Isolation and *X*-Ray Structure of [(μ-H)$Ru_3(CO)_9$(μ_3-PhNCPh)], the Catalytically Active Cluster in $Ru_3(CO)_{12}$-catalysed Transfer Hydrogenation of Benzylideneaniline

Amithaba Basu,[a] Sumit Bhaduri,[a]* Krishna Sharma,[a] and Peter G. Jones[b]

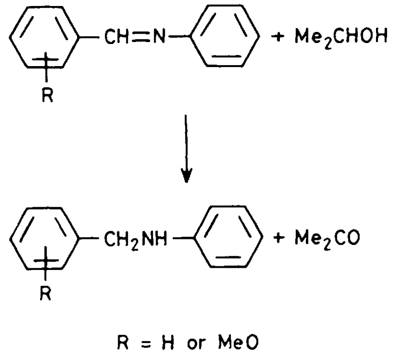
[a] *Alchemie Research Centre, P.O. Box 155, Thane-Belapur Road, Thane 400 601, Maharashtra, India*
[b] *Institut für anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, Federal Republic of Germany*

(μ-H)$Ru_3(CO)_9$(μ_3-PhNCPh) (**1**) has been isolated from an $Ru_3(CO)_{12}$-based catalytic system for the transfer hydrogenation of benzylideneaniline and found to be catalytically active; the *X*-ray structure of (**1**) is reported.

Homogeneous hydrogen-transfer reactions of a wide variety and synthetic utility are known to be efficiently catalysed by tri- and tetra-nuclear ruthenium clusters.[1] However, as for most other cluster-catalysed reactions, there is little direct evidence for the participation of cluster intermediates.[2] This is especially true for the precatalyst $Ru_3(CO)_{12}$, since it is generally converted into complexes that have not been structurally characterized. Using benzylideneaniline as the acceptor, propan-2-ol as the donor, and $Ru_3(CO)_{12}$ as the precatalyst (see Scheme 1), we have been able to test the catalytic activities of the isolable complexes formed during the reaction. The trinuclear ruthenium cluster (**1**), characterized by single crystal *X*-ray diffraction, has been found to be the only catalytically active species. Furthermore, the observed catalytic activity with analogues of benzylideneaniline can be rationalized on the basis of the molecular structure of (**1**).

Conversion data on the transfer hydrogenation of benzylideneaniline and some of its analogues, with $Ru_3(CO)_{12}$ as the precatalyst, are presented in Table 1. After the catalytic reduction of benzylideneaniline itself, three ruthenium carbonyl complexes could be isolated by column chromatography. These were (**1**) (*ca.* 45%), [$Ru(CO)_2$-($PhN{=}CHC_6H_4)_2$] (*ca.* 30%), and an as yet unidentified species with multiple carbonyl bands in its i.r. spectrum (*ca.* 25%). The mononuclear complex was identified by comparison with an authentic sample.[3] Whereas (**1**) is catalytically active for the transfer hydrogenation of benzylideneaniline, the other two complexes are inactive. The species (**1**) can be recovered quantitatively at the end of the catalytic run.

The molecular structure of (**1**) is shown in Figure 1.† The ruthenium atoms define an isosceles triangle with one long and two short metal–metal bonds. The hydrogen-abstracted benzylideneaniline unit PhNCPh, acting as a five-electron donor, lies over the Ru_3 triangle, bonding to all the Ru atoms. It is probable that the NC moiety is randomly disordered. The long Ru–Ru bond is bridged *via* the lone pair of the nitrogen atom and a formal σ-bond from the carbon; a π-bond is formed to the other Ru atom. The hydride bridges the long Ru–Ru bond, as is usual in this type of compound. The C–N bond length corresponds to a bond order between 1 and 2. Although a few reports have appeared on the interaction between $Ru_3(CO)_{12}$ and ligands with imine groups, quantitative information on the metal/C–N interaction has remained elusive.[4]



Scheme 1

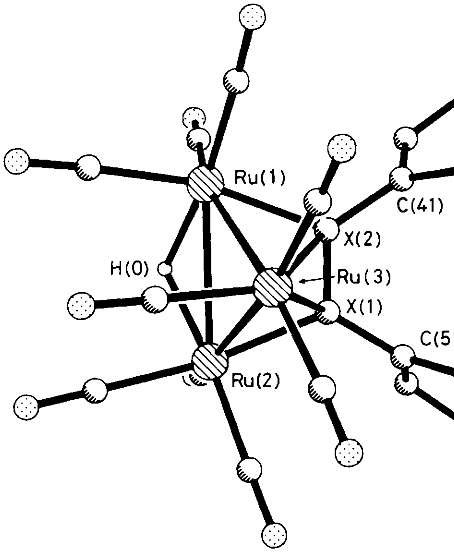


Figure 1. The molecule of (**1**) in the crystal, showing the atom numbering scheme; radii arbitrary, phenyl H omitted for clarity.

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† *Crystal data:* $C_{22}H_{11}NO_9Ru_3$, $M = 736.6$, monoclinic, $P2_1/n$, $a = 9.179(2)$, $b = 17.330(3)$, $c = 15.465(4)$ Å, $\beta = 102.56(2)°$, $U = 2401$ Å^3, $Z = 4$, $D_x = 2.03$ g cm^{-3}, $F(000) = 1416$, $\mu(\text{Mo-}K_\alpha) = 1.85$ mm^{-1}, crystal size 0.6 × 0.4 × 0.25 mm (orange prism). Data collection and reduction: 6431 profile-fitted intensities[5] measured with Stoe-Siemens four-circle diffractometer ($2\theta_{max.}$ 57°), 6086 unique, 5318 with $F > 4\sigma(F)$ used for all calculations. Empirical absorption correction based on Ψ-scans. Cell constants refined from 2θ values of 40 reflections in the range 20—23°. Structure solution and refinement: heavy-atom method, refinement on F to $R = 0.028$, $R' = 0.028$. All non-H atoms anisotropic; bridging H located in difference map and refined freely; C and N atoms of C=N moiety indistinguishable and both refined as C with occupation factor 1 1/12. Weighting scheme $w^{-1} = \sigma^2(F) + 0.000075\ F^2$. Selected bond lengths (Å): Ru(1)–Ru(2) 2.931(1), Ru(1)–Ru(3) 2.706(1), Ru(2)–Ru(3) 2.716(1), Ru(1)–H 1.78(4), Ru(2)–H 1.79(4), Ru(1)–X(2) 2.092(2), Ru(2)–X(1) 2.081(2), X(1)–X(2) 1.357(3) (mixed C/N sites represented as 'X'). Full details of the crystal structure determination have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, W. Germany. All requests for this material should quote the reference number CSD 52408 and a full literature citation. Atomic co-ordinates, bond lengths and angles, and thermal parameters *only* have also been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Transfer hydrogenations with $Ru_3(CO)_{12}$.[a]

Substrate	Conversion (%)
PhCH=NPh	80
o-$MeOC_6H_4CH$=NPh	0
m-$MeOC_6H_4CH$=NPh	47
p-$MeOC_6H_4CH$=NPh	45

[a] All reactions were carried out at 82 °C with $Ru_3(CO)_{12}$ (32 mg, 0.05 mmol) and substrate (5 mmol) in propan-2-ol (15 ml). Reaction time was 5 h.

From Figure 1, it is apparent that an analogous structure derived from *o*-$MeOC_6H_4CH$=NPh would entail appreciable steric interaction between the carbonyls and the methoxy group. This presumably explains why no analogue of (**1**) can be isolated from the corresponding reaction and, in turn, the inability of $Ru_3(CO)_{12}$ to effect transfer hydrogenation of the *ortho*-derivative (Table 1).

Finally, it should be noted that (**1**) undergoes reversible carbonylation,‡ a reaction typical of unsaturated clusters.[2] This implies the availability of an unsaturated form of (**1**). Attempts to isolate the adduct $[HRu_3(CO)_{10}(PhNCPh)]$ as a solid result in decarbonylation and formation of (**1**). It is probable that the catalytic activity of (**1**) is associated with its unsaturated form.

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‡ $\nu_{max.}$ (hexane) $[HRu_3(CO)_{10}(PhNCPh)]$: 2098m, 2080w, 2064 vs, 2048s, 2026vs, 2010s, 2004sh,s, and 1990 m; (**1**): 2094s, 2070s, 2038vs, 2028s, 2008s, 2000s,sh, and 1984s cm^{-1}; δ_H $[(CD_3)_2CO]$ (**1**): 7.3 and −18.1; $[HRu_3(CO)_{10}(PhNCPh)]$ 7.2 and −14.6.

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