Ruthenium-cluster-catalysed Reductive Carbonylation of Nitrobenzene: X-Ray Structure of $[Ph_4P][Ru_3(CO)_{10}(PhNCHO)]$, a Catalytic Intermediate

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The ruthenium cluster $[Ph_4P][Ru_3(CO)_{10}(PhNCHO)]$ has been structurally characterised and shown to play an important role, along with its precursor $[Ph_4P][HRu_3(CO)_9(PhNCO)]$, in the hydroxide- or methoxide-promoted reductive carbonylation of nitrobenzene.

The selectivities and activities of $Ru_3(CO)_{12}$ -based catalytic systems in the reductive carbonylation of nitrobenzene are known to be greatly influenced by the solvents and anionic promoters.¹⁻³ Thus in a biphasic system with water as one of the solvents and HO⁻ as the promoter, aniline is the exclusive product.^{1b--d} However, with MeO⁻ as promoter and 2-methoxyethanol as the solvent, formanilide is preferentially formed.^{1a} Here we report the X-ray structure of the tetraphenylphosphonium salt of $[Ru_3(CO)_{10}(PhNCHO)]^-$ (1).[‡] We also present results that indicate involvement of (1) and its structurally characterised⁴ precursor, $[HRu_3(CO)_{9}-(PhNCO)]^-$ (2) in the overall catalytic cycle.

The carbonylation of (2) under ambient conditions leads to slow ($t_1 \ge 48$ h) but quantitative formation of (1), which has been isolated as salts of various cations. After many attempts, a crystal suitable for X-ray structure determination was obtained from the [PPh₄]⁺ salt.§ The crystal quality was however only moderate. As has been found for the analogous osmium clusters,⁵ the formamide ligand co-ordinates through the nitrogen and oxygen atoms across one edge of the ruthenium triangle (see Figure 1). The average Ru–Ru distances in (1) and (2) are 2.840 and 2.758 Å⁴ respectively. The N–C and C–O bond lengths, 1.30(2) and 1.25(2) Å in (1)

Crystal data for $[C_{24}H_{20}P]^+[C_{17}H_6NO_{11}Ru_3]^-: M = 1043$, orthorhombic, space group *Pbca*, a = 17.504(4), b = 17.384(6), c = 27.290(6) Å, U = 8304 Å³, Z = 8, $D_c = 1.67$ g cm⁻³, F(000) = 4112, λ (Mo- K_{α}) = 0.71069 Å, μ = 1.2 mm⁻¹. Yellow plate, 0.75 × 0.4 × 0.04 mm. Data were collected using a Stoe-Siemens four-circle diffractometer, monochromated Mo- K_{α} radiation, 7839 intensities to $2\theta_{\text{max}}$ 45°, 5382 unique (R_{int} 0.077), 2747 with $F > 4\sigma(F)$ used for all calculations (program system SHELX, locally modified by its author Prof. G. M. Sheldrick). Cell constants refined from 2θ values of 52 reflections in the range 20–22°. Absorption correction based on ψ -scans, with transmissions 0.70–0.78. Structure solution by the heavy-atom method, followed by full-matrix least squares refinement. Ru, P, N, O atoms anisotropic, C isotropic, idealised rigid phenyl groups in cation, H atoms at calculated positions using riding model. Final R 0.083, R_w 0.065. 261 Parameters, weighting scheme w^{-1} = $\sigma^2(F) + 0.0003 F^2$, S 1.5, max. $\Delta/\sigma 0.001$, max. $\Delta\rho 0.8 \text{ e} \text{ Å}^{-3}$. Full details of the crystal structure determination (atomic co-ordinates, bond lengths and angles, thermal parameters, and structure factors) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Fed. Rep. of Germany. Any request for this material should quote a full literature citation and the reference number CSD 53413. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

 $true [(Ph_3P)_2N]^+$ salt of (1) crystallises triclinic with approximate cell constants 10.77, 15.56, 16.57 Å, 109.3, 91.6, 100.7°. The crystal quality was however no better than that of the $[Ph_4P]^+$ salt, and no complete structure determination was attempted.



Scheme 1



Figure 1. The $[Ru_3(CO)_{10}(PhNCHO)]^-$ anion (1) in the crystal of its $[Ph_4P]^+$ salt. Radii are arbitrary; phenyl H omitted for clarity. Selected bond lengths (Å): Ru(1)-Ru(2) 2.865(2), Ru(1)-Ru(3) 2.871(2), Ru(2)-Ru(3) 2.773(2), N-C(11) 1.42(2), N-Ru(3) 2.17(1), N-C(17) 1.30(2), O(11)-C(17) 1.25(2), O(11)-Ru(2) 2.13(1).

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and 1.458(7) and 1.225(6) Å in (2), indicate considerable double bond character for the N–C bond in the formamido ligand.⁵ The hydrogen atom on the formamido carbon could not be located in the X-ray structure analysis, but is seen in the ¹H n.m.r. spectrum and is consistent with the absence of v_{X-H} (X = N or O) in the i.r. spectrum.¶

At ambient temperatures under a CO atmosphere both (1) and (2) react with water (t_1 ca. 2 h) to give formanilide and aniline respectively as the major ($\geq 80\%$) organic products, accompanied by the formation of Ru₃(CO)₁₂. Under similar conditions, reaction of (1) with methanol also leads to the formation of formanilide and Ru₃(CO)₁₂. Cluster (2) however remains largely ($\geq 80\%$) unreacted in methanol under CO over a period of 2 h. These observations can be rationalised according to equations (1) and (2). Finally, in a separate experiment, the reaction between [HRu₃(CO)₁₁]⁻ and PhNO₂ was found to lead to the formation of (2) in low yields ($\leq 10\%$).

$$1) + 2CO + ROH \rightarrow Ru_3(CO)_{12} + PhNHCHO + RO^-$$

$$(R = Me, H) \quad (1)$$

$$(2) + 2CO + H_2O \rightarrow Ru_3(CO)_{12} + PhNH_2 + HO^-$$
 (2)

Based on the above observations, a *model* catalytic cycle as shown in Scheme 1 may be proposed. Step (i) is a well-

established reaction that has been studied in detail.⁶ It is reasonable to assume that catalytic quantities of $[HRu_3(CO)_{11}]^-$ are also formed under conditions (protic solvents and MeO⁻ promoter) where trace quantities of water are likely to be present. Since step (iv) is considerably faster than step (iii), aniline is obtained quantitatively in the presence of large quantities of water. When only trace quantities of water are present, step (iv) is avoided to a considerable extent and formanilide is obtained as the major product.

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[¶] Selected data for (1): Satisfactory elemental analyses for $C_{53}H_{36}N_2P_2O_{11}Ru_3$, the [(PPh₃)₂N]⁺ salt, and $C_{41}H_{26}NPO_{11}Ru_3$, the [Ph₄P]⁺ salt. I.r. (CH₂Cl₂) 2076 w, 2060 w, 2018 s, 1992 vs, br., 1962 m, sh, 1942 m, 1856 vw, 1795 m, br. ¹H n.m.r. [(CD₃)₂CO] for the [Bu₄N]⁺ salt, δ 6.82 (s, 1H), 6.9 (m, 5H), no Ru–H signal between +10 and -60 p.p.m.