

Preliminary communication

**CATALYTIC OLEFIN HYDROGENATION WITH
 NONACARBONYLTRIS(TRIPHENYLPHOSPHINE)TRIRUTHENIUM AND
 ITS DERIVATIVES. CRYSTAL STRUCTURE OF
 $[\text{Ru}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-PPh}_2)(\mu\text{-O=CPh})]$**

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Summary

The complexes $[\text{Ru}_3(\text{CO})_7(\text{PPh}_2)_2(\text{C}_6\text{H}_4)]$ and $[\text{Ru}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-PPh}_2)(\mu\text{-O=CPh})]$ were obtained by pyrolysis of $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ and tested as catalysts for the hydrogenation of cyclohexene and 2-cyclohexen-1-one. The structure of $[\text{Ru}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-PPh}_2)(\mu\text{-O=CPh})]$ was established by a single crystal X-ray diffraction study.

In recent years tertiary-phosphine-substituted derivatives of $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ have been used as homogeneous catalysts primarily, but not exclusively, for hydrogenation reactions [1]. In these reports the desirability of phosphine-substituted carbonyl clusters as catalysts arises from the following considerations: first, the stabilities of the substituted derivatives are usually greater than that of $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ under a particular set of reaction conditions; secondly, clusters substituted with chiral phosphines have been shown to be capable of influencing the enantiomeric distribution of the products. To the best of our knowledge $[\text{Ru}_3(\text{CO})_9\text{L}_3]$ ($\text{L} = \text{PR}_3$) has not been tested as a homogeneous hydrogenation catalyst. This paper describes the catalytic activities of $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ (I) and of derivatives obtained from mild pyrolysis of I. We also report a single crystal X-ray structure determination of $[\text{Ru}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-PPh}_2)(\mu\text{-O=CPh})]$ (II), one of the derivatives thus obtained.

Results and discussion

Complex I shows moderate activity as a catalyst for the hydrogenation of olefins (see Table 1, Experiment (i) and (ii)); as the reactions proceed the colour of the solutions changes from purple to orange-red. At the end of the reactions the known [2] hydrido carbonyls $[\text{H}_4\text{Ru}_4(\text{CO})_{12-x}(\text{PPh}_3)_x]$ ($x = 1$ to 4) can be isolated from the reaction mixture. Increasing the initial hydrogen pressure has no significant effect on the yields of the saturated products, but at the end of the reaction $[\text{H}_4\text{Ru}_4(\text{CO})_8(\text{PPh}_3)_4]$ is isolated almost exclusively ($> 80\%$) from the reaction mixture. A control experiment between I and hydrogen in the absence of olefin shows that the formation of the hydrido carbonyls is not dependent on the presence of the olefinic substrate.

An increase in temperature without a simultaneous increase in the initial pressure of hydrogen results in significantly higher conversion in the hydrogenation of 2-cyclohexen-1-one. However, infrared spectroscopy during the reaction indicates that the catalytic intermediates in this case are not the tetraruthenium hydrido carbonyls. The carbonyl complex isolated at the end of the catalytic run is found to be $[\text{Ru}_3(\text{CO})_7(\text{PPh}_2)_2(\text{C}_6\text{H}_4)]$ (III); its catalytic activity has thus been independently tested. While III shows higher catalytic activity than I for the hydrogenation of 2-cyclohexen-1-one, the activities for the hydrogenation of cyclohexene are comparable. An X-ray structure determination of III has recently been reported [3]. Since it contains a benzyne ligand, III was also tested as a catalyst for aromatic ring hydrogenation reactions. III is inactive with respect to ring hydrogenation but shows moderate activity for the hydrogenation of nitrobenzene to aniline (see Table 1, Experiment (v) and (vi)). In this case, the solution IR spectra remain unchanged throughout the reaction and thus no other species is formed to a detectable extent.

Pyrolysis of I in refluxing decalin (b.p. 197–196°C) is known [4] to give a variety of di- and tri-nuclear ruthenium carbonyls including III. We find that pyrolysis of I at lower temperatures ($\sim 109^\circ\text{C}$) increases the yields of III

TABLE 1^a

Experiment	Catalyst	Reactant	Products (turnover number/h)
(i)	I	2-Cyclohexen-1-one	Cyclohexanone (2.0), Cyclohexanol (1.3)
(ii)	II	Cyclohexene	Cyclohexane (3.1)
(iii)	III	2-Cyclohexen-1-one	Cyclohexanone (13.0) Cyclohexanol (1.0)
(iv)	III	Cyclohexene	Cyclohexane (3.8)
(v)	III	Benzene	No reaction ^b
(vi)	III	Nitrobenzene	Aniline (2.0)
(vii)	II	2-Cyclohexen-1-one	Cyclohexanone (9.8), Cyclohexanol (1.5)
(viii)	II	Cyclohexene	Cyclohexane (3.5)

^a All reactions carried out with an initial hydrogen pressure of 25 psi at 70°C, 0.025 mmol catalyst, 0.5 mmol of reactant for 5 h with cyclohexane as solvent. Neat cyclohexene was used as solvent in experiment (ii), (iv) and (viii). Reported procedures [7] were adopted to show that decomposition to metal particles did not take place under the reaction conditions. ^b No reaction with initial hydrogen pressure of 100 psi.

substantially. Under these conditions a new dinuclear acyl complex $[\text{Ru}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-PPh}_2)(\mu\text{-O=CPh})]$ (II) is also formed in low yields; it was characterized by X-ray structure determination. II has similar catalytic activity to III for cyclohexene hydrogenation. However, it is evident on the basis of infrared spectroscopy that under the conditions employed, II acts as a catalyst precursor and undergoes conversion to some other, as yet uncharacterized, carbonyl species. It was tested as a catalyst for ring and nitrobenzene hydrogenations and found to be inactive in both cases.

It is interesting to note that an equivalent formulation of II, " $\text{Ru}_2(\text{CO})_6(\text{PPh}_3)_2$ " can be arrived at by removing one of the three " $\text{Ru}(\text{CO})_3(\text{PPh}_3)$ " units from the parent compound I. The steric strain in I may lead to the formation of this unsaturated species, which may then undergo intramolecular rearrangement to II. Synthesis and crystal structure have recently been reported [5] for the μ -acyl-phosphido-bridged diruthenium complex $[\text{Ru}_2(\text{CO})_6(\mu\text{-O=CCHC}(\text{Ph})\text{NEt}_2)(\text{PPh}_2)]$ (IV). The Ru—Ru bond lengths (2.750(1) and 2.7540(5) Å), acyl C—O bond lengths (1.262(3) and 1.275(6) Å) and Ru—P—Ru angles of the bridging phosphido groups (71.4(1) and 71.6(0)°) for II and IV, respectively, indicate that phosphine substitution of a carbonyl group or changing the 'R' group in the bridging 'RCO' unit has little effect on the overall structure.

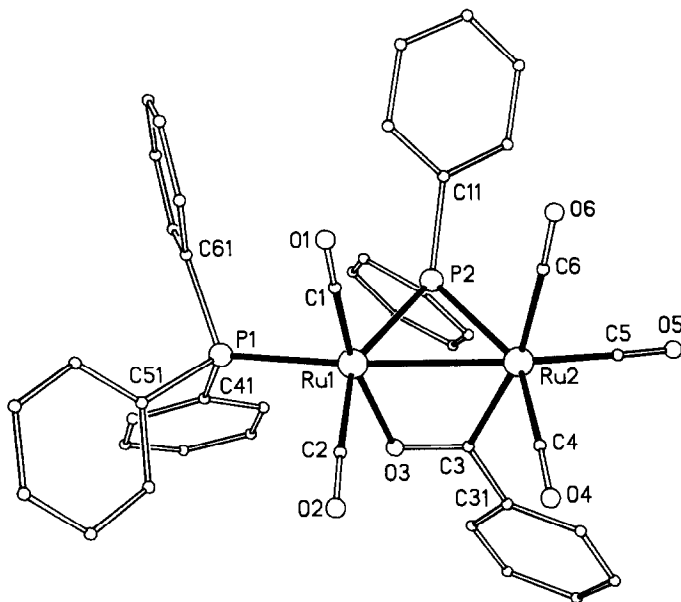


Fig. 1. The structure of II in the crystal, showing the atom numbering scheme (radii arbitrary, H atoms omitted). Selected bond lengths (Å): Ru(1)—Ru(2) 2.750(1), Ru(1)—P(1) 2.387(1), Ru(1)—P(2) 2.365(1), Ru(1)—O(3) 2.158(2), Ru(2)—P(2) 2.349(1), Ru(2)—C(3) 2.082(2), C(3)—O(3) 1.262(3). The Ru(1)—O(3)—C(3)—Ru(2) unit is planar (r.m.s. deviation 0.03 Å) and makes a dihedral angle of 84.5° with the Ru(1)—P(2)—Ru(2) plane.

Experimental

Synthesis of I and the catalytic experiments were carried out as previously reported [4,6].

Pyrolysis of I. Complex I (0.15 mmol) was refluxed in sodium-dried degassed toluene (50 ml) under nitrogen for 5 h. The colour of the solution changed from intense purple to faint purple-red. After removal of toluene the products were subjected to thin layer chromatography with hexane and dichloromethane (90/10) as eluant. Two bands, a purple one followed by a yellow-green, were obtained. Both the bands were isolated and the products were recrystallized from hexane. The purple band gave III (0.11 mmol) which was characterized on the basis of IR in cyclohexane: 2057s, 2020s, 2009vs, 1998s, 1968s, 1955s, cm^{-1} and by its unit cell constants [3]. The yellow-green band gave II (0.03 mmol). IR in cyclohexane: 2080w, 2054s, 2006vs, 1996s, 1948m, 1590m cm^{-1} . ^1H NMR, multiplet at δ 7.30 and 6.75 ppm, intensity ratio 5/1.

*Crystal data**. II, $\text{C}_{42}\text{H}_{30}\text{O}_6\text{P}_2\text{Ru}_2$, $M_r = 894.8$. Triclinic, $P\bar{1}$, a 9.987(2), b 10.923(3), c 18.708(4) Å, α 87.33(2), β 82.22(2), γ 70.98(2)°, U 1911.6 Å³, $Z = 2$, D_x 1.55 g cm^{-3} , $F(000) = 896$, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 0.9 mm^{-1} . 7950 profile-fitted reflections ($2\theta_{\text{max}}$ 55°), absorption correction from azimuthal scan data, crystal size 0.7 × 0.25 × 0.38 mm, 7846 unique data, 6953 with $F > 4\sigma(F)$ used for all calculations; heavy-atom method, final R 0.026, R_w 0.029 (non-H atoms anisotropic, isotropic H included in refinement using a riding model). See Fig. 1.

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*Further crystallographic details (atom coordinates, complete bond lengths and angles, structure factors, temperature factors) can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, F.R.G. Please quote reference number CSD 51412 and the full literature citation.