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Synthesis, characterization and molecular structure of a triruthenium carbonyl cluster containing both phenylimido and nitrosobenzene ligands

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The μ_3-imido cluster $[Ru_3(CO)_{10}(\mu_3\text{-NPh})]$ reacted with an excess of nitrosobenzene in tetrahydrofuran to give $[Ru_3(CO)_7(\mu_3\text{-NPh})_2(\mu\text{-}\eta^2\text{-ONPh})_2]$ which consists of a triruthenium metal core capped on two sides by two phenylimido ligands with two nitrosobenzene moieties bridging the two non-bonding Ru···Ru edges *via* the nitroso group.

The reactivity of imido clusters $[M_3(CO)_{10}(\mu_3\text{-NPh})]$ (M = Fe,[1] Ru[2] or Os[3]) has been extensively investigated over the past decade. The ruthenium complex $[Ru_3(CO)_{10}(\mu_3\text{-NPh})]$ **1** is studied with enthusiasm as it possesses various synthetic utilities and the μ_3-imido ligands are believed to be key intermediates in the catalytic reduction of nitrobenzene.[4] It has also been shown that the μ_3-imido ligands will undergo coupling reactions with carbene and alkyne ligands to give carbamates[5] and pyridones.[6] Herein, we report the isolation of an unprecedented trinuclear carbonyl cluster containing both bridging phenylimido and nitrosobenzene ligands from the reaction of complex **1** with nitrosobenzene.

The imido cluster $[Ru_3(CO)_{10}(\mu_3\text{-NPh})]$ **1** reacts with an excess of nitrosobenzene in tetrahydrofuran (thf) at room temperature to give a dark green solid $[Ru_3(CO)_7(\mu_3\text{-NPh})_2(\mu\text{-}\eta^2\text{-ONPh})_2]$ **2**,† in 20% yield upon TLC separation on silica. The ^1H NMR spectrum of **2** in CD_2Cl_2 shows two multiplets with a relative intensity of 1 : 1 at δ 6.67 and 7.00 attributed to the protons of the phenyl rings. In the IR spectrum a signal due to a bridging carbonyl appears at 1885 cm^{-1}. The positive FAB mass spectrum of **2** exhibits an envelope centred at *m*/*z* 896 with an isotopic distribution characteristic of three ruthenium atoms. In order to elucidate the structure of **2** an X-ray analysis has been carried out on a dark green crystal grown by slow evaporation of an *n*-heptane solution at −20 °C.‡

The molecular structure of complex **2** is shown in Fig. 1 together with selected bond parameters. The metal framework consists of a triangular Ru_3 core triply capped on two sides by two phenylimido ligands together with two additional nitrosobenzene moieties bridging to two adjacent edges of the ruthenium triangle *via* the nitroso group in a μ-η^2 fashion. The phenylimido moieties symmetrically cap both sides of the isosceles triruthenium plane with an average Ru–N distance of 2.090 Å, similar to that observed in $[Ru_3(CO)_9(\mu_3\text{-NPh})_2]$ **3**.[9] Within the ruthenium triangle, only one direct metal–metal bond exists and this is bridged by a carbonyl group parallel to the triruthenium plane. The Ru(1)–Ru(1*) bond is rather short [2.601(2) Å] compared to the Ru–Ru bond length in **1** [2.746(5) Å].[10] The other two non-bonded Ru···Ru vectors are bridged by two nitrosobenzene moieties *via* the nitroso group in a μ-η^2 manner such that Ru(2) is *trans*-co-ordinated by two oxygen atoms [Ru–O 2.029(6) Å] while Ru(1) is co-ordinated by the nitrogen atom [Ru–N 2.051(7) Å] of a nitroso group. The N–O bond distance within the co-ordinated nitrosobenzene ligand [1.334(9) Å] is longer than that in free nitrosobenzene [1.265(4) Å][11] but is comparable to N–O bond distances in complexes such as $[Fe_2(CO)_6(\mu\text{-NCHMe}_2)(\mu\text{-}\eta^2\text{-ONCMe}_2)]$ [1.371(5)],[12] $[Fe_2(CO)_6(\mu\text{-NCMe}_2)(\mu\text{-}\eta^2\text{-ONCMe}_2)]$ [1.351(6)][13] and $[Co_2(cp)_2(\mu\text{-NCPh}_2)(\mu\text{-}\eta^2\text{-ONCPh}_2)]$ (cp = C_5H_5) [1.343(6) Å].[14] All of the reported complexes with μ-η^2-nitroso groups are dimetallic in nature with the metal–metal bond remaining intact. On the contrary, in cluster **2**, two Ru–Ru bonds are opened up by the μ-η^2-nitrosobenzene ligands resulting in a rather small separation (2.39 Å) between the N atoms of the phenylimido groups. The co-ordinated nitrosobenzene moieties are essentially planar with a maximum deviation of 0.02 Å. The phenyl rings of both the phenylimido and nitrosobenzene ligands are almost perpendicular to each other as evidenced by the dihedral angle of 94.4°. The triply

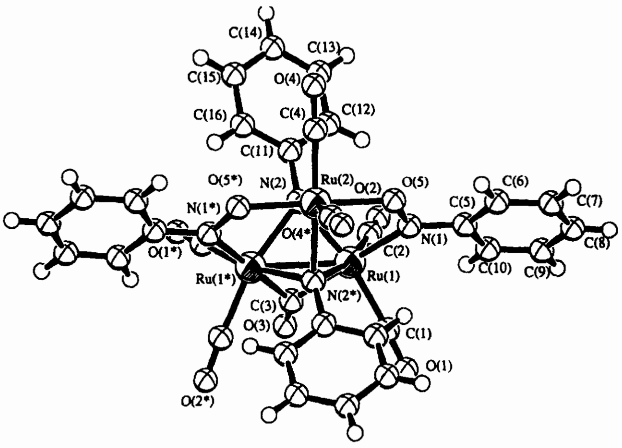

Fig. 1 Molecular structure of complex **2** showing the atom-numbering scheme, with selected bond distances (Å) and angles (°). Ru(1)–Ru(1*) 2.601(2), Ru(1)–N(1) 2.051(7), Ru(1)–N(2) 2.086(6), Ru(2)–N(2) 2.099(7), Ru(2)–O(5) 2.029(6), Ru(1)···Ru(2) 3.115(2), N(1)–C(5) 1.44(1), N(2)–C(11) 1.43(1), Ru(1)–N(2)–Ru(1*) 77.5(2), Ru(1)–N(2)–Ru(2) 95.9(3), Ru(1)–N(1)–O(5) 133.4(7), Ru(2)–O(5)–N(1) 116.7(5), Ru(1)–N(2)–C(11) 129.9(5), Ru(2)–N(2)–C(11) 118.1(5)

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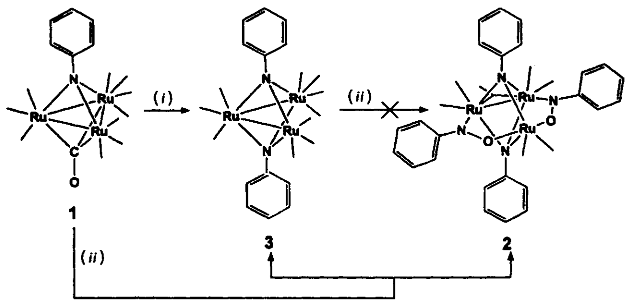
† Analytical data for complex **2** (Found: C, 25.10; H, 0.95; N, 2.85. $C_{31}H_{20}N_4O_9Ru_3$ requires C, 24.70; H, 1.00; N, 2.75%). IR [*n*-hexane, ν(CO)] 2084s, 2059s, 2049vs, 2027s, 2003s, 1885m cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.00 (m) and 6.67 (m). FAB mass spectrum: *m*/*z* 896 (calc. 896), M^+.

‡ Crystal data. **2** $C_{31}H_{20}N_4O_9Ru_3$, $M = 895.73$, monoclinic, space group *C*2/*c* (no. 15), $a = 15.024(3)$, $b = 10.181(4)$, $c = 21.922(3)$ Å, $\beta = 102.95(1)°$, $U = 3267(1)$ Å^3; $Z = 4$, $D_{calc} = 1.821$ g cm^{-3}, $F(000) = 1752$, Mo-Kα radiation, *T* 295 K, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 14.28 cm^{-1}. Dark green block, 0.20 × 0.20 × 0.22 mm. 2279 Unique data measured on a Rigaku AFC7R diffractometer ($2\theta_{max} = 45°$); 1673 observed reflections [$I > 3\sigma(I)$]. Absorption correction based on ψ-scan methods was applied. Structure solved by direct methods (SIR 92)[7] and Fourier-difference techniques, refined by full-matrix least-squares analysis on *F*, with non-hydrogen atoms refined anisotropically. $R = 0.041$ and $R' = 0.043$, $w = [\sigma^2(F_o)]^{-1}$. Calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[8] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/248.



Scheme 1 (*i*) PhNO, thf; (*ii*) excess PhNO, thf, room temperature

bridging phenylimido and the μ-η^2-nitrosobenzene ligands act as 4e and 3e donors respectively; the co-ordination sphere of **2** is completed by a total of seven terminal and bridging carbonyls to give a cluster valence electron count of 52 which is electron precise according to the effective atomic number rule if only one metal–metal bond is present.

From a structural point of view, it is tempting to propose the bis(phenylimido) cluster $[Ru_3(CO)_9(\mu_3\text{-}NPh)_2]$ **3**,[15] as an intermediate in the formation of **2**. However, the pre-formed cluster **3** does not react with excess nitrosobenzene under similar reaction conditions (Scheme 1) to those used to generate complex **2** from **1**.

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References

1 J. S. Song, S. H. Han, S. T. Nguyen, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1990, **9**, 2386.
2 S. Bhaduri, H. Khwaja, N. Sapre, K. Sharma, A. Basu, P. G. Jones and G. Carpenter, *J. Chem. Soc., Dalton Trans.*, 1990, 1313.
3 D. L. Ramage, G. L. Geoffroy, A. L. Rheingold and B. S. Haggerty, *Organometallics*, 1992, **11**, 1242.
4 S. Bhaduri, K. S. Gopalkrishnan, W. Clegg, P. G. Jones, G. M. Sheldrick and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1984, 1765.
5 G. D. Williams, R. R. Whittle, G. L. Geoffroy and A. L. Rheingold, *J. Am. Chem. Soc.*, 1987, **109**, 3936; S. H. Han, J. S. Song, P. D. Macklin, S. T. Nguyen, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1989, **8**, 2127.
6 S. H. Han, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1987, **6**, 2380.
7 G. Cascarano, L. Favia and C. Giacovazzo, SIR 92, *J. Appl. Crystallogr.*, 1992, **25**, 310.
8 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.
9 W. Clegg, G. M. Sheldrick, D. Stalke, S. Bhaduri and K. S. Gopalkrishnan, *Acta Crystallogr., Sect. C*, 1984, **40**, 927.
10 S. Bhaduri, K. S. Gopalkrishnan, G. M. Sheldrick, W. Clegg and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1983, 2339.
11 D. A. Dieterich, I. C. Paul and D. Y. Curtin, *J. Am. Chem. Soc.*, 1974, **96**, 6372.
12 S. Aime, G. Gervasio, L. Milone, R. Rossetti and P. L. Stanghellini, *J. Chem. Soc., Dalton Trans.*, 1978, 534.
13 G. P. Khare and R. J. Doedens, *Inorg. Chem.*, 1976, **15**, 86.
14 T. Carofiglio, S. Stella, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1989, 1957.
15 J. A. Smieja and W. L. Gladfelter, *Inorg. Chem.*, 1986, **25**, 2667.

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