Synthesis and Crystal Structure of $[(Ph_3P)_2N][HRu_3(CO)_9(PhNCO)]$, a Ruthenium Cluster with a Phenyl Isocyanate Ligand

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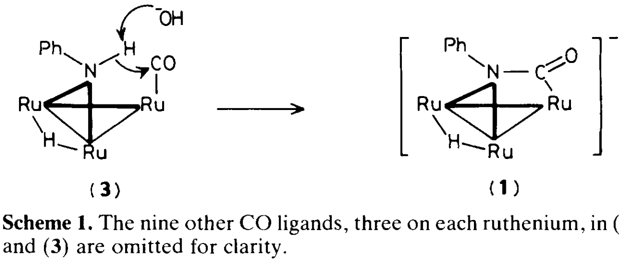
The ruthenium cluster $[PPN][HRu_3(CO)_9(PhNCO)]$ $\{[PPN] = (Ph_3P)_2N\}$ has been synthesised by intramolecular nucleophilic attack on CO and characterised by *X*-ray structure determination.

Reductive carbonylations of nitroaromatic compounds to produce isocyanates and carbamate esters are of considerable industrial importance.[1] Catalytic systems based on $Ru_3(CO)_{12}$ have been described that are selective for the formation of aniline,[2a,d] formanilide,[2a] carbamate esters,[2b] or phenyl isocyanate.[2c] Studies of the reactivity of metal clusters containing μ_3-NPh ligands and of their relevance in these catalytic systems have recently been reported.[3a—c] Here we report the isolation and structural characterisation of $[PPN][HRu_3(CO)_9(PhNCO)]$ (**1**) $\{[PPN] = (Ph_3P)_2N\}$ and its relationship with ruthenium clusters containing the μ_3-NPh ligand. Osmium clusters with *N*-arylformamido and related ligands have been reported,[4] but to our knowledge (**1**) is the first cluster in which phenyl isocyanate is bound to the metal framework.

The attempted carbonylation of μ_3-PhN clusters under a variety of thermal and photochemical conditions did not lead to PhNCO-containing clusters. We therefore resorted to an alternative strategy, involving intramolecular nucleophilic attack on a carbonyl ligand by a formal μ_2-NPh$^-$ moiety generated *in situ* (Scheme 1). The cluster $HRu_3(CO)_{10}(NHPh)$ (**3**) is obtained from the reaction of aniline with $Ru_3(CO)_{12}$.[5] Treatment of (**3**) with a stoicheiometric amount of KOH in methanol, followed by the addition of (PPN)Cl and evaporation of the solvent, gives a residue from which (**1**) can be extracted with diethyl ether.† In solution at



(**3**) (**1**)

Scheme 1. The nine other CO ligands, three on each ruthenium, in (**1**) and (**3**) are omitted for clarity.

$$\begin{tikzcd}[row sep=large, column sep=large]
\underset{(\mathbf{3})}{HRu_3(CO)_{10}(PhNH)} \arrow[r, shift left, "-CO"] \arrow[d, shift left, "OH^-"] & \underset{(\mathbf{4})}{H_2Ru_3(CO)_9(PhN)} \arrow[l, shift left, "+CO"] \arrow[d, shift left, "OH^-"] \\
\underset{(\mathbf{1})}{[HRu_3(CO)_9(PhNCO)]^-} \arrow[r, "-CO"] \arrow[u, shift left, "H^+"] & \underset{(\mathbf{2})}{[HRu_3(CO)_9(PhN)]^-} \arrow[u, shift left, "H^+"]
\end{tikzcd}$$

Scheme 2

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† *Selected data.* For (**1**): Satisfactory elemental analysis for $C_{52}H_{36}N_2P_2O_{10}Ru_3$. I.r. (CH_2Cl_2) 2066w, 2034s, 2006vs, 1980s,br, 1928w,sh, 1610m,br; cm^{-1}; ^{1}H n.m.r. (CD_2Cl_2): Ru–H at δ −14.0. For (**2**): Satisfactory elemental analysis for $C_{51}H_{36}N_2P_2O_9Ru_3$. I.r. (CH_2Cl_2) 2056w, 2026s, 1994vs, 1966s,br, 1915w,sh; cm^{-1}; ^{1}H n.m.r. (CD_2Cl_2): Ru–H at δ −16.3. A preliminary *X*-ray structure determination of (**2**) confirms the presence of the μ_3-NPh ligand (S. Bhaduri, H. Khwaja, P. G. Jones, and G. B. Carpenter, to be published).

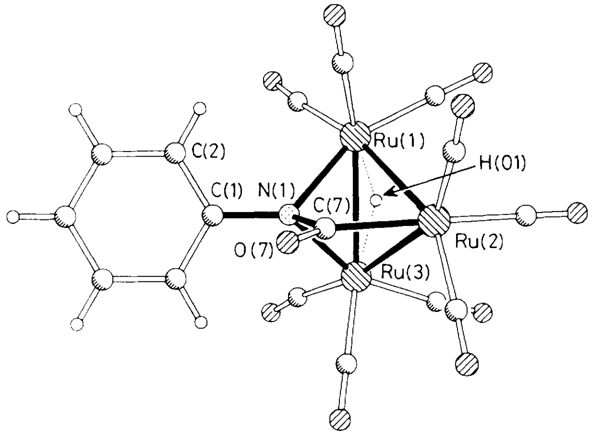

Figure 1. The $[HRu(CO)_9(PhNCO)]^-$ anion in the crystal of (**1**) (radii arbitrary). Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.753(1), Ru(1)–Ru(3) 2.773(1), Ru(2)–Ru(3) 2.749(1), Ru(1)–N(1) 2.139(4), Ru(2)–C(7) 2.040(6), Ru(3)–N(1) 2.147(4), Ru–H 1.74 (av.), C(1)–N(1) 1.444(7), N(1)–C(7) 1.458(7), C(7)–O(7) 1.225(6), C(1)–N(1)–C(7) 114.5(4), N(1)–C(7)–O(7) 120.3(5), N(1)–C(7)–Ru(2) 106.9(3).

25 °C, (**1**) undergoes irreversible loss of CO, forming the μ_3-NPh cluster (**2**) quantitatively (Scheme 2).† The cluster (**2**) can also be prepared by treating $H_2Ru_3(CO)_9(NPh)$ (**4**)[3c,5] with methanolic KOH.

Single crystal *X*-ray analysis established the structure of (**1**) (Figure 1).‡ The Ru–Ru bond lengths are similar to those in μ_3-NPh-capped ruthenium clusters[3c,7] and the hydride ligand, identified from the *X*-ray analysis, bridges Ru(1)–Ru(3). This position is consistent with potential energy calculations.[8] The bond lengths of the isocyanate group, N(1)–C(7) 1.458(7) and C(7)–O(7) 1.225(6) Å, are consistent with the assumption of an N–C single bond and a double C=O bond.

Although (**3**) and (**4**) are interconvertible, (**2**) cannot be recarbonylated to (**1**) at 25 °C and 300 p.s.i. Whereas the treatment of (**2**) with non-co-ordinating acids leads quantitatively to (**4**), only about 30% of (**3**) is obtained from (**1**) under similar conditions; $H_4Ru_4(CO)_{12}$, (**4**), and an as yet uncharacterised cluster are the other products (approximate yields 10, 40, 20%, respectively).

When heated at 80 °C under CO, (**1**) and (**2**) both give phenyl isocyanate (60%); at 80 °C under CO–H_2 (1 : 1), they both give aniline (100%). In both cases these are the sole organic products. This indicates that (**1**) may play an important role as a catalytic intermediate in the reductive carbonylation of nitrobenzene.

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‡ *Crystal data* for (**1**), $C_{52}H_{36}N_2O_{10}P_2Ru_3$, M = 1214, monoclinic, $P2_1/c$, a = 18.096(3), b = 16.453(3), c = 17.671(4) Å, β = 106.98(2)°, U = 5031.8 Å^3, Z = 4, D_c = 1.60 g cm^{-3}, $F(000)$ = 2416, μ(Mo-K_α) = 1 mm^{-1}. The structure was solved by the heavy atom method and refined anisotropically to R 0.051, R_w 0.039 for 5770 unique observed reflections.[6] Aromatic hydrogens were included using a riding model. The hydride ligand was located in a difference synthesis and refined subject to the restraint of equal Ru–H bond lengths. Further details of the structure determination (atomic co-ordinates, complete bond lengths and angles, thermal parameters, structure factors) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote the full literature citation and the reference number CSD 52760. Atomic co-ordinates, bond lengths and angles, and thermal parameters have also been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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