A Novel High-nuclearity Rhodium Carbonyl Cluster Compound Containing Two Interstitial Nitrogen Atoms: Synthesis and X-Ray Structure of the Anion $[Rh_{14}N_2(CO)_{25}]^{2-}$

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The novel anion $[Rh_{14}N_2(CO)_{25}]^{2-}$, obtained by pyrolysis of $[Rh_6N(CO)_{15}]^-$, contains a metal-centred tetradecanuclear metallic polyhedron, with two interstitial nitrogen atoms, both five-connected to rhodium atoms.

High-nuclearity metal-atom clusters (with more than 6 metals) containing interstitial nitrogen atoms are rather uncommon species. The few known examples were all obtained on starting from the trigonal prismatic species $[M_6N(CO)_{15}]^-$ (M = Co, Rh),[1,2] and they include the mixed-metal anions $[Rh_6MN(CO)_{15}]^{2-}$ (M = Co, Ir)[3] and $[PtRh_{10}N(CO)_{21}]^{3-}$ (ref. 4), and the homometallic species $[Rh_7N(CO)_{15}]^{2-}$ (ref. 3), $[Rh_{12}HN_2(CO)_{23}]^{3-}$ (ref. 5) and $[Co_{14}N_3(CO)_{26}]^{3-}$.[6] These compounds show that new skeletal geometries can be stabilized by the encapsulated nitrides, which often occupy unusual and irregular interstitial sites. Continuing our investigations on this cluster family, we report here the synthesis and X-ray crystal structure of the novel dianion $[Rh_{14}N_2(CO)_{25}]^{2-}$, which has the peculiarity that the two nitrides are encapsulated in a metal-centred compact polyhedron.

The $[Rh_{14}N_2(CO)_{25}]^{2-}$ anion is synthesized† by prolonged pyrolysis of $Na[Rh_6N(CO)_{15}]$ in refluxing propan-2-ol; slightly higher yields are obtained in the presence of acetic acid. Pyrolysis can also be carried out in diglyme at 140 °C with somewhat shorter reaction times. IR monitoring of the reaction shows that in the early stages some intermediate species are formed, which eventually disappear to give the product together with some insoluble black material. The product has been isolated as the pure crystalline tetrapropylammonium salt in 50–55% yields. The IR spectrum of $(NPr_4)_2[Rh_{14}N_2(CO)_{25}]$ in MeCN show bands at 2023vs, 1970vw, 1880(sh), 1862m and 1840(sh) cm^{-1}. No hydridic signals were found in the ^1H NMR spectrum in C_3D_6O either at room temperature or at −90 °C.

The structure of the $(NPr_4)^+$ salt has been investigated by single-crystal X-ray analysis.‡ The anion of overall idealized

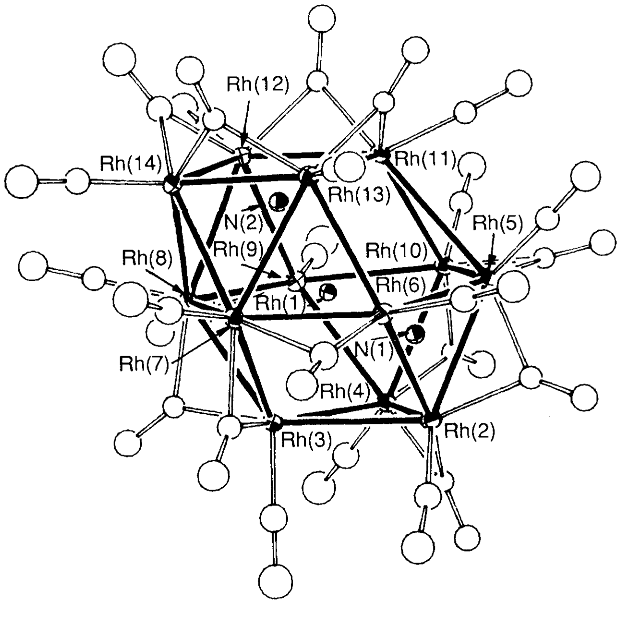

Fig. 1 An overall view of the anion $[Rh_{14}N_2(CO)_{25}]^{2-}$

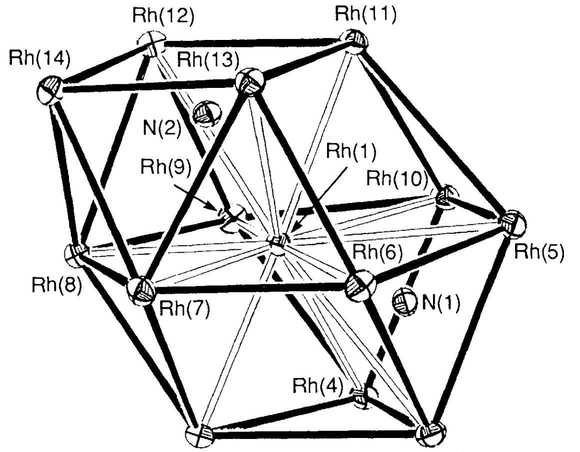

Fig. 2 A view of the $Rh_{14}N_2$ moiety. The Rh–Rh distances (Å) are as follows: 1–2 3.077, 1–3 2.626, 1–4 3.146, 1–5 2.995, 1–6 2.712, 1–7 2.624, 1–8 2.657, 1–9 2.651, 1–10 3.098, 1–11 2.741, 1–12 3.253, 1–13 3.205, 2–3 2.963, 2–4 2.786, 2–5 2.817, 2–6 2.888, 3–4 2.993, 3–7 2.824, 3–8 2.823, 4–9 2.898, 4–10 2.801, 5–6 2.843, 5–10 2.787, 5–11 3.098, 6–7 2.739, 6–13 2.834, 7–8 2.768, 7–13 2.957, 7–14 2.822, 8–9 2.775, 8–12 2.924, 8–14 2.844, 9–10 2.825, 9–12 2.856, 10–11 3.159, 11–12 2.823, 11–13 2.838, 12–14 2.779, 13–14 2.759, e.s.d.s. 0.001 Å.

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† *Synthesis*: A solution of $Na[Rh_6N(CO)_{15}]$ (0.46 g) in propan-2-ol (25 ml) containing acetic acid (1 ml) was refluxed under nitrogen with stirring in an oil bath at 115 °C for about 15 h, with the evolved CO occasionally being pumped off. The colour changed from yellow to brown to reddish brown, while some black material separated. The cooled solution was evaporated to dryness *in vacuo*, the residue was extracted with methanol (20 ml) and the solution filtered. A 0.5% solution of $(NPr_4)Br$ in propan-2-ol (70 ml) was carefully layered over the methanolic solution. When the solvent diffusion was complete (about 2 weeks), the mother liquor was syringed off and the crystals were washed with propan-2-ol, water, and propan-2-ol again, and vacuum dried; yield 50–55%. Satisfactory elemental analyses were obtained. These crystals were suitable for the X-ray analysis. Comparable yields were obtained by heating a solution of $Na[Rh_6N(CO)_{15}]$ (0.95 g) in diglyme (30 ml) at 140 °C for 10–11 h.

‡ *Crystal data* for $C_{49}H_{56}N_4O_{25}Rh_{14}$: M = 2541.7, triclinic, space group $P\bar{1}$ (No. 2), with a = 16.198(4), b = 17.609(3), c = 15.416(3) Å, α = 114.32(2), β = 116.33(2), γ = 82.12(2)°, U = 3585.6 Å^3, Z = 2, D_c = 2.354 g cm^{-3}, μ(Mo-Kα) = 31.5 cm^{-1}, Mo-Kα radiation (λ = 0.71073 Å). The intensity data were collected on a CAD4 Enraf-Nonius diffractometer by the ω-scan method, within the limits $3 < \theta < 25°$. An empirical absorption correction was applied (transmission factors in the range 0.84–1.00). The structure was solved by direct methods and Fourier methods and refined by full-matrix least-squares on the basis of 8343 independent significant $[I > 3\sigma(I)]$ reflections. Only the metal atoms and the nitrides were treated anisotropically. The final values of the agreement indices R and R_w were 0.039 and 0.058, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

C_s symmetry, is illustrated in Fig. 1 and the bare cluster in Fig. 2. The ideal mirror plane passes through Rh(1), Rh(3), Rh(11) and Rh(14), and the two nitride atoms. The Rh_{14} metallic array can be rationalized as a 3-layer compact fragment (3–7–4 metal atoms), which can be described as a monocapped centred cuboctahedron [capping atom Rh(14)], with one broken edge [Rh(12)···Rh(13)]. The central metal atom, Rh(1), is bound to 12 surface metals [from Rh(2) to Rh(13)] as in closest-packing, with six shorter and almost normal bonds [range 2.624(1)–2.741(1) Å, mean 2.669 Å], and six longer bonds, ranging from 2.995(1) to 3.253(1) Å. These long bonds are associated with the cavities containing the interstitial nitrides. Of the 27 surface metal–metal bonds 25 are scattered in the range 2.739(1)–2.993(1) Å (mean 2.839 Å); two bonds are longer [Rh(5)–Rh(11) 3.098(1), Rh(10)–Rh(11) 3.159(1) Å]. The two interstitial nitrogen atoms are located in different cavities: N(1) lies in a semi-octahedral (or square-pyramidal) environment, with a shorter contact to the central metal [Rh(1)–N(1) 1.907(5) Å] and four longer interactions to the surface atoms [Rh–N(1) range 2.009(5)–2.054(6) Å, mean 2.030 Å]; N(2) occupies a 7-metal cavity [two layers: a square Rh(11,12,13,14) and a triangle Rh(1,7,8)] but it is connected to only five metals, the central metal [Rh(1)–N(2) 1.947(5) Å] and the four atoms of the Rh(11,12,13,14) square [Rh–N(2) range 2.043(5)–2.135(5) Å, mean 2.081 Å].

These results confirm two features observed for interstitial nitrides in high-nuclearity rhodium clusters: (i) the N atoms are located in trigonal prismatic, in semi-octahedral or in larger irregular cavities but, in this case, in spite of the possibility that a higher metallic coordination number could be obtained, the preferred one is invariably 5; (ii) the N atoms are located close to surface square faces of the type $M_4(\mu\text{-}CO)_4(CO)_4$. The 25 carbonyl ligands are bound 13 terminally, one per surface metal atom, ten symmetrical edge-bridging and two [on edges Rh(6)–Rh(7) and Rh(8)–Rh(9)] with quite asymmetrical edge-bridging.

It is worth noting that the metal skeleton in $[Rh_{14}N_2(CO)_{25}]^{2-}$ is more compact than those present in the related high-nuclearity species $[Rh_{12}HN_2(CO)_{23}]^{3-}$ and $[Co_{14}N_3(CO)_{26}]^{3-}$; it represents essentially a fragment of closest-packed metal atoms, as those present in large cluster species without interstitial heteroatoms, with some distortions due to the steric and electronic requirements of the two encapsulated nitrogen atoms.

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