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# 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.

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The use of $Ru_3(CO)_{12}$ as a precatalyst in transfer hydrogenation reactions involving primary or secondary alcohols as donors and $\alpha,\beta$-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.

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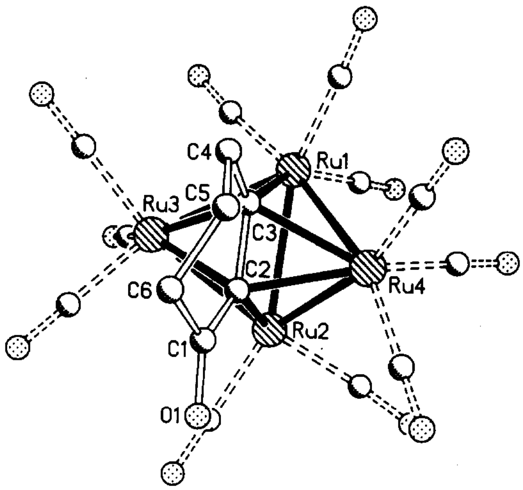
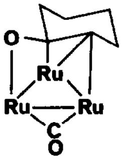


Fig. 1. The molecule of **1** in the crystal (H atoms omitted, radii arbitrary). Selected bond lengths (Å): Ru(1)-Ru(2) 2.858(1), Ru(1)-Ru(3) 2.765(1), Ru(1)-Ru(4) 2.742(1), Ru(2)-Ru(3) 2.713(1), Ru(2)-Ru(4) 2.743(1), C(2)-C(3) 1.466(4), C(1)-O(1) 1.210(4), Ru(1)-C(3) 2.124(3), Ru(3)-C(3) 2.244(3), Ru(4)-C(3) 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 $^1$H 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 $\pi$-bonded to the "wingtip" metal atoms and $\sigma$-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, $\beta$ 92.07(2)°, $V$ 2358 Å$^3$, $Z$ 4, $D_x$ 2.35 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) 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-$K_\alpha$ 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 $\psi$-scans were applied (transmissions 0.77–0.91). Cell constants were refined from $2\theta$ 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

1 Y. Blum and Y. Shvo, J. Organomet. Chem., 263 (1984) 93 and references therein; A. Basu, S. Bhaduri and K.R. Sharma, J. Organomet. Chem., 319 (1987) 407.

2 A. Basu, S. Bhaduri and H. Khwaja, J. Organomet. Chem., 319 (1987) C28; S. Bhaduri, K.S. Gopalkrishnan, W. Clegg, P.G. Jones, G.M. Sheldrick and D. Stalke, J. Chem. Soc., Dalton Trans., (1984) 1765; A. Basu, S. Bhaduri, K.R. Sharma, P.G. Jones and G.M. Sheldrick, Chem. Commun., in press.

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.