

Conversion of a Nitrile Ligand into an Amido Group on a Cluster Surface; X-Ray Characterisation of $[\text{HOs}_4(\text{CO})_{12}\{\mu_3\text{-N}(\text{CO})\text{Me}\}(\text{MPPh}_3)]$ ($\text{M} = \text{Au}$ or Cu)

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The reaction of $[\text{H}_3\text{Os}_4(\text{CO})_{12}(\text{NCMe})_2]^+$ with $[\text{N}(\text{PPh}_3)_2]\text{NO}_2$ yields $[\text{HOs}_4(\text{CO})_{12}\{\mu_3\text{-N}(\text{CO})\text{Me}\}]^-$ by a novel conversion of an acetonitrile ligand into an amido group on the cluster surface; the anion reacts with $[\text{MPPh}_3]^+$ ($\text{M} = \text{Au}$ or Cu) to produce the neutral derivatives $[\text{HOs}_4(\text{CO})_{12}\{\mu_3\text{-N}(\text{CO})\text{Me}\}(\text{MPPh}_3)]$ which have been characterised by X-ray diffraction.

The interaction of $[\text{N}(\text{PPh}_3)_2]\text{NO}_2$ (**1**) with metal clusters has been developed as a method for enhancing cluster reactivity. The following reactions of (**1**) have been observed: (i) nucleophilic nitrosylation of $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}$ or Os), $\text{H}_3\text{Os}_4(\text{CO})_{12}(\mu\text{-I})$, $\text{Ru}_5\text{C}(\text{CO})_{15}$, $\text{Ru}_6\text{C}(\text{CO})_{17}$, and $\text{Os}_{10}\text{C}(\text{CO})_{24}\text{I}_2$;!¹ (ii) double deoxygenation of (**1**) to form nitrido and isocyanate derivatives of Co, Rh, and Ir carbonyl clusters;² (iii) deprotonation of hydrido carbonyl metal clusters;³ (iv) incorporation of the nitrite ion within the cluster unit in $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$;⁴ (v) catalysis of substitution reactions in triruthenium compounds by (**1**).⁵

The reaction of the bis-acetonitrile cation $[\text{H}_3\text{Os}_4(\text{CO})_{12}(\text{NCMe})_2]^+$ (**2**) with (**1**) has been reported to afford the anionic species $[\text{HOs}_4(\text{CO})_{12}(\text{NCMe})_2]^-$, on the basis of spectroscopic data.⁶ Our recent investigation of this process has revealed a novel type of interaction in which oxygen is transferred from the nitrite ion to a co-ordinated acetonitrile ligand. The reaction is summarised in Scheme 1. Although incorporation of an amido group into a triosmium cluster can be achieved by displacement of the acetonitrile ligands in

$\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ in the presence of the appropriate amide under refluxing conditions,⁷ the reaction herein reported represents an unprecedented example of the conversion of an acetonitrile ligand into an amido group on a cluster surface. The anionic species $[\text{HOs}_4(\text{CO})_{12}\{\mu_3\text{-N}(\text{CO})\text{Me}\}]^-$ (**3**) was obtained in 50% yield as its $[\text{N}(\text{PPh}_3)_2]^+$ salt from the reaction of (**2**) with (**1**) in acetonitrile at room temperature.† Reaction of the cations $[\text{MPPh}_3]^+$ ($\text{M} = \text{Au}$ or Cu), formed from Ph_3PMCl in the presence of $\text{Tl}[\text{PF}_6]$, with (**3**) in CH_2Cl_2 solution at room temperature yields the neutral species $[\text{HOs}_4(\text{CO})_{12}\{\mu_3\text{-N}(\text{CO})\text{Me}\}(\text{MPPh}_3)]^\ddagger$ [$\text{M} = \text{Au}$ (**4**), or Cu (**5**)].

† Spectroscopic data: i.r., $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$, (**3**) 2045s, 2010s, 1992s, 1968sh, 1932sh, and 1658 cm^{-1} (amide); (**4**) 2096m, 2066s, 2029vs, 1989s, 1968sh, 1949sh, and 1600 cm^{-1} (amide); (**5**) 2088m, 2060s, 2027vs, 1990s, and 1600 cm^{-1} (amide); ¹H n.m.r. (CDCl_3), δ (**3**) 2.67 (Me, s) and -16.02 (OsH, s); (**4**) 2.58 (Me, s) and -18.57 (OsH, s); (**5**) 2.58 (Me, s) and -18.20 (OsH, s); satisfactory elemental analysis was obtained for (**3**).

Although the mechanism of the interaction between (1) and (2) has not been established, this reactivity shows the dual behaviour of the nitrite ion as both as deprotonating and a nucleophilic reagent.

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References

- 1 R. E. Stevens, T. J. Yanta, and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1981, **103**, 4981; J. Puga, R. Sánchez-Delgado, and D. Braga, *Inorg. Chem.*, 1985, **24**, 3971; K. Henrick, B. F. G. Johnson, J. Lewis, J. Mace, M. McPartlin, and J. Morris, *J. Chem. Soc., Chem. Commun.*, 1985, 1671; B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, M. McPartlin, and A. Sironi, *J. Organomet. Chem.*, 1983, **253**, C5; R. J. Goudsmit, P. F. Jackson, B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, M. D. Vargas, D. Braga, K. Henrick, M. McPartlin, and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1985, 1795.
 - 2 R. E. Stevens, P. C. C. Liu, and W. L. Gladfelter, *J. Organomet. Chem.*, 1985, **287**, 133.
 - 3 J. Puga, R. Sánchez-Delgado, A. Andriollo, J. Ascanio, and D. Braga, *Organometallics*, 1985, **4**, 2064; M. A. Collins, B. F. G. Johnson, J. Lewis, J. M. Mace, J. Morris, M. McPartlin, W. J. Nelson, J. Puga, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1983, 689.
 - 4 E. D. Morrison, G. L. Geoffroy, A. L. Rheingold, and W. C. Fultz, *Organometallics*, 1985, **4**, 1413.
 - 5 G. Lavigne and H. D. Kaesz, *J. Am. Chem. Soc.*, 1984, **106**, 4647.
 - 6 B. F. G. Johnson, J. Lewis, W. J. Nelson, J. Puga, P. R. Raithby, and K. H. Whitmire, *J. Chem. Soc., Dalton Trans.*, 1983, 1339.
 - 7 B. F. G. Johnson, J. Lewis, T. I. Odiaka, and P. R. Raithby, *J. Organomet. Chem.*, 1981, **216**, C56; T. I. Odiaka, *ibid.*, 1985, **284**, 95.
 - 8 D. Braga, B. F. G. Johnson, J. Lewis, J. M. Mace, M. McPartlin, J. Puga, W. J. H. Nelson, P. R. Raithby, and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1982, 1081.
 - 9 B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 314; D. Braga, K. Henrick, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, A. Sironi, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1983, 1131; B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. D. Vargas, D. Braga, and M. McPartlin, *J. Organomet. Chem.*, 1983, C59.
 - 10 SHELX76, G. M. Sheldrick, University of Cambridge, 1976.
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