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Preliminary communication

Isolation and X-ray structure determination of $Ru_4(CO)_{12}(C_6H_6O)$, a precatalyst for the transfer hydrogenation of cyclohex-1-en-2-one

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Abstract

$Ru_4(CO)_{12}(C_6H_6O)$ (**1**) and $Ru_3(CO)_{10}(C_6H_8O)$ (**2**) have been obtained from the reaction of $Ru_3(CO)_{12}$ with cyclohex-1-en-2-one; **1** has been characterized by an X-ray structure determination. Both **1** and **2** have been found to be active precatalysts for the transfer hydrogenation of cyclohex-1-en-2-one.

The use of $Ru_3(CO)_{12}$ as a precatalyst in transfer hydrogenation reactions involving primary or secondary alcohols as donors and α,β-unsaturated ketones as acceptors has recently been reported [1]. Structural characterization of isolable complexes formed in the reaction between $Ru_3(CO)_{12}$ and a suitable acceptor (e.g. cyclohex-1-en-2-one) is of obvious importance for determining the possible role of such complexes in the catalytic cycle. Such an approach has proved to be useful in the investigation of other reactions in which $Ru_3(CO)_{12}$ is a precatalyst [2]. Here we report that complexes **1** and **2**, isolated from the reaction between $Ru_3(CO)_{12}$ and cyclohex-1-en-2-one, are active precatalysts for the transfer hydrogenation of the same acceptor.

Reaction of $Ru_3(CO)_{12}$ with cyclohex-1-en-2-one in cyclohexane at 80 °C for 16 h gives a red-brown solid (**1**) and a red oil (**2**), which can be separated by column chromatography and characterized by spectroscopic techniques [3 *]. The proposed mode of bonding of "C_6H_8O" in **2** is consistent with the absence of metal hydrides

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* Reference number with asterisk indicates a note in the list of references.

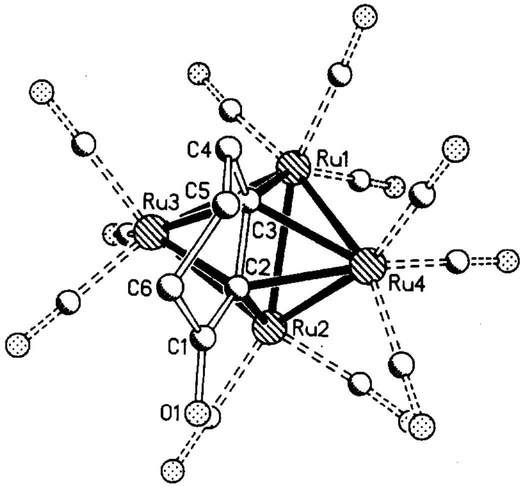
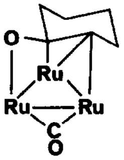


Fig. 1. The molecule of **1** in the crystal (H atoms omitted, radii arbitrary). Selected bond lengths (Å): Ru(1)–Ru(2) 2.858(1), Ru(1)–Ru(3) 2.765(1), Ru(1)–Ru(4) 2.742(1), Ru(2)–Ru(3) 2.713(1), Ru(2)–Ru(4) 2.743(1), C(2)–C(3) 1.466(4), C(1)–O(1) 1.210(4), Ru(1)–C(3) 2.124(3), Ru(3)–C(3) 2.244(3), Ru(4)–C(3) 2.254(3), Ru(2)–C(2) 2.148(3), Ru(3)–C(2) 2.208(3), Ru(4)–C(2) 2.190(3). One carbonyl group at Ru(2) is eclipsed.

and ketone and olefin functions (as shown by ^1H and ^{13}C NMR and IR data [3 *]). The diagram of **2** omits the three terminal CO groups on each Ru atom for clarity. The bridging CO is associated with an IR band at 1890 cm^{-1}.



(**2**)

The molecular structure of **1** as determined by X-ray diffraction is shown in Fig. 1. The four ruthenium atoms adopt a butterfly configuration. The C_6H_6O ligand lies over the metal skeleton with the ethylenic C–C bond parallel to the Ru(1)–Ru(2) "hinge" bond; it is π-bonded to the "wingtip" metal atoms and σ-bonded to the hinge atoms to form a distorted octahedral core, as found in other ruthenium clusters [4]. The C(2)–C(3) bond length is 1.466(4) Å, confirming the multiple bond character (typical values in such complexes are ca. 1.43–1.46 Å). There is no interaction between the keto oxygen atom and the metal framework (IR band at 1680 cm^{-1}). The Ru–Ru bond lengths (2.713–2.858 Å, the "hinge" bond being the longest) are also typical for such ruthenium clusters [4].

When isopropyl alcohol is used as the donor, $Ru_3(CO)_{12}$, **1** and **2** are all active precatalysts for the transfer hydrogenation of cyclohex-1-en-2-one to cyclohexanol via cyclohexanone [5 *]. In all three cases the clusters are converted to other carbonyl species still to be identified.

X-Ray structure determination of 1

Crystal data. $C_{18}H_6O_{13}Ru_4$, *M* 834.5. Monoclinic, space group $P2_1/n$, *a* 9.599(2), *b* 16.260(4), *c* 15.120(3) Å, β 92.07(2)°, *V* 2358 Å^3, *Z* 4, D_x 2.35 g cm^{-3}, μ(Mo-K_α) 2.5 mm^{-1}, *F*(000) 1584.

Data collection and processing. A red-brown, almost opaque block, 0.55 × 0.4 × 0.3 mm, was used to record 5796 profile-fitted intensities [6] on a Stoe-Siemens four-circle diffractometer (Mo-K_α radiation, $2\theta_{max}$ 57°). Of 5464 unique reflections, 4988 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX76/SHELXS). Absorption corrections based on ψ-scans were applied (transmissions 0.77–0.91). Cell constants were refined from 2θ values of 40 reflections in the range 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined anisotropically to *R* 0.027, R_w 0.027 (H atoms included using a riding model; extinction correction of the form $F_{corr} = F_c/[1 + xF_c^2/\sin 2\theta]^{0.25}$ with $x = 2.2(1) \times 10^{-6}$; weighting scheme $w^{-1} = \sigma^2(F) + 0.0001F^2$; 317 parameters).

Full details of the structure (atom coordinates, bond lengths and angles, structure factors, temperature factors) have been deposited with the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2 (F.R.G.). Any request for this material should quote the reference number CSD 52443 and the full literature citation.

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References

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3 IR (cm^{-1}) in hexane, **1**: 2098w, 2071s, 2048vs, 2024s, 1983m, 1680w; **2**: 2104vw, 2093w, 2076m, 2056vs, 2032w, sh, 2020s, 2004s, 1990w, 1890m. ^{1}H NMR, (ppm) in CD_2Cl_2, **1**: 3.38 (2H, t), 2.70 (2H, m), 2.18 (2H, m); **2**: 2.19 (2H, m), 1.59 (4H, m), 1.26 (2H, m). No Ru-H signals for **1** or **2** between 0 and −60. ^{13}C (^{1}H) NMR (ppm) in $CDCl_3$, **2**: 51.37, 37.98, 29.65 (2C), 24.32, 19.90. Molecular ion peaks **1**: 834 with 12 successive CO losses; **2**: 679 with 10 successive CO losses.

4 P.F. Jackson, B.F.G. Johnson, J. Lewis, P.R. Raithby, G.J. Hall, M. McPartlin and W.J.H. Nelson, J. Chem. Soc., Chem. Commun., (1980) 1190 and references therein.

5 In all the cases with a precatalyst (0.05 mmol) to substrate molar ratio of 1/100 in isopropyl alcohol (10 ml) at 80 °C, complete conversion to cyclohexanol could be achieved in 16 h.

6 W. Clegg, Acta Crystallogr., 37A (1981) 22.