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Synthesis and structural characterisation of tetraruthenium μ_4-nitrene clusters containing tolylacetylene (HC_2Tol). Molecular structures of $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu_4\text{-}\eta^2\text{-}HC_2Tol)]$ and $[Ru_4(CO)_9(\mu\text{-}CO)_2\{\mu_4\text{-}NC(O)OMe\}(\mu_4\text{-}\eta^2\text{-}HC_2Tol)]$

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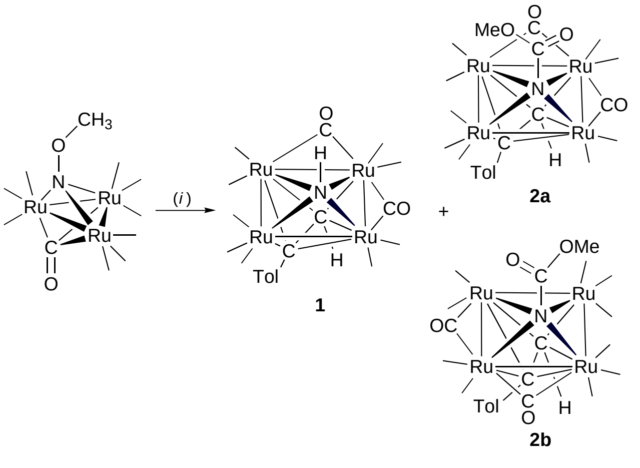
Two structurally characterized tetraruthenium carbonyl clusters, $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu_4\text{-}\eta^2\text{-}HC_2Tol)]$ **1** and $[Ru_4(CO)_9(\mu\text{-}CO)_2\{\mu_4\text{-}NC(O)OMe\}(\mu_4\text{-}\eta^2\text{-}HC_2Tol)]$ **2**, have been isolated from the reaction between $[Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)]$ and tolylacetylene (HC_2Tol) in refluxing *n*-octane.

The chemistry of transition-metal clusters containing a μ_4-nitrene ligand, in particular μ_4-NH, has not been well developed. In contrast, a large number of μ_3-nitrene clusters are known and they are found to be a key intermediate for the catalytic nitroarene carbonylation reactions.[1,2] Blohm and Gladfelter[3] have shown that protonation of the tetraruthenium nitrido cluster anion $[Ru_4(CO)_{12}(\mu_4\text{-}N)]^-$ in the presence of diphenylacetylene produced the μ_4-NH containing species $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)]$.[3] Reactions of triruthenium nitrene clusters $[Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}NPh)]$ with diphenylacetylene were found to produce the μ_4-nitrene cluster $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}NPh)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)]$.[4] It appears that the alkynes are important auxiliary ligands that favour the formation and isolation of μ_4-nitrene species. Recently we reported a series of penta- and hexa-nuclear ruthenium μ_4-nitrene carbonyl clusters prepared from the thermolysis or pyrolysis of $[Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)]$.[5] However, preparative methods for μ_4-nitrene species reported so far are not very specific and lead to low yields of the products, hence their reactivity studies are hindered. Herein, we report the reactivity of tolylacetylene (HC_2Tol) towards the triruthenium carbonyl cluster $[Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)]$, which resulted in the isolation of two tetraruthenium clusters containing μ_4-nitrene ligands in more accessible yields.

Heating of $[Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOMe)]$ with excess tolylacetylene in refluxing *n*-octane for 5 h afforded a brown reaction mixture. Two new yellow clusters $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu_4\text{-}\eta^2\text{-}HC_2Tol)]$ **1** and $[Ru_4(CO)_9(\mu\text{-}CO)_2\{\mu_4\text{-}NC(O)OMe\}(\mu_4\text{-}\eta^2\text{-}HC_2Tol)]$ **2** were isolated in 35% yield each by preparative TLC on silica, see Scheme 1. Owing to the similarity in the chromatographic behaviour of clusters **1** and **2**, they could not be separated. Indeed the compounds could only be obtained in the form of solvated co-crystals containing equimolar amounts of **1** and **2** which were then characterized by spectroscopy ‡ and chemical and structural analysis.§

X-Ray analysis showed that the asymmetric unit contains two identical molecules of cluster **1**, two isomeric molecules of cluster **2** and a *n*-hexane solvate molecule. Intermolecular hydrogen bonds are found between the μ_4-NH of **1** and the carbonyl oxygen atom in the μ_4-NC(O)OMe group of **2**, see Fig. 1. The molecular geometries of clusters **1** and **2** are similar in that, the four ruthenium atoms form a slightly twisted square-base arrangement with a quadruply bridging $TolC_2H$ ligand. Both **1** and **2** have two CO-bridged Ru–Ru bonds [ave 2.691(1) Å] and two unbridged Ru–Ru bonds [ave 2.747(1) Å]. The square tetraruthenium planes Ru(1)–Ru(2)–Ru(3)–Ru(4) and Ru(9)–Ru(10)–Ru(11)–Ru(12) are coplanar with a mean deviation from the least squares planes of less than 0.19 and 0.20 Å respectively. The nitrene N atom symmetrically caps the square base with average Ru–N distances of 2.150(9) Å for **1** and 2.183(8) Å for **2** and it lies 0.99 and 1.05 Å above the basal plane for **1** and **2** respectively. In cluster **1**, the hydrogen atom was located by Fourier-difference synthesis using low angle data at 0.84 Å from the μ_4-nitrene nitrogen atom. The ^1H NMR spectrum of **1** showed a triplet, at δ 1.96 ($J_{NH} = 49.3$ Hz), which is similar to that of $[Ru_4(CO)_{11}(\mu_4\text{-}NH)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)]$.[3] The two molecules of cluster **2** in the asymmetric unit differ in the alkyne orientation and are presented as **2a** and **2b** in Scheme 1.



Scheme 1 (*i*) Tolylacetylene, *n*-octane, 120 °C

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‡ Spectroscopic data for the mixture of clusters **1** and **2**. IR: [ν(CO), *n*-hexane, cm^{-1}] 2089w, 2059vs, 2049s, 2037vs, 2026m, 2008m, 1987m, 1904w, 1856m; [ν(NH), KBr disc, cm^{-1}] 3347w (Found: C, 30.0; H, 1.4; N, 1.7. Calc. for $C_{90}H_{54}N_4O_{48}Ru_{16}$: C, 30.23; H, 1.52; N, 1.57%). Cluster **1**. ^1H NMR ($CDCl_3$): 6.79 (m, 2 H), 6.20 (m, 2 H), 3.86 (s, 1 H), 2.17 (s, 3 H) and 1.96 (t, 1 H, $J_{NH} = 49.3$ Hz). FAB mass spectrum: *m*/*z* 843 (calc. 843), M^+. Cluster **2**. ^1H NMR ($CDCl_3$): 6.79 (m, 2 H), 6.20 (m, 2 H), 3.94 (s, 1 H), 2.94 (s, 3 H) and 2.17 (s, 3 H). FAB mass spectrum: *m*/*z* 901 (calc. 901), M^+.

§ Crystal data for co-crystal of $[\mathbf{1}\cdot\mathbf{2}]_2\cdot C_6H_{14}$, $C_{90}H_{54}N_4O_{48}Ru_{16} = 2(C_{20}H_9NO_{11}Ru_4)\cdot 2(C_{22}H_{11}NO_{13}Ru_4)\cdot C_6H_{14}$, $M = 3576.53$, triclinic, space group $P\bar{1}$ (no. 2), $a = 17.763(1)$, $b = 18.481(1)$, $c = 19.185(1)$ Å, $\alpha = 112.21(2)$, $\beta = 100.68(2)$, $\gamma = 92.53(2)°$, $U = 5684(1)$ Å^3, $Z = 2$, $D_c = 2.089$ g cm^{-3}, $F(000) = 3420$. Mo-Kα radiation, $T = 298$ K, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 21.45 cm^{-1}, yellow block 0.19 × 0.28 × 0.31 mm, 19 366 unique data measured on a MAR research image-plate scanner, 11 156 observed reflections [$I > 3\sigma(I)$]. An approximation of absorption by inter-image scaling was applied. $R = 0.048$ and $R' = 0.065$, $w = [\sigma^2(F_o)]^{-1}$. CCDC reference number 186/857.

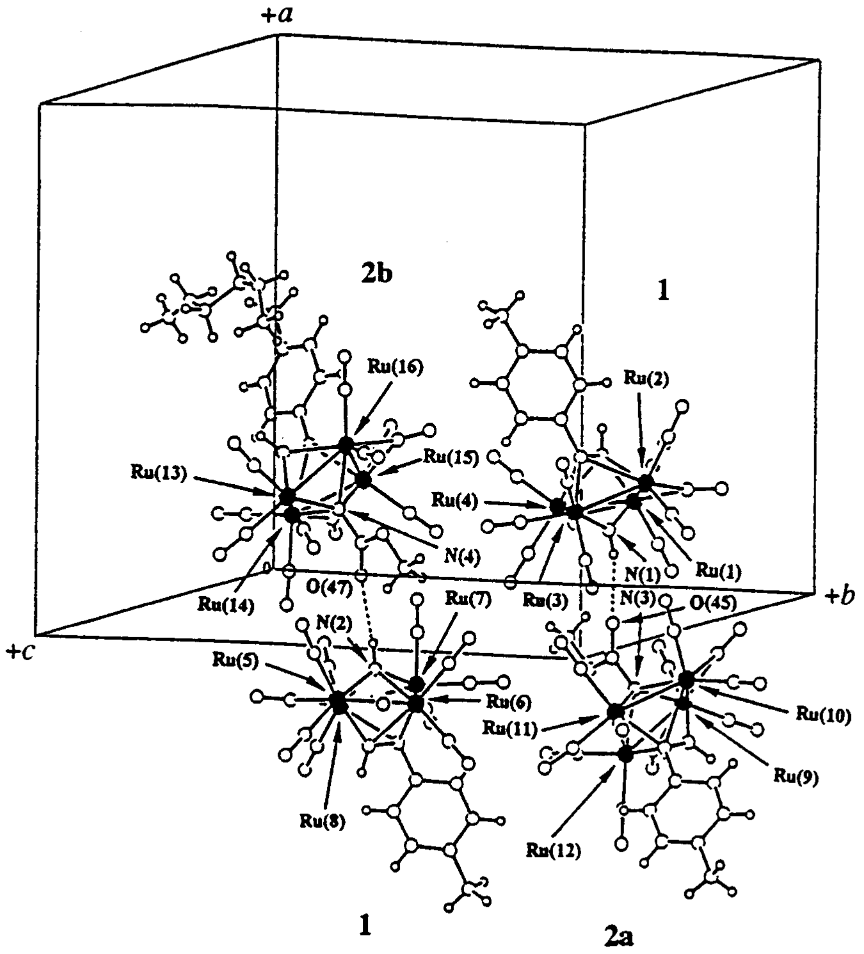

Fig. 1 Molecular structure of clusters **1** and **2** in the asymmetric unit with selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.670(1), Ru(1)–Ru(4) 2.692(1), Ru(2)–Ru(3) 2.717(1), Ru(3)–Ru(4) 2.783(1), Ru(1)–N(1) 2.157(9), Ru(2)–N(1) 2.136(9), Ru(3)–N(1) 2.146(9), Ru(4)–N(1) 2.172(8), N(1)–H 0.82, Ru(9)–Ru(10) 2.684(1), Ru(9)–Ru(12) 2.706(1), Ru(10)–Ru(11) 2.727(1), Ru(11)–Ru(12) 2.778(1), Ru(9)–N(3) 2.192(8), Ru(10)–N(3) 2.162(7), Ru(11)–N(3) 2.174(8), Ru(12)–N(3) 2.217(8), C(72)–O(45) 1.21(1); Ru(2)–Ru(1)–Ru(4) 84.23(4), Ru(1)–Ru(2)–Ru(3) 95.74(4), Ru(2)–Ru(3)–Ru(4) 81.64(4), Ru(1)–Ru(4)–Ru(3) 93.74(4), Ru(10)–Ru(9)–Ru(12) 83.64(4), Ru(9)–Ru(10)–Ru(11) 95.84(4), Ru(10)–Ru(11)–Ru(12) 81.50(4), Ru(9)–Ru(12)–Ru(11) 94.17(4)

However, we believe that they exist in one form in solution as indicated by ^{1}H NMR studies. Unfortunately low-temperature ^{1}H NMR experiments could not reveal the signals due to the individual isomers at 220 K. The NC(O)OMe moiety in **2** can be regarded as a carbamate derivative which is essentially coplanar (maximum deviation 0.004 Å in **2a** and 0.0008 Å in **2b**). It is mutually perpendicular to the metal plane as is evident from the dihedral angle of 91.4° between the planes N(3)–C(72)–O(45)–O(46) and Ru(9)–Ru(10)–Ru(11)–Ru(12). Although the exact mechanism is not known, clusters **1** and **2** are products of a reaction involving the Ru-assisted cleavage of the bound methoxynitrido moiety. This moiety is implicated as a metal–surface-bound intermediate in a number of chemical processes such as nitrogen oxide reduction.[6] Further work on the study of the intermediates which might be involved is underway.

Acknowledgements

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