

Characterisation of an Osmium Cluster Carbonyl Containing a Weakly Co-ordinated Amine Ligand; X-Ray Crystal and Molecular Structure of $[\text{Os}_3(\text{CO})_9(\text{NO})_2(\text{NMe}_3)]$

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Summary The X-ray structure of the first trialkylamine metal cluster, $[\text{Os}_3(\text{CO})_9(\text{NO})_2(\text{NMe}_3)]$, has been determined; the large steric requirements of the trialkylamine is reflected in the long Os-N distance of the co-ordinated group.

ONE of the most effective methods for initiating ligand substitution reactions¹ in metal carbonyl systems, under relatively mild conditions, has been the use of trialkylamine oxide in the presence of the ligand. The success of the method depends upon the facility of the reagent to create a vacant co-ordination site by oxidation of a bonded carbon monoxide to carbon dioxide. Owing to the low co-ordination ability of the trialkylamine generated because of the large bulk and high steric restraints of the amine, the other ligand groups present may then favourably compete for this co-ordination site. The application of this reagent to cluster carbonyls has been successfully employed for $[\text{Os}_3(\text{CO})_{12}]$ and, using this method because of the mild conditions of the reaction, it has been possible to prepare hitherto inaccessible derivatives.²

The extension of this reagent to higher clusters of osmium has been less successful as significant concentrations of complexes with co-ordinated tertiary amine have been isolated. The presence of co-ordinated amine has been established in the complex $[\text{Fe}(\text{CO})_4(\text{NMe}_3)]$.³ Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NO})_2]$ with trimethylamine oxide under normal conditions has been found to yield a product involving a co-ordinated amine $[\text{Os}_3(\text{CO})_9(\text{NO})_2(\text{NMe}_3)]$. The i.r. spectrum of this complex has absorption bands at 2103 m, 2075 w, 2062 s, 2023 vs, 2003 s, 1993 m, and 1943 m

(cm^{-1}) which were assigned to carbonyl vibrations, and one at 1443 m (cm^{-1} , CHCl_3 solvent) due to the nitrosyl ligand. The ^1H n.m.r. spectrum showed a singlet at τ 7.37, and the molecular ion in the mass spectrum occurred at m/e 943, indicating the presence of a co-ordinated amine. We have undertaken the X-ray structure analysis of this compound to establish the co-ordination requirements of the tertiary amine group, and determine the steric restraints involved with this ligand group.

Crystals of the complex were obtained in the form of brown, elongated rectangular blocks, and were mounted in 0.5 mm Lindemann capillaries under nitrogen since the compound was slightly air-sensitive.

Crystal data: $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_{11}\text{Os}_3$, $M = 941.82$, triclinic, $a = 12.859(3)$, $b = 10.549(2)$, $c = 17.356(5)$ Å, $\alpha = 112.63(2)^\circ$, $\beta = 99.52(2)^\circ$, $\gamma = 93.62(2)^\circ$, $U = 2122.3$ Å³, $Z = 4$, $D_c = 2.95$ g cm^{-3} ; $\mu(\text{Mo-K}\alpha) = 179.6$ cm^{-1} , space group $P\bar{1}$. 10,134 intensities ($2\theta_{\text{max}} = 60.0^\circ$) were measured on a Syntex P2₁ diffractometer using graphite monochromated Mo-K α radiation. Data were corrected for Lorentz-polarisation factors and for absorption, and merged to give 5739 unique observed intensities [$I > 5\sigma(F)$]. The six unique Os atoms were located by multisolution Σ_2 sign expansion, and the C, N, and O atoms from a subsequent electron-density difference synthesis. The methyl hydrogens were constrained to lie in geometrically idealised positions (C-H, 1.08 Å; H-C-H, 109.5°), and the methyl groups refined as rigid bodies. The structure was refined by blocked cascade least-squares (Os anisotropic, C, N, and O isotropic, H common isotropic) with a weighting scheme $\omega = [\sigma^2(F) + 0.00145 F^2]^{-1}$. The final residuals were $R = 0.055$ and $R^1 = [\Sigma\omega^2\Delta/\Sigma\omega^2 |F_o|] = 0.057$.

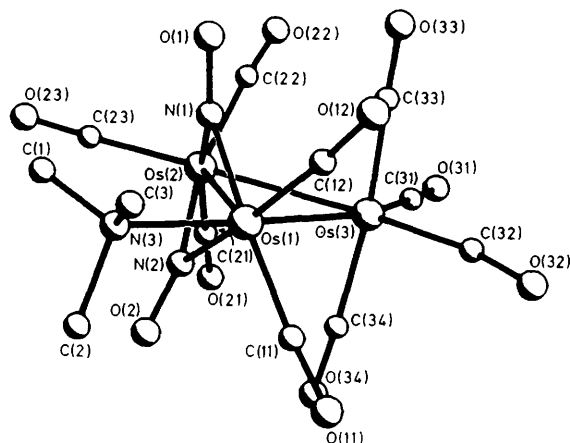


FIGURE. The molecular geometry of $[\text{Os}_3(\text{CO})_9(\text{NO})_2(\text{NMe}_3)]$, including the atom number scheme. Hydrogen atoms have been omitted for clarity. Bond lengths: Os(1)–Os(2), 3.197(2); Os(1)–Os(3), 2.885(2); Os(2)–Os(3), 2.875(2); Os(1)–N(1), 2.05(1); Os(1)–N(2), 2.05(1); Os(1)–N(3), 2.22(2); Os(2)–N(1), 2.05(1); Os(2)–N(2), 2.05(1) Å; bond angles: Os(1)–N(1)–Os(2), 102.4(5)°.

The asymmetric unit contains two independent, but structurally similar molecules, one of which is shown in the Figure; some important bond parameters are also included. The co-ordination of tertiary amines to organometallic species is rare, and the use of the bulky nature of tertiary amines and the related secondary amides has been skilfully employed by Bradley and his co-workers to produce metals in low and unusual co-ordination environments.

In the amido species $[\text{Cr}(\text{NPr}^1_2)_3]^4$ and $[\text{W}(\text{NMe}_2)_6]^5$ the complexes are considered to be stabilised by N–M $p\pi-d\pi$ bonding with relatively short M–N bonding; the bulk of the ligands prevents co-ordination of other groups. In contrast, the N–Os distance in $[\text{Os}_3(\text{CO})(\text{NO})_2(\text{NMe}_3)]$ is long, and is only *ca.* 0.05 Å shorter than the Os–P distance of 2.27 Å in $[\text{Os}_3(\text{CO})_9(\text{NO})_2(\text{POMe})_3]^6$. The long Os–N bond length reflects the good 'leaving group' properties of this ligand as observed in the preparation of many derivatives of $[\text{Os}_3(\text{CO})_{12}]$ by reaction with Me_3NO .⁴ Typical H(methyl)–N(nitrosyl) and H(methyl)–C(carbonyl) contact distances are 2.70 and 2.81 Å, respectively, which are close to the sum of the van der Waals radii. A shorter Os–N bond length would result in severe steric congestion between the amine and the carbonyl and nitrosyl ligands in the cluster.†

The geometry of $[\text{Os}_3(\text{CO})_9(\text{NO})_2(\text{NMe}_3)]$ resembles that of $[\text{Ru}_3(\text{CO})_{10}(\text{NO})_2]^7$ with the NMe_3 ligand replacing an equatorial carbonyl group. The two nitrosyl ligands symmetrically bridge the same Os–Os edge. The long Os–Os distance suggests that there is little direct metal–metal bonding, and that the ' $\text{Os}_2(\text{NO})_2$ ' unit should be considered as an 'open 4-centre system' with the nitrosyls acting as 3-electron donors. The other Os–Os distances are similar to the average Os–Os bond length of 2.877(3) Å in $[\text{Os}_3(\text{CO})_{12}]$.⁸

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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