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Synthesis, X-ray structure, and catalytic properties of a ruthenium cluster with a carbohydrate ligand

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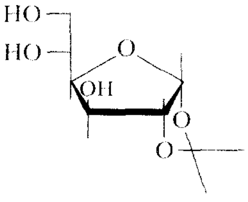
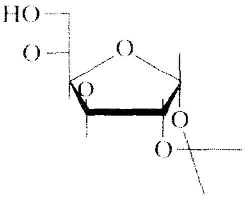
Abstract

The cluster $Ru_3(CO)_{12}$ reacts with 1,2-*O*-isopropylidene-α-D-glucofuranose (H_2L) or 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose to give $Ru_3(CO)_8(L)$, a chiral cluster with a carbohydrate ligand. The structure has been established by a single crystal X-ray diffraction study.

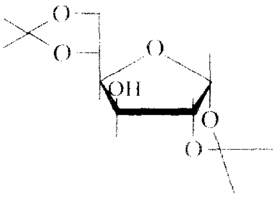
Ruthenium carbonyl clusters have recently been used as precatalysts in a variety of hydrogenation and transfer hydrogenation reactions [1]. Chiral derivatives are of potential use in asymmetric reactions of the same type. We report here the synthesis, characterisation, and catalytic properties of a triruthenium cluster $Ru_3(CO)_8(L)$ (**1**) obtained from the reaction of $Ru_3(CO)_{12}$ with 1,2-*O*-isopropylidene-α-D-glucofuranose (H_2L). Titanium complexes with similar carbohydrate ligands have recently been shown to have applications in organic syntheses [2]. To the best of our knowledge, **1** is the first example of a ruthenium carbonyl cluster with chirality based on a carbohydrate ligand.



(H_2L)



(L)



(L′)

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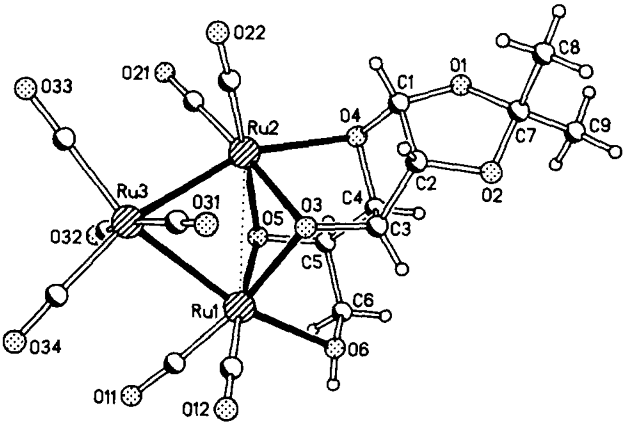

Fig. 1. The molecule of complex **1** in the crystal (radii are arbitrary; water of crystallisation omitted).

The cluster **1** was obtained from the reaction of $Ru_3(CO)_{12}$ with H_2L in cyclohexane at 80°C in 40% yield. It was separated from $H_4Ru_4(CO)_{12}$, the other major product, by thin layer chromatography with hexane/dichloromethane (1 : 1) as eluant. Cluster **1** was also obtained in lower yields (< 25%) by the reaction of $Ru_3(CO)_{12}$ with 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose (L′) in cyclohexane in the presence of traces of water. Changing the orientation of the hydroxyl group at C3 has a notable effect on the course of the reaction; no product could be isolated when 1,2 : 5,6-di-*O*-isopropylidene-α-D-allofuranose (L″) was used. The formulation of **1** is consistent with spectroscopic data *, and was confirmed by an X-ray structural study of crystals of its monohydrate grown from methanol/water. The molecular structure is shown in Fig. 1.

The metal atoms define an isosceles triangle with Ru(1)–Ru(2) 3.002 Å, a distance we consider too long to be regarded as a bond. Ru(3), which bears four CO groups, does not interact with the carbohydrate moiety, but Ru(2) and Ru(1) form bonds to O(3), O(5), O(4) and O(3), O(5), O(6) respectively. The structure analysis shows that oxygens O(3) and O(5) are deprotonated: all other H atoms (including those of water) were located, O(5) has a tetrahedral environment including a hydrogen bond to the water molecule, and O(3) is too close to a carbonyl oxygen to allow room for a hydrogen atom. Thus the short Ru–O bonds to O(5) and O(3) (av. 2.146 Å) involve the deprotonated oxygens, whereas Ru(1)–O(6) and Ru(2)–O(4) are appreciably longer (2.256, 2.377 Å). The NMR data also support this formulation; the signals from C(3) and C(5) in **1** show downfield shifts of *ca.* 4 and 7 ppm compared with the free ligand H_2L. The ligand L acts as a 10e donor, with three electrons each from O(3) and O(5) and two each from O(4) and O(6). The total number of valence electrons is therefore fifty, leading to the breaking of one metal–metal bond.

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* Spectroscopic data for **1**: IR (dichloromethane) 2098m, 2024s,sh, 2008vs, 1984m, 1928s cm^{-1}. ^1H NMR ($CDCl_3$ plus dmso-d_6) δ 6.36 (d, 1H), 4–4.5 (m, 6H), 1.43 (s, 3H), 1.31 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD) 113.3, 107.06, 86.91, 84.24, 79.67, 78.05, 66.14, 26.51, 26.01. The circular dichroism spectrum shows a positive Cotton effect at 340 nm. $[\alpha]^{25}$ 43.6 (c = 0.25, MeCOOEt).

Table 1

Hydrogenation and transfer hydrogenation with **1** [a]

Substrate	Conversion (%)	Enantiomeric excess (%)
α-Acetamidocinnamic acid [b]	25	17
Methyl α-acetamidocinnamate [b]	0	
Acetophenone [b]	14	5
Acetophenone [c]	22	10

[a] All reactions carried out with a 100:1 substrate to **1** molar ratio. [b] THF, 110°C, 200 p.s.i. of H_2, 6 h. No reaction at ambient temperatures up to 500 p.s.i. of H_2. [c] Propan-2-ol, 82°C, 12 h, hydrogen-transfer reaction.

Cluster **1** reacts with a mixture of CO and H_2 (1:1, 80°C, 200 p.s.i.) to give quantitative yields of $H_4Ru_4(CO)_{12}$ and H_2L. Since $Ru_3(CO)_{12}$ reacts selectively with L′, the reaction can be exploited to separate L′ (as H_2L) from an equimolar racemic mixture of L′ and L″.

The potential of **1** as a precatalyst for model hydrogenation and transfer hydrogenation reactions has been evaluated; some representative results are shown in Table 1. It is clear that **1** is a poor precatalyst both in terms of catalytic efficiency and optical induction. Work is in progress with phosphine-substituted derivatives of **1** and other easily available ruthenium clusters containing non-phosphine chiral ligands.

X-Ray structure determination of compound 1

Crystal data. $C_{17}H_{14}O_{14}Ru_3 \cdot H_2O$, $M = 763.51$, monoclinic, space group $P2_1$, $a = 10.943(2)$, $b = 9.532(2)$, $c = 12.804(2)$ Å, $\beta = 109.75(1)°$, $U = 1257.0$ Å^3, $Z = 2$, $D_x = 2.017$ Mg m^{-3}, $F(000) = 740$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu = 1.85$ mm^{-1}, $T = 293$ K.

Data collection and reduction. Brown prism 0.35 × 0.15 × 0.08 mm, Stoe 4-circle diffractometer, monochromated Mo-K_α radiation, $2\theta_{max}$ 55°, 6643 absorption-corrected intensities, 5755 unique (R_{int} 0.023), 5250 with $F > 4\sigma(F)$ used for all calculations (program system Siemens SHELXTL PLUS).

Structure solution and refinement. Ru atoms by hand interpretation of Patterson function, other atoms in difference syntheses. Anisotropic refinement on F to R 0.030, wR 0.030; H atoms using riding model; weighting scheme $w^{-1} = \sigma^2(F) + 0.00015F^2$; absolute configuration by η refinement ($\eta = -1.01(7)$, whereupon the structure was inverted for the final cycles); 315 parameters, S 1.2, max. Δ/σ 0.001, max. $\Delta\rho$ 0.7 e Å^{-3}. Further details of the structure determination (complete bond lengths and angles, atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD-55884.

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