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Preliminary communication

Synthesis and crystal and molecular structure of $\text{Os}_3(\text{CO})_9[1,1,1\text{-tris(isocyanomethyl)ethane}]$: a novel tris-isocyanide ligand capped triosmium cluster

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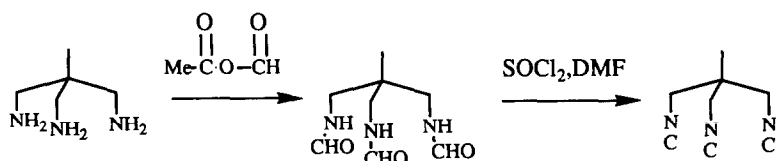
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Abstract

Reaction of 1,1,1-tris(isocyanomethyl)ethane (trisNC) (**3**) with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ gives the tripod-capped cluster $[\text{Os}_3(\text{CO})_9(\text{trisNC})]$ (**4**), which has been fully characterised by spectroscopic and X-ray crystallographic techniques.

A common feature of the chemistry of transition metal clusters is their breakdown to smaller clusters or mononuclear complexes, and this is particularly common for first row transition metal systems where the metal–metal bonds are weak [1]. A number of methods have been used to overcome this problem by stabilising polynuclear species in cluster-mediated chemical transformations. Metal–metal bonds may be stabilised by using bridging or capping phosphorus [2] or sulphur [3] donor ligands, or the metals may be “clamped” together by bi- or polydentate phosphine ligands [2]. There have been few attempts to use chelating ligands with N, C or O atoms as the donors, although the coordination of monodentate ligands with these donor atoms to clusters is very common. Previous attempts using the potentially tridentate ligand *cis,cis*-1,3,5-trisocyanocyclohexane in reactions with $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) failed to give a capped trimetal cluster product [4]. In this context, we now report the synthesis of a new and potentially tridentate isocyanide ligand, 1,1,1-tris(isocyanomethyl)ethane (**3**), and its reaction with the activated triosmium cluster, $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$, which gives a product, $[\text{Os}_3(\text{CO})_9(1,1,1\text{-tris(isocyanomethyl)ethane})]$ (**4**), in which the ligand caps the metal triangle.

The ligand 1,1,1-tris(isocyanomethyl)ethane (trisNC) (**3**) may be prepared conveniently in a two-step synthesis from the known compound **1** [5] (Scheme 1), and has been characterised by spectroscopic methods *. The reaction of **3** with the disubstituted triosmium cluster $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ [6], in CH_2Cl_2 , followed by



Scheme 1. Synthesis of the ligand 1,1,1-tris(isocyanomethyl)ethane.

purification by tlc affords the yellow product, $[\text{Os}_3(\text{CO})_9(\text{trisNC})]$ (**4**), in 55% yield. This complex has been characterised by spectroscopic techniques **, and the molecular geometry established by a single-crystal X-ray analysis.

The molecular structure of **4** *** is shown in Fig. 1, which includes some important bond parameters. The molecule sits on a crystallographic mirror plane which bisects the Os(2)–Os(2a) edge and passes through the Os(1), C(11), O(11), C(1), N(1), C(3), C(5) and C(6) atoms. The metal triangle is essentially equilateral, with an edge length ca. 0.03 Å longer than found in the parent osmium carbonyl, $[\text{Os}_3(\text{CO})_{12}]$ [7]. Each Os atom is co-ordinated to three terminal carbonyl ligands, two in equatorial sites and one in an axial site. The tridentate trisNC ligand symmetrically caps the metal triangle, and may be described as a tripod ligand. The Os–C(isocyanide) and C–N distances in **4** are similar to those reported in $[\text{Os}_3(\text{CO})_{11}(\text{CN}^t\text{Bu})]$ [8] and $[\text{Os}_3(\text{H})(\mu\text{-H})(\text{CO})_{10}(\text{CN}^t\text{Bu})]$ [9], where the isocyanide ligands occupy axial sites on the Os_3 triangle, the Os–C–N units are essentially linear, and the C–N–C fragments show only small deviations from linearity. The angle at C(5) are close to tetrahedral, consistent with formal sp^3 hybridisation for this atom. As observed previously [8,9], the axial Os–C (carbonyl) bonds, *trans* to the isocyanide, are slightly longer than the equatorial Os–C (carbonyl) bonds, *trans* to a metal–metal edge. This reflects the greater competition between the carbonyl and the isocyanide for π -electron density from the metal. The overall structure of **4** is reminiscent of that of $[\text{Ru}_3(\text{CO})_9\{\text{MeSi}(\text{PBu}_2)_3\}]$ [10], where the $(\text{MeSi}(\text{PBu}_2)_3)$ ligand acts as a tripod, co-ordinating to all three metals through the phosphorus donors. However, it should be pointed out that the ruthenium cluster could only be obtained in 16% yield and that donor atoms from the second row of the Periodic Table were required.

* 3 IR ($\nu(\text{NC})/\text{cm}^{-1}$) (CH_2Cl_2) 2145vs; ^1H NMR (CDCl_3) δ 3.51 (s, 6H, CH_2), 1.28 (s, 3H, CH_3); ^{13}C NMR (CDCl_3) δ 160.91 (s, N=C), 45.7 (s, CH_2); 38.29 (q, CCH_3); 18.05 (s, CH_3); mass spec., m/e 147.

** IR ($\nu(\text{CO})/\text{cm}^{-1}$) (CH_2Cl_2) 2054vs, 2007s, 1945s; ($\nu(\text{NC})/\text{cm}^{-1}$) 2245vw, 2204w, 2161m; ^1H NMR (CD_2Cl_2) δ 3.52 (s, 6H, CH_2); 1.28 (s, 3H, CH_3); mass spec., m/e 973.

*** Crystal data for **4**: $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_9\text{Os}_3$, M 973.9, monoclinic, a 8.378(2), b 11.872(2), c 10.714(2) Å, β 90.60(3)°, V 1065.6(4) Å³, Z = 2, D_c 3.035 g cm⁻³, $F(000)$ = 872, μ 179.24 cm⁻¹ for Mo- K_α radiation (λ 0.71069 Å), T 290 K, space group $P2_1/m$. The structure was determined by direct methods and refined to a minimum of $\sum w(F_o - F_c)^2$ from 1287 reflections with $2\theta < 45^\circ$ and $F > 4\sigma(F)$ (σ from counting statistics only) measured with a Stoe diffractometer and on-line profile fitting. Final R 0.024, wR 0.025 for 156 parameters including anisotropic thermal parameters for all non-hydrogen atoms and constrained hydrogen atoms. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

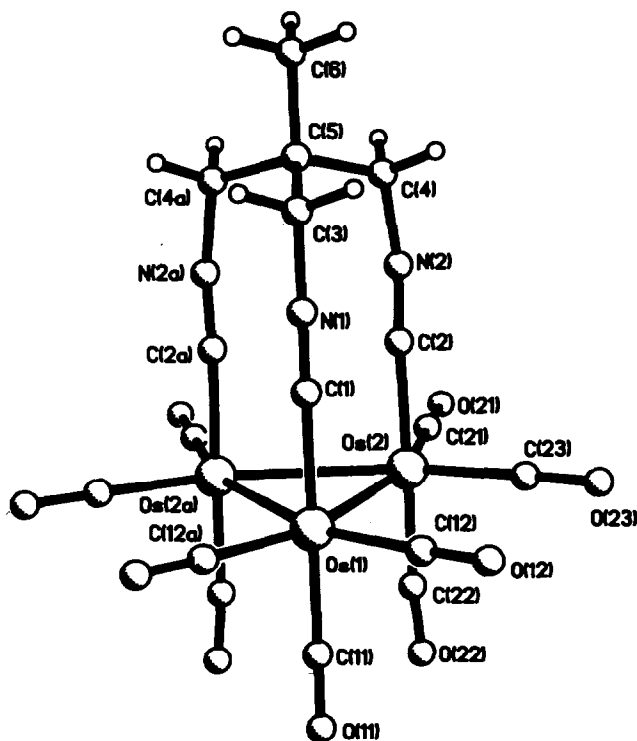


Fig. 1. The molecular structure of $[\text{Os}_3(\text{CO})_9(\text{trisNC})]$ (4) showing atom numbering scheme. Bond lengths: Os(1)–Os(2), 2.889(1); Os(2)–Os(2a), 2.903(1); Os(1)–C(1), 2.00(1); Os(2)–C(2), 1.99(1); C(1)–N(1), 1.17(2); C(2)–N(2), 1.17(2); N(1)–C(3), 1.41(2); N(2)–C(4), 1.44(2); C(3)–C(5), 1.52(2); C(4)–C(5), 1.50(1); Os(1)–C(11), 1.96(2); Os(1)–C(12), 1.90(1); Os(2)–C(21), 1.89(1); Os(2)–C(22), 1.93(1); Os(2)–C(23), 1.90(1) Å; bond angles: Os(2)–Os(1)–Os(2a), 60.3(1); Os(1)–Os(2)–Os(2a), 59.8(1); C(11)–Os(1)–C(1), 176.7(6); C(22)–Os(2)–C(2), 178.3(4); Os(1)–C(1)–N(1), 177.0(12); Os(2)–C(2)–N(2), 176.4(6); C(1)–N(1)–C(3), 170.2(13); C(2)–N(2)–C(4), 169.1(8); N(1)–C(3)–C(5), 117.4(11); N(2)–C(4)–C(5), 115.4(8); C(3)–C(5)–C(4), 111.4(7), C(4)–C(5)–C(4a), 111.9(10); C(3)–C(5)–C(6), 109.2(10); C(4)–C(5)–C(6), 106.4(7)°.

Treatment of $[\text{Os}_3(\text{CO})_9(\text{tricNC})]$ (4) with $\text{Me}_3\text{NO}/\text{MeCN}$ followed by addition of a further equivalent of 3 affords the disubstituted complex, $[\text{Os}_3(\text{CO})_6(\text{trisNC})_2]$ (5), in moderate yield. In this product it is assumed that the second tris NC ligand also caps the Os_3 triangle to give the bicapped structure as shown in Fig. 2.

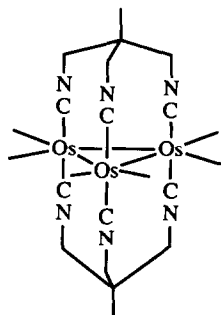


Fig. 2. Possible structure for $[\text{Os}_3(\text{CO})_6(\text{trisNC})_2]$ (5).

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