

118. Quantitative Formation in Water of $[\text{Ru}(\text{CO})(\text{H}_2\text{O})_5]^{2+}$ from Hexaaquaruthenium(II) and Carbon Monoxide

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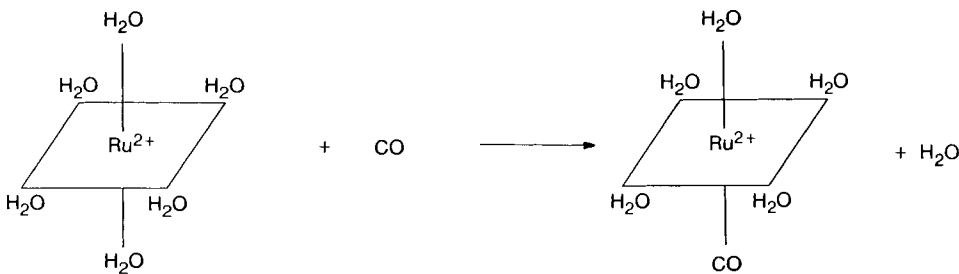
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High-pressure ^{17}O - and ^{13}C -NMR show that $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ reacts quantitatively with carbon monoxide (50 bar) in water to form $[\text{Ru}(\text{CO})(\text{H}_2\text{O})_5]^{2+}$.

If organometallic chemistry in aqueous solution would be successful, it could help to solve ecological problems. We wish to report here a simple prototype of this kind of chemistry obtained by reacting a metal aquaion, $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$, directly with carbon monoxide under pressure in aqueous solution (*Scheme*).

Scheme



$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ has a high affinity for π -acidic ligands such as nitrogen heterocycles, nitriles, and olefines [1]. We have extended this study to investigate the reaction with CO at low pressures of 1 to 2 bar. The appearance of a CO stretching vibration at 1980 cm^{-1} in the reaction mixture of $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ and CO in THF was considered as evidence for the formation of a CO complex. This observation prompted us to intensify our study of this chemical system. The reaction indicated in the *Scheme* was performed in a sapphire NMR tube supporting pressures up to 100 bar [2], and was followed by ^{17}O - and ^{13}C -NMR. $[\text{Ru}(\text{H}_2\text{O})_6](\text{TsO})_2$, prepared according to a procedure described in [3], was first enriched with acidified (0.1M TsOH) 10% H_2^{17}O at ambient temperature and pressure under inert atmosphere. The half-life of the water exchange is less than 1 min ($k_{\text{ex}}^{\text{H}_2\text{O}} = 0.018\text{ s}^{-1}$ at 298 K) [4]. The NMR spectrum of this solution shows the free H_2O signal (chemical-shift reference) and the characteristic signal of $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ at -192 ppm . The sample was then

pressurized with CO at 50 bar, and mixed for 2 d on a shaker. As a function of time, we observe the disappearance of the ^{17}O signal of the $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ and the appearance of two new resonances at -154.8 and -29.3 ppm corresponding to the equatorial and axial water O-atoms of $[\text{Ru}(\text{CO})(\text{H}_2\text{O})_5]^{2+}$, respectively (*Fig.*). The ratio of observed integrals is in reasonable agreement with the theoretical value of 4, considering the difficulty of accurate integration of the axial H_2O signal very close to the 550 times larger free H_2O signal.

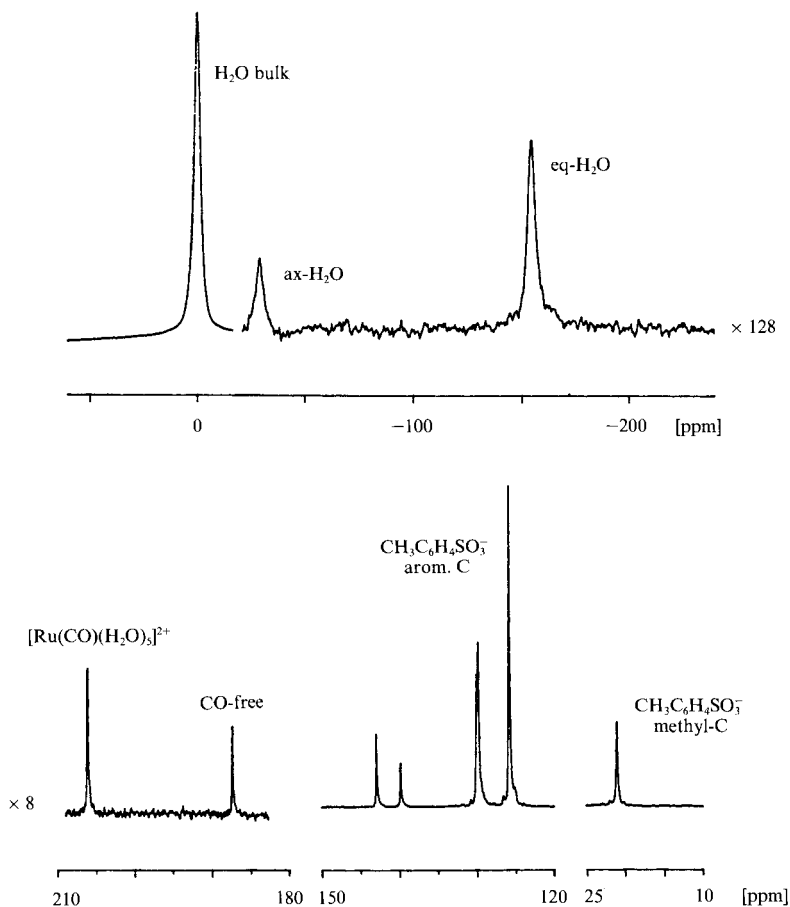


Figure. 54.24-MHz ^{17}O -NMR spectrum (top) and ^{13}C -NMR spectrum (bottom) of a 0.1 M $[\text{Ru}(\text{CO})(\text{H}_2\text{O})_5](\text{TsO})_2$ and 0.1 M TsOH aqueous solution (10% ^{17}O -enriched water), under 50 bar pressure of CO at 298 K ($[\text{CO}]_{\text{free}}$ in solution = 0.037 M)

During the same time, ^{13}C -NMR shows the growth of a new signal at 205.5 ppm due to the coordinated CO, beside that due to free CO in solution at 187 ppm. The ^{13}C integrals indicate the coordination of one CO per Ru. During the reaction, the colour of the solution changes from purple to yellow. After release of the CO pressure the NMR spectra remain unchanged for hours, except the disappearance of the free CO signal. The

colour of the solution remains yellow as well and does not return to purple. The FT-IR spectra of the final solution (ambient pressure) show the characteristic stretching frequency of coordinated CO at 1971 cm^{-1} . For comparison, free CO appears at 2134 cm^{-1} , and in the analogous $[\text{Ru}(\text{NH}_3)_5(\text{CO})]\text{X}_2$ complexes, it has been reported between 1925 and 1955 cm^{-1} [5] [6].

$[\text{Ru}(\text{CO})(\text{H}_2\text{O})_5]^{2+}$ is the first (monocarbonyl)aqua ion reported. This opens interesting new perspectives including similar reactions with other small molecules or metal ions, and also in the study of the change in reactivity of the coordinated H_2O molecules due to CO coordination.

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