II) ion and the appearance of two new resonances at δ −160.1 and −46.9 corresponding to the equatorial (eq) and axial (ax) water oxygens of $[Ru(CH_2{=}CH_2)(H_2O)_5]^{2+}$, respectively [Fig. 1(*a*)], were observed. The ratio of integrals is in reasonable agreement with the theoretical value of 4, considering the difficulty of accurate integration of the axial water signal very close to the 555 times larger free water signal. At the same time the ^{13}C NMR spectrum [Fig. 1(*b*)] shows a triplet signal at δ 68.7 (the triplet due to free $CH_2{=}CH_2$ in solution at δ 125.6, $J_{^{13}C-^1H}$ coupling constant of 161.3 Hz; $SiMe_4$ reference. The observed $J_{^{13}C-^1H}$ coupling constant for $[Ru(CH_2{=}CH_2)(H_2O)_5]^{2+}$ is 161.6 Hz. The ^1H NMR spectrum [Fig. 1(*c*)] shows a singlet at δ 5.04 corresponding to the π-bonded $CH_2{=}CH_2$ next to signals due to free dissolved ethylene (δ 5.46), water (δ 4.87) and the tosylate protons (δ 2.38, 7.36 and 7.70). After release of the ethylene pressure, the water was evaporated from this solution under

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† NMR spectra were taken on a Bruker AC-200 instrument equipped with a widebore cryomagnet (4.7 T).

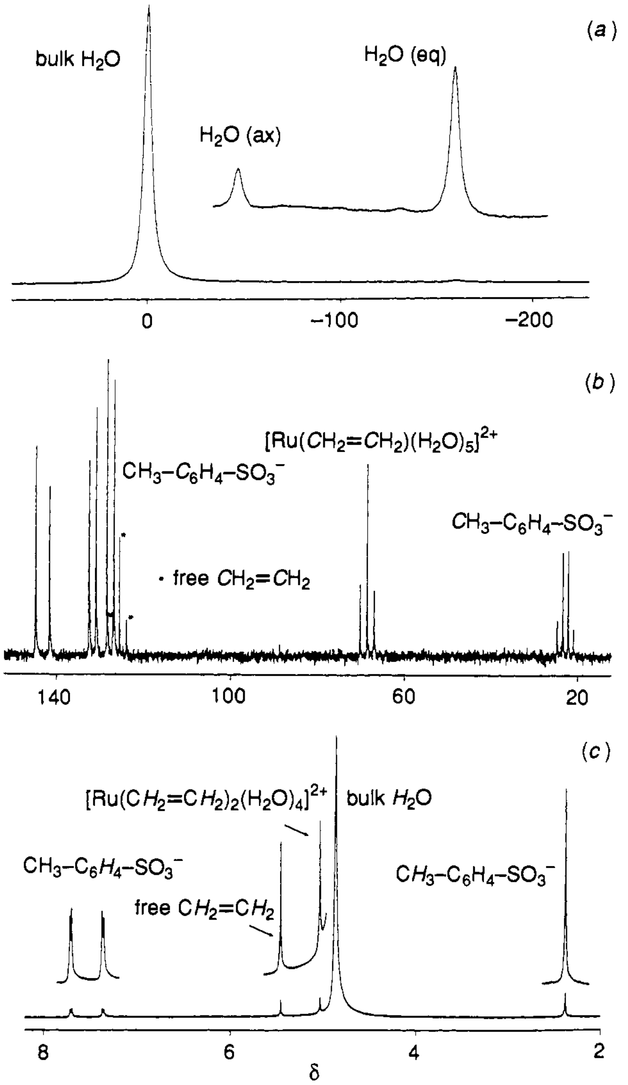


Fig. 1 (*a*) 54.24 MHz ^{17}O, (*b*) 50.32 MHz ^{13}C and (*c*) 200 MHz ^{1}H NMR spectra of a 0.1 mol dm^{-3} $[Ru(CH_2{=}CH_2)(H_2O)_5](tos)_2$ aqueous solution (in 10% [^{17}O] enriched water), under ethylene pressure at 298 K

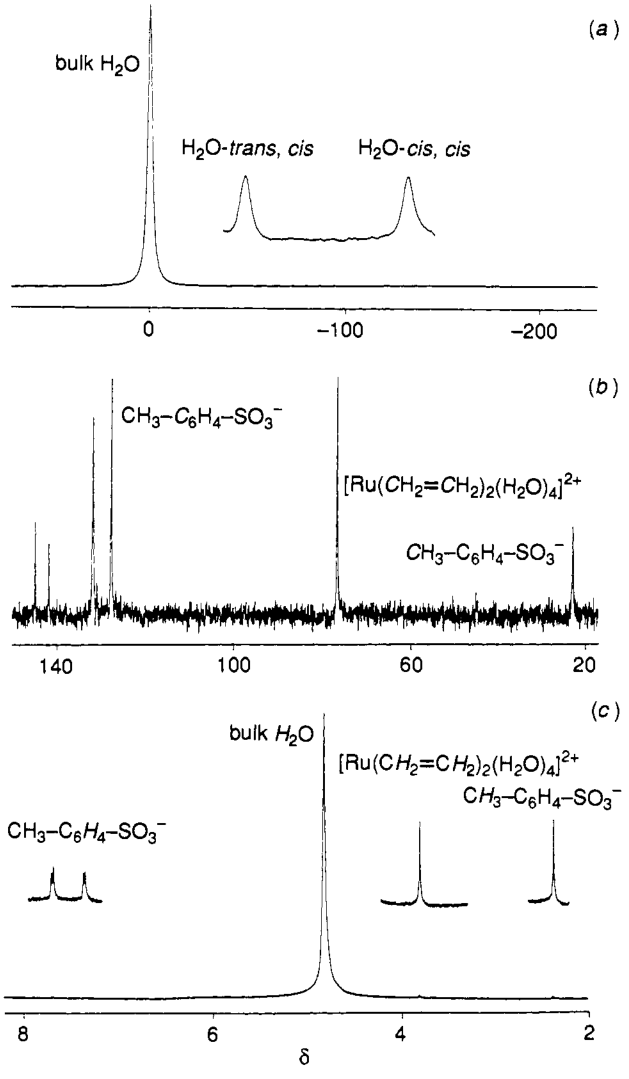
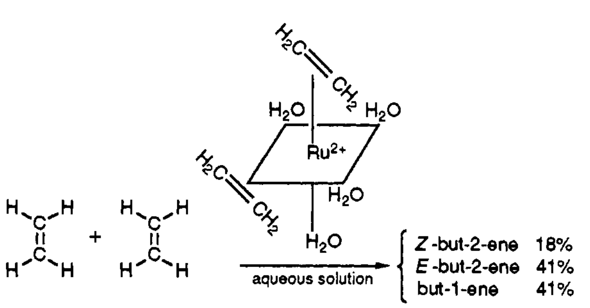


Fig. 2 (*a*) 54.24 MHz ^{17}O, (*b*) 50.32 MHz proton decoupled ^{13}C and (*c*) 200 MHz ^{1}H NMR spectra of a 0.1 mol dm^{-3} $[Ru(CH_2{=}CH_2)_2(H_2O)_4](tos)_2$ aqueous solution (in 10% [^{17}O]enriched water) at 298 K



(3)

vacuum and the brown solid $[Ru(CH_2{=}CH_2)(H_2O)_5](tos)_2$ was analysed.‡

A second identical solution (0.1 mol dm^{-3} Ru^{II}, 60 bar ethylene) was mixed for 18 h. The ^{17}O NMR spectrum [Fig. 2(*a*)] now shows two signals with 1:1 intensity ratio at δ −49.52 and −132.1, which can be assigned to the *cis,trans* and *cis,cis* water oxygens of the bis complex, respectively. The decoupled ^{13}C NMR [Fig. 2(*b*)] shows a signal at δ 76.6, due to the four equivalent carbons in $[Ru(CH_2{=}CH_2)_2(H_2O)_4]^{2+}$. In the ^{1}H NMR spectrum [Fig. 2(*c*)] there is a singlet at δ 3.81 corresponding to the bonded $CH_2{=}CH_2$ in the bis complex.§ The water was evaporated from this solution under vacuum and the dark-brown solid $[Ru(CH_2{=}CH_2)_2(H_2O)_4](tos)_2$ was analysed.‡

A third identical solution was shaken for three days and showed the appearance of an organic phase above the aqueous solution, containing $[Ru(CH_2{=}CH_2)_2(H_2O)_4]^{2+}$. The ^{13}C NMR spectra of this new organic phase, separated under pressure, show the characteristic signals of butenes[9,10]¶ in the following ratios: [*Z*-but-2-ene] : [*E*-but-2-ene] : [but-1-ene] 1 : 2.2 : 2.2 (eqn. 3). A slight amount of dissolved ethylene was also observed, but no higher oligomers could be detected. As expected the release of pressure caused the evaporation of the organic phase; b.p. (°C) [*p* = 1 bar]: 3.7 (*Z*-but-2-ene), 0.88 (*E*-but-2-ene) and −6.3 (but-1-ene). The aqueous catalytic dimerisation reaction is not stereoselective, and all the possible butenes are formed except 2-methylpropene.

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‡ Satisfactory elemental analyses were obtained.

§ The spectra were taken after release of ethylene pressure, there is no free dissolved ethylene in the solution.

¶ Observed: but-1-ene δ 139.1 (d), 111.9 (t), 26.0 (t) and 10.8 (q); *E*-but-2-ene δ 125.0 (d) and 16.4 (q) *Z*-but-2-ene, δ 123.3 (d) and 11.9 (q) and the dissolved ethylene δ 121.4 (t).

It is known that $[Ru(H_2O)_6]^{2+}$ can catalyse the ring-opening metathesis polymerisation of strained olefins[11,12] and the isomerisation of olefins, in particular the useful transformation of allyl to vinyl ethers.[13] We have now shown that $[Ru(H_2O)_6]^{2+}$ can efficiently catalyse under mild experimental conditions the dimerisation of ethylenes in fully aqueous solution and we have characterised the reaction intermediates. This observation is attractive with respect to ecological considerations and will stimulate the research for similar reactions with other small molecules and metal ions in aqueous solution.[||]

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[||] Non-aqueous catalytic dimerisation of olefins have been described recently: *e.g.* with $[RuH(\eta^5\text{-}C_8H_{11})_2]BF_4$ in CH_2Cl_2[14], with Pd and/or Ru catalyst in approtic organic solvent[15] and with ruthenium(III) salts and Al halides in an environment free of water.[16]