

Preliminary communication

Synthesis and characterisation of hexanuclear ruthenium clusters containing a μ_4 -nitrene ligand. Crystal structures of $[\text{Ru}_6(\text{CO})_{15}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})\{\mu_3\text{-}\eta^2\text{-N}(\text{H})\text{C}(\text{O})\text{OMe}\}]$ and $[\text{Ru}_6(\text{CO})_{16}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})(\mu\text{-NCO})]$

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Abstract

Two hexaruthenium carbonyl clusters $[\text{Ru}_6(\text{CO})_{15}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})\{\mu_3\text{-}\eta^2\text{-N}(\text{H})\text{C}(\text{O})\text{OMe}\}]$ **1** and $[\text{Ru}_6(\text{CO})_{16}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})(\mu\text{-NCO})]$ **2** have been isolated from the pyrolysis of $\text{H}_2\text{Ru}_3(\text{CO})_9\text{NOCH}_3$, and single-crystal X-ray structure analysis shows that both **1** and **2** have a square planar arrangement of four ruthenium atoms capped by a μ_4 -nitrene ligand, with two additional ruthenium atoms bridging two opposite Ru–Ru edges of the square base to form a ‘boat’ form metal framework.

Keywords: Ruthenium; Clusters; Nitrene; Carbonyl; Crystal structure

Nitrosyl-containing metal clusters [1–3] have been investigated extensively owing to their higher reactivity towards electrophilic attack by alkylating agents [4]. However, little attention has been given to the reactivity of the O-alkylated nitrosyl compounds. Herein, we report a thermal coupling reaction of trinuclear ruthenium cluster containing a triply bridging methoxynitrido group, $[\text{H}_2\text{Ru}_3(\text{CO})_9\text{NOCH}_3]$ [4,5] to give Ru_6 nitrene clusters.

Heating of $[\text{H}_2\text{Ru}_3(\text{CO})_9\text{NOCH}_3]$ at 140°C for 2 hours¹ affords $[\text{HRu}_3(\text{CO})_{10}\text{NH}_2]$ [9] as the major

product (ca. 50%) along with two hexanuclear ruthenium clusters $[\text{Ru}_6(\text{CO})_{15}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})\{\mu_3\text{-}\eta^2\text{-N}(\text{H})\text{C}(\text{O})\text{OMe}\}]$ **1** and $[\text{Ru}_6(\text{CO})_{16}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})(\mu\text{-NCO})]$ **2**². Dark green crystals of **1** and dark blue crystals of **2** suitable for single crystal X-ray analysis were grown by slow evaporation

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¹ A sample of $\text{H}_2\text{Ru}_3(\text{CO})_9\text{NOCH}_3$ (200 mg, 0.333 mmol) was sealed in a Carius tube under reduced pressure. The tube was kept in an oven at 140°C for 2 hours. The dark green residue was then extracted with dichloromethane until the extract became colorless. The solvent was removed from the combined dark green extracts and the residue was chromatographed on TLC plate with n-hexane/dichloromethane mixture (9:1) as eluent. A green ($R_f \sim 0.45$) and blue band ($R_f \sim 0.4$), respectively yielded **1** and **2**, each in ca. 5% yield.

² Spectroscopic Data for **1**: IR (n-hexane) $\nu(\text{CO})$ 2095w, 2065vs, 2051s, 2025s, 2010vs, 2003s, 1993w and 1983w cm^{-1} ; ¹H NMR (CDCl_3): δ 5.55 (t, $\tau_{\text{NH}} = 46$ Hz, 1H), 3.75 (s, 3H), 2.83 (s, 3H) and -0.82 (br, 1H); FAB mass spectrum: m/z 1203, M^+ ; Elemental analysis (Found: C, 20.5; H, 0.6; N, 2.4%. $\text{C}_{20}\text{H}_8\text{N}_2\text{O}_{20}\text{Ru}_6$ Calc. C, 19.97; H, 0.67; N, 2.33%).

2: IR (n-hexane) $\nu(\text{CO})$ 2099w, 2071vs, 2056s, 2049s, 2039vs, 2012m, 1984w, 1875w and 1847w cm^{-1} ; ¹H NMR (CDCl_3): δ 5.70 (t, $\tau_{\text{NH}} = 43$ Hz, 1H) and 3.74 (s, 3H); FAB mass spectrum: m/z 1171, $(\text{M-CO})^+$; Elemental analysis (Found: C, 20.5; H, 0.3; N, 2.6%. $\text{C}_{20}\text{H}_4\text{N}_2\text{O}_{20}\text{Ru}_6$ requires C, 20.04; H, 0.34; N, 2.34%).

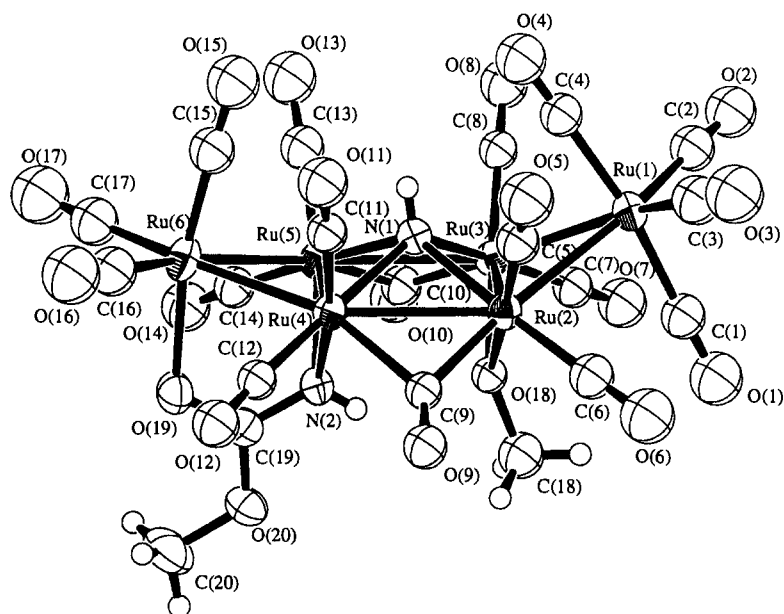


Fig. 1. The structure of $[\text{Ru}_6(\text{CO})_{15}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})\{\mu_3\text{-}\eta^2\text{-N(H)C(O)OMe}\}]$ **1** showing the atom numbering scheme. Selected bond distances (Å) and angles ($^\circ$): Ru(1)–Ru(2) 2.833(1), Ru(2)–Ru(3) 2.969(1), Ru(4)–Ru(6) 2.719(1), Ru(5)–Ru(6) 2.733(1), Ru(1)–Ru(3) 2.839(1), Ru(2)–Ru(4) 2.811(1), Ru(3)–Ru(5) 2.826(1), Ru(4)–Ru(5) 2.878(1), Ru(2)–O(18) 2.092(5), Ru(3)–O(18) 2.101(5), Ru(4)–N(2) 2.193(6), Ru(5)–N(2) 2.189(6), Ru(6)–O(19) 2.193(5), Ru(2)–N(1) 2.173(6), Ru(3)–N(1) 2.174(6), Ru(4)–N(1) 2.191(6), Ru(5)–N(1) 2.200(6), O(19)–C(19) 1.254(9), O(20)–C(20) 1.45(1), N(2)–C(19) 1.357(10), N(1)–H(1) 0.8(1), N(2)–H(8) 0.7(1), Ru(3)–Ru(2)–Ru(4) 89.06(3), Ru(2)–Ru(3)–Ru(5) 89.08(3), Ru(2)–Ru(4)–Ru(5) 91.24(3), Ru(4)–Ru(6)–O(19) 82.8(1), Ru(3)–Ru(5)–Ru(4) 90.62(3), Ru(4)–N(2)–Ru(5) 82.1(2), O(19)–C(19)–O(20) 120.1(7), O(20)–C(19)–N(2) 115.3(7).

of $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ (1:2) solution at 0°C ³. The molecular structures and selected bond parameters for **1** and **2** are shown in Figs. 1 and 2 respectively.

³ Crystal Data for **1**: $[\text{Ru}_6(\text{CO})_{15}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})\{\mu_3\text{-}\eta^2\text{-N(H)C(O)OMe}\}]$, $\text{C}_{20}\text{H}_8\text{N}_2\text{O}_{20}\text{Ru}_6$, $M = 1202.70$, Triclinic, space group $P\bar{1}$ (No. 2), $a = 11.773(4)$, $b = 15.993(9)$, $c = 9.367(2)$ Å, $\alpha = 94.00(2)$, $\beta = 107.92(2)$, $\gamma = 104.22(2)^\circ$, $U = 1606.5(7)$ Å³, $Z = 2$, $D_{\text{calc}} = 2.484$ g cm⁻³, $F(000) = 1132$, Mo K α radiation, temperature 298K, $\lambda = 0.71073$ Å, $\mu(\text{Mo K}\alpha) = 28.35$ cm⁻¹, green block $0.22 \times 0.26 \times 0.30$ mm, 3362 observed diffractometer data [$I > 3\sigma(I)$]. Structure solved by direct methods (SIR88) [10] and Fourier difference techniques, refined by full-matrix least-squares analysis (Ru, N and non-hydrogen atoms of N(H)C(O)OMe moiety anisotropic, hydrogen atoms attached to nitrogen atoms were located by difference Fourier synthesis, while other hydrogen atoms were generated in their idealized positions C–H, 0.96 Å) to $R = 0.031$, $R_w = 0.033$, $\omega = 4F_o^2 / [\sigma^2(F_o)^2 + 0.006(F_o^2)^2]$.

Crystal Data for **2**: $[\text{Ru}_6(\text{CO})_{16}(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})(\mu\text{-NCO})]$, $\text{C}_{20}\text{H}_4\text{N}_2\text{O}_{20}\text{Ru}_6$, $M = 1198.67$, Monoclinic, space group $P2_1/c$ (No. 14), $a = 9.094(4)$, $b = 11.718(4)$, $c = 30.334(4)$ Å, $\beta = 93.97(2)^\circ$, $U = 3224(1)$ Å³, $Z = 4$, $D_{\text{calc}} = 2.469$ g cm⁻³, $F(000) = 2248$, Mo K α radiation, $\lambda = 0.71073$ Å, temperature 298K, $\mu(\text{Mo K}\alpha) = 28.24$ cm⁻¹, blue needle $0.12 \times 0.14 \times 0.34$ mm, 1896 observed reflections [$I > 3\sigma(I)$]. Structure determined by a combination of direct methods (SIR88) [10] and difference Fourier techniques and refined by full-matrix least-squares analysis (Ru and N of the $\mu_4\text{-NH}$ group anisotropic, hydrogen atoms on $\mu_4\text{-NH}$ was located by difference Fourier synthesis while other hydrogen atoms were placed in their idealized positions C–H, 0.96 Å) to $R = 0.041$, $R_w = 0.043$, $\omega = 4F_o^2 / [\sigma^2(F_o)^2 + 0.003(F_o^2)^2]$. Program used teXsan [11]. Tables of atomic coordinates, thermal parameters, and a complete list of bond lengths and angles for both **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre.

The metal frameworks of **1** and **2** are structurally related as they both involve of a square planar arrangement of 4 ruthenium atoms, Ru(2)–Ru(3)–Ru(4)–Ru(5) symmetrically capped by a quadruply bridging nitrene ligand. The opposite edges of the square base are bridged by two additional ruthenium atoms which lie above the square plane on the side of the nitrene ligand to form a 'boat' form metal core similar to $[\text{Ru}_6(\text{CO})_{14}(\mu\text{-CO})_2(\mu_4\text{-S})\{\mu_3\text{-}\eta^2\text{-EtNCSNHEt}\}(\mu_3\text{-}\eta^2\text{-EtNCNHEt})]$ [6] and $[\text{Ru}_6(\text{CO})_{16}(\mu\text{-CO})_2(\mu\text{-OH})_2(\mu_4\text{-S})]$ [7]. The Ru(4)–Ru(5)–Ru(6) substructure of **1** is bridged by a $\mu_3\text{-}\eta^2\text{-N(H)C(O)OMe}$ ligand, and in **2** there is only a cyanato ligand bridging the edge Ru(4)–Ru(5). Both **1** and **2** have a bridging methoxy group at the edge Ru(2)–Ru(3) and two bridging carbonyls at Ru(2)–Ru(4) and Ru(3)–Ru(5). Their coordination spheres are completed by terminal carbonyls to give a Cluster Valence Electrons (CVE) count of 94 [6,7]. The nitrene N atom lies 0.81 Å for **1** and 0.82 Å for **2** above the square planar basal plane of Ru(2)–Ru(3)–Ru(4)–Ru(5), to form square pyramidal configuration. The average Ru–N distances of the nitrene are 2.185 Å and 2.190 Å for **1** and **2**, respectively, i.e. slightly longer than that in $[\text{Ru}_4(\text{NH})(\text{PhCCPh})(\text{CO})_{11}]$ [8] (2.145 Å). In **2** the dihedral angles between the plane Ru(2)–Ru(3)–Ru(4)–Ru(5) and Ru(1)–Ru(2)–Ru(3) as well as Ru(4)–Ru(5)–Ru(6) are 153.6° and 151.0° respectively. In **1** the dihedral angle between the plane Ru(2)–Ru(3)–Ru(4)–Ru(5) and Ru(1)–Ru(2)–Ru(3) is 150.6° . However, the dihedral angle between the plane Ru(2)–

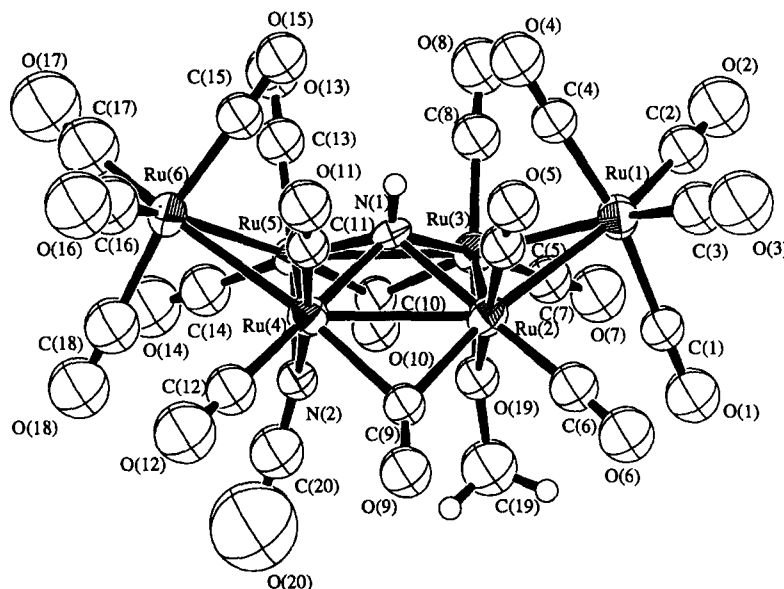


Fig. 2. The structure of $[\text{Ru}_6(\text{CO})_6(\mu\text{-CO})_2(\mu_4\text{-NH})(\mu\text{-OMe})(\mu\text{-NCO})]$ **2** showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.786(3), Ru(2)–Ru(3) 2.922(2), Ru(4)–Ru(6) 2.800(2), Ru(5)–Ru(6) 2.812(2), Ru(1)–Ru(3) 2.792(3), Ru(2)–Ru(4) 2.813(2), Ru(3)–Ru(5) 2.818(3), Ru(4)–Ru(5) 2.941(3), Ru(2)–O(19) 2.10(1), Ru(3)–O(19) 2.08(1), Ru(4)–N(2) 2.09(1), Ru(5)–N(2) 2.09(1), Ru(2)–N(1) 2.19(1), Ru(3)–N(1) 2.18(1), Ru(4)–N(1) 2.19(2), Ru(5)–N(1) 2.20(2), N(1)–H(1) 0.9(2), N(2)–C(20) 1.19(2), O(20)–C(20) 1.21(3), Ru(3)–Ru(2)–Ru(4) 90.38(7), Ru(2)–Ru(3)–Ru(5) 89.99(7), Ru(2)–Ru(4)–Ru(5) 89.70(6), Ru(2)–O(19)–Ru(3) 88.6(5), Ru(3)–Ru(5)–Ru(4) 89.90(6), O(20)–C(20)–N(2) 173(3), Ru(4)–N(2)–Ru(5) 89.4(6), Ru(5)–N(2)–C(20) 136(1).

Ru(3)–Ru(4)–Ru(5) and Ru(4)–Ru(5)–Ru(6) in **1** is increased to 168.3° owing to the chelating effect of the $\mu_3\text{-}\eta^2\text{-N(H)C(O)OMe}$ ligand. This N(H)C(O)OMe moiety in **1** can be regarded as a carbamate derivative, and is essentially coplanar (maximum deviation 0.023 Å).

The ^1H NMR spectrum of **1** exhibits two singlets at δ 3.75 and 2.83 due to methoxy group resonance and broad peaks at δ 5.55 and -0.82 that are assigned to the μ_4 -nitrene and the amido hydrogen, respectively. Similarly, the singlet at δ 3.74 and broad peak at δ 5.70 are assigned to the bridging methoxy group and the μ_4 -nitrene ligand, respectively, in the spectrum of **2**. The nitrene hydrogen atoms of **1** and **2** were located from difference Fourier synthesis at 0.8(1) and 0.9(2) Å from N(1). The distance is very similar to that in $\mu_4\text{-NH}$ in $[\text{Ru}_4(\text{NH})(\text{PhCCPh})(\text{CO})_{11}]$ [8]. We believe that the nitrene hydrogen comes from a hydride ligand of the $[\text{H}_2\text{Ru}_3(\text{CO})_9\text{NOCH}_3]$.

Acknowledgements

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