Isotope Labelling Studies on the Ruthenium-catalysed Hydroformylation of Ethylene: Indirect Evidence for Catalysis at Intact Clusters

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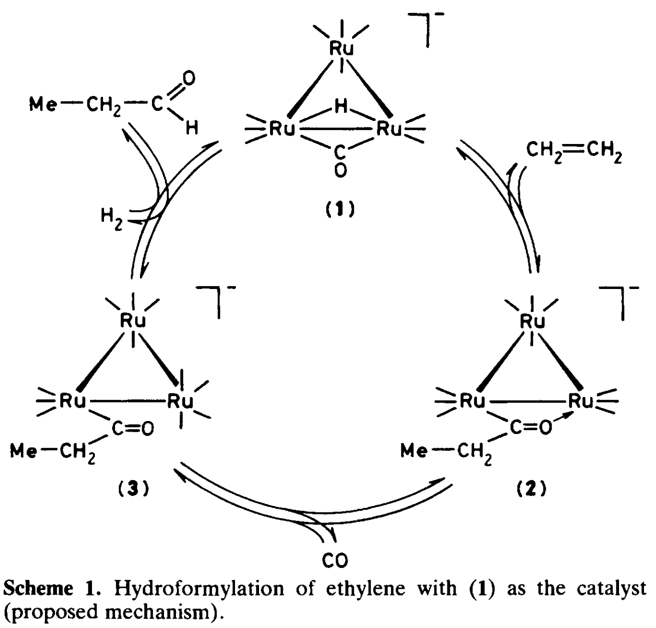
Isotope labelling studies suggest that the hydroformylation of ethylene catalysed by the cluster anion $[Ru_3H(CO)_{11}]^-$ proceeds through the intermediacy of intact Ru_3 clusters.

Ever since transition-metal clusters have been discussed as catalysts,[1] various attempts to establish the implication of polynuclear metal species throughout a catalytic reaction have been reported.[2—5] However, not only is an unambiguous proof of genuine cluster catalysis still awaited, sound mechanistic conceptions concerning the course of a catalytic reaction at polymetallic centres also remain absent.[6] We have found by complementary isotope labelling experiments that the hydroformylation of ethylene, catalysed by the cluster anion $[Ru_3H(CO)_{11}]^-$ (**1**),[7] may be interpreted in terms of a reaction cycle, the elementary steps of which involve exclusively intact Ru_3 clusters.

According to our findings, the cluster anion (**1**) is attacked by the ethylene molecule; the hydride ligand is transferred to the incoming C_2H_4 unit which combines with the electrophilic C atom of the carbonyl bridge, resulting in the formation of the μ_2-η^2(C,O)-propionyl ligand of the intermediate (**2**) (Scheme 1). By CO uptake, (**2**) is presumably transformed into the intermediate (**3**) which reacts with hydrogen to yield propionaldehyde and the original cluster anion (**1**). The elementary steps of this cycle must be reversible, because in spite of the remaining presence of (**1**) the hydroformylation decays after approximately 300 cycles; however after evaporation of the product and repressurising of the autoclave with the

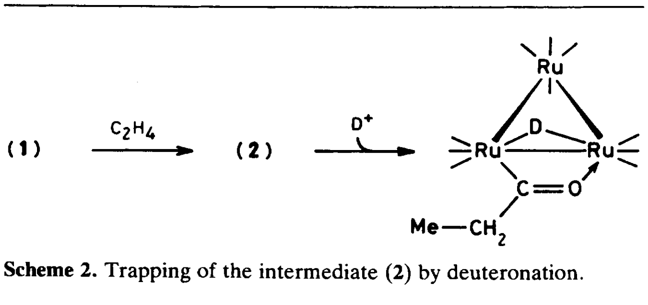


Scheme 1. Hydroformylation of ethylene with (**1**) as the catalyst (proposed mechanism).

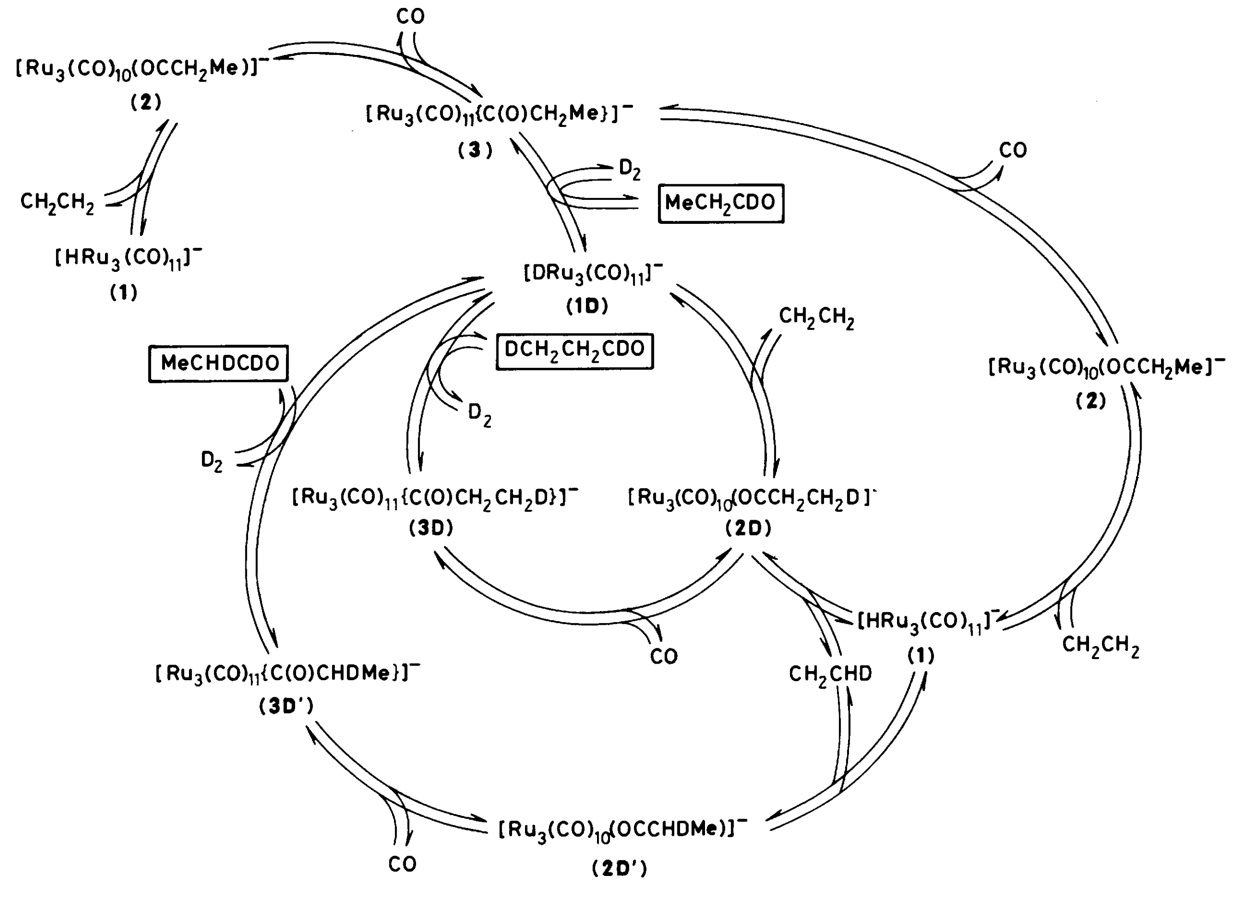
Table 1. Isotope distribution in the deuteriated propionaldehyde formed in the deuterioformylation of ethylene with (**1**) as the catalyst.[a]

Solvent	Degree of monodeuteriation[b] (% D) Methyl	Methylene	Formyl	Yield (%)
DMF[c]	80	12	97	74
THF	76	5	98	71
CH_3CN	78	8	98	66
CD_3CN	71	8	98	68

[a] 10 ml of solution, 150 mg of $[NEt_4][Ru_3H(CO)_{11}]$, 2.4 g of C_2H_4, 100 °C, total pressure 52 bar (D_2:C_2H_4:CO 13:13:26), 4.5 h. [b] Determined by integration of the n.m.r. signals (accuracy ± 5%). ^2H n.m.r. ($CDCl_3$), (13.7 MHz, 1000 Hz ^1H decoupled): δ 0.94 (CH_2D), 2.20 (CHD), and 9.76 (CDO) p.p.m.; ^1H n.m.r. ($CDCl_3$, 250 MHz): δ 1.04 (CH_3, J_{HH} 7.2 Hz), 1.02 (CH_2D, J_{HH} 7.2, J_{HD} 1.9 Hz), 2.04 (CHD, J_{HH} 7.2, J_{HD} 1.1 Hz), 2.06 (CH_2, J_{HH} 7.2 Hz), and 9.72 (CHO), all signals resolved. [c] DMF = dimethylformamide.



Scheme 2. Trapping of the intermediate (**2**) by deuteronation.



Scheme 3. Deuterioformylation of ethylene with (**1**) as the catalyst.

reaction gases the catalytic activity of the solution is regenerated. Although the anionic intermediates (**2**) and (**3**) could not be isolated, the key processes of this cycle, *i.e.* transfer of the hydride from the metal framework to the incoming ethylene and incorporation of the hydrogen molecule in both aldehyde and cluster anion, were established by isotope labelling experiments.

The intermediate (**2**) was trapped by acidification; the protonation of a tetrahydrofuran (THF) solution of (**1**) pressurised with ethylene (25 °C, 40 bar, 4 h) gives the known[8] neutral cluster $[Ru_3(\mu_2\text{-}H)(\mu_2\text{-}\eta^2\text{-}OCCH_2CH_3)(CO)_{10}]$ containing the $\mu_2\text{-}\eta^2$(C,O)-propionyl ligand as assumed for (**2**). The deuteronation as distinct from the protonation demonstrates the intermediacy of the anion (**2**) (Scheme 2); the THF solution of (**1**) pressurised with ethylene (25 °C, 40 bar, 4 h) reacts with CF_3CO_2D to give the cluster $[Ru_3(\mu_2\text{-}D)(\mu_2\text{-}\eta^2\text{-}OCCH_2CH_3)(CO)_{10}]$† specifically deuteriated in the hydride position, as established by ^1H and ^2H n.m.r. spectroscopy (94 atom % D). This result shows that the hydride bridge in (**1**) is involved in the reaction with ethylene; it is removed from the metal framework and reformed only upon acidification.

On the basis of the mechanism proposed in Scheme 1 three different propionaldehyde species are to be expected for the deuterioformylation of ethylene (Scheme 3). In the initial cycle ethylene is added to (**1**); the anion (**2**) thus formed reacts by incorporation of CO to give the anion (**3**), which is cleaved by D_2 to yield CH_3CH_2CDO and the deuteriated anion (**1D**). The same sequence of reactions is repeated in the main cycle, but with the deuteriated anion (**1D**). Consequently, a deuteride instead of a hydride is transferred to the incoming ethylene leading to the aldehyde DCH_2CH_2CDO, which is the main product of the catalytic reaction. Because of the reversibility of the elementary steps two side-cycles arising from the elimination of deuterioethylene from (**2D**) have to be considered: the protic anion (**1**) thus formed can react with CH_2CH_2 or with CH_2CHD under inverse addition resulting in the formation of the propionaldehydes CH_3CH_2CDO and $CH_3CHDCDO$ as side-products with decreasing probability. The ^1H and ^2H n.m.r. spectroscopic analysis of the product mixture reveals that indeed three different propionaldehyde species are formed when D_2 is employed in place of H_2; the formyl position is completely deuteriated within the error limits and the methyl and methylene positions show respectively 76 and 5% monodeuteriation with a slight dependence upon solvent being observed (Table 1). The observed isotope distribution demonstrates that hydrogen is introduced into the formyl position of the propionaldehyde as well as into the bridging position of the cluster anion; the hydride bridge is subsequently transferred to the incoming ethylene. These findings do not unambiguously exclude cluster disintegration, but they are consistent with the reaction cycle proposed in Scheme 1 which involves exclusively intact Ru_3 clusters.

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† Isolated in 20% yield by preparative t.l.c. (silica, cyclohexane). ^1H n.m.r. ($CDCl_3$) δ 0.92 (3H, t, CH_3) and 2.97 (2H, q, CH_2); ^2H n.m.r. ($CDCl_3$) δ −13.91(s) p.p.m.; i.r. (cyclohexane) ν_{CO} 2104w, 2068vs, 2057vs, 2030s, 2019s, 2010m, 2004m, 1996sh, and 1969vw cm^{-1}.

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