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## Preliminary Communication

# Synthesis and crystal structure of $Ru_3(CO)_6(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}CyNC)(CyNC)_2$ (Ph), an open trinuclear cluster complex containing an isocyanide ligand acting as a 4-electron donor

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### Abstract

Moderate heating of $Ru_3(CO)_{10}$(dppm) with CyNC (1:3) for 2 h under nitrogen, 68°C and purification by TLC affords moderate yield of the yellow complex $Ru_3(CO)_6(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}CyNC)(CyNC)_2(Ph)$ (1), which has been shown by X-ray crystallography to contain an open $Ru_3$ cluster with one isocyanide ligand acting as a 4e donor and bonded to all three metal atoms, representing a novel type of bonding of isocyanide on a $Ru_3$ cluster. Another interesting feature of 1 is the trapping on the cluster of the phenyl group lost from the dppm ligand.

*Key words:* Ruthenium; Phosphorus; Isocyanide; Cluster; Crystal structure

There is currently much interest in the extended interactions that are possible between unsaturated ligands and metal clusters but impossible in mononuclear complexes. Studies of such interactions may help understanding of the interaction between such molecules and metal surfaces, and hence of the mode of heterogeneous action of catalysts. Transition metal clusters containing isocyanide ligands are still relatively rare, especially those with isocyanide ligand not in a terminal bonding mode [1]. This communication reports the formation of an open $Ru_3$ complex with an isocyanide ligand acting as a 4-electron donor.

Moderate heating of $Ru_3(CO)_{10}$(dppm) and CyCN [Cy = cyclohexyl, $C_6H_{11}$] (1:3) for 2 h under nitrogen at 68°C followed by separation by TLC [Kieselgel $GF_{254}$, $CH_2Cl_2$/acetone/petroleum ether, 10:2:88 as eluant] affords moderate yields of a yellow complex $Ru_3(CO)_6(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}CyNC)(CyNC)_2(Ph)$ (1) (Found: C, 52.28; H, 4.61; N, 4.06; $C_{52}H_{55}O_6N_3P_2Ru_3$ calcd.: C, 52.79; H, 4.69; N, 3.55%), the structure of which has been determined by a single crystal X-ray diffraction study *.

The structure of 1 is shown in Fig. 1, with relevant bond distances and angles in the caption. There are a number of interesting features in this molecule. Thus it contains an open array of $Ru_3$ atoms capped by a dephenylated dppm ligand ($PPhCH_2PPh_2$) in the same way as in $Ru_3(\mu\text{-}H)(\mu_3\text{-}PhECH_2EPh_2)(CO)_9$ (E = P, As) [2] and $HRu_3(CO)_8(\mu\text{-}C_6H_4N_2)(\mu_3\text{-}PhAsCH_2AsPh_2)$ [3]. However, in the formation of these related complexes the Ph removed from the dppm ligand is lost, whereas in the formation of 1 it is trapped on the cluster bonded to one of the metal atoms [Ru(1)].

There are three isocyanide molecules attached to the complex, two of which are terminally bonded with the third bridging all three metal atoms. The usual 18e requirement suggests that this bridging isocyanide ligand acts as a four electron donor. The bond length ClNC–NlNC 1.294 (14) and the Cy–N–C angle of 121.1(9)° are consistent with the reduction in bond order, as in $Ru_5(CO)_{14}(CN^tBu)_2$ [4].

The bridging CNCy group lies across the open triangular face so that the C atom is bonded to the Ru(1)

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* Crystal data for $C_{52}H_{55}O_6N_3P_2Ru_3$: $M = 1183.2$, orthorhombic, space group $Pna2_1$, $a = 20.361(2)$, $b = 12.233(3)$, $c = 20.679(2)$ Å, $U = 5150.6$ Å$^3$, $Z = 4$, $D_c = 1.53$ g cm$^{-3}$, $\mu = 8.75$ cm$^{-1}$, 5036 independent reflections measured of which 3747 reflections with $I > 2.5\sigma(I)$ used in refinement. Determination of cell constants and data collection were carried out at room temperature with Mo-K$\alpha$ radiation on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. Data were recorded by a $2\theta/\theta$ scan and were corrected for Lorentz-polarization effects. The structure was solved by use of SHELXS86 [5] to reveal the Ru atoms and successive difference Fourier syntheses with SHELX76 [6] to reveal the remaining non-hydrogen atoms. The structure was refined by the blocked full-matrix least-squares procedure based on $F$ with the hydrogen atoms riding in calculated positions (C–H 0.96 Å) to a final $R = 0.0704$ ($R_{\text{enantiomer}} = 0.0707$) $R_w = 0.0747$ and ($R_{w\,\text{enantiomer}} = 0.0752$). All calculations were carried out on an IBM 4361/4381 computer at the Computer Centre of the Universiti Sains Malaysia.

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while the N=C moiety lies above the Ru(2)–Ru(3) bond. The π-interaction between N=C and Ru(2) and Ru(3) is confirmed by the short Ru(2)–Ru(3) distance [2.817(2) Å] which is appreciably shorter than the CO-bridged Ru(1)–Ru(2) bond [2.868(1) Å]. Such shortening of the M–M bond in isocyanide complex was also observed in $Fe_3(CO)_9(\mu_3$-$\eta^2$-$CN^tBu)$ [7].

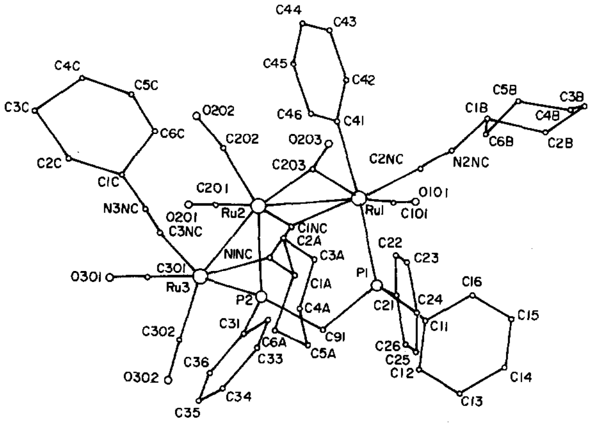

Fig. 1. PLUTO [8] plot of complex (12)($C_{52}H_{55}O_6N_3P_2Ru_3$). Selected atomic distances (Å) and angles (°): Ru2–Ru1 2.868(1), P1–Ru1 2.424(4), C41–Ru1 2.174(10), C(101–Ru1 1.850(11), C203–Ru1 2.513(13), C1NC–Ru1 1.980(9), C2NC–Ru1 2.053(13), Ru3–Ru2 2.817(2), P2–Ru2 2.333(4), C201–Ru2 1.885(11), C202–Ru2 1.915(15), C203–Ru2 1.950(14), C1NC–Ru2 2.115(9), P2–Ru3 2.307(3), C301–Ru3 1.844(12), C303–Ru3 1.886(13), N1NC–Ru3 2.140(10), C3NC–Ru3 1.977 (14); C2NC–Ru1–C101 92.7(5), C2NC–Ru1–C203 81.2(4), Ru3–Ru2–Ru1 106.9(1), P2–Ru2–Ru1 93.6(1), P2–Ru2–Ru3 52.2(1), C201–Ru2–Ru3 99.5(3), C201–Ru2–P2 89.4(4), C202–Ru2–Ru3 93.6(4), C202–Ru2–C201 94.6(6), C203–Ru2–Ru1 59.3(4), C203–Ru2–C201 91.8(5), C203–Ru2–C202 96.5(6), C1NC–Ru2–Ru1 43.6(3), C1NC–Ru2–Ru3 64.6(3), C1NC–Ru2–P2 76.5(3), C1NC–Ru2–C202 92.2(5), P2–Ru3–Ru2 53.0(1), C301–Ru3–Ru2 91.4(0.4), C301–Ru3–P2 92.1(4), C303–Ru3–C301 94.8(6), N1NC–Ru3–Ru2 73.0(3), N1NC–Ru3–P2 82.5(3), C3NC–Ru3–C301 93.4(6), C3NC–Ru3–C303 97.7(6), C3NC–Ru3–N1NC 85.8(5), P1–Ru1–Ru2 88.2(1), C41–Ru1–Ru2 88.9(3), C41–Ru1–P1 177.1(3), C101–Ru1–P1 96.1(4), C101–Ru1–C41 86.4(4), C203–Ru1–Ru2 41.8(3), C203–Ru1–P1 96.0(3), C203–Ru1–C41 81.6(4), C203–Ru1–C101 166.7(5), C1NC–Ru1–Ru2 47.5(3), C1NC–Ru1–P1 85.2(3), C1NC–Ru1–C41 93.1(4), C1NC–Ru1–C101 97.3(4), C1NC–Ru1–C203 89.2(4), C2NC–Ru1–Ru2 122.6(3), C2NC–Ru1–P1 92.8(4), C2NC–Ru1–C41 88.5(5).

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