Synthesis and X-ray structure of a cluster complex with facial coordination of cyclooctatetraene to a Co_2Ni triangle

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The reaction between $[(\eta\text{-}C_5H_5)NiCo_3(CO)_9]$ and cyclooctatetraene yields $[Co_2Ni(CO)_6(\mu_3\text{-}\eta^2:\eta^3:\eta^3\text{-}C_8H_8)]$ with a cyclooctatetraene ligand in the facial coordination mode to a heterometallic Co_2Ni triangle.

The facial coordination of the cyclic π-perimeters C_nH_n (n = 5–8) to a molecular metal cluster is well documented.[1–4] Examples include the complexes $[\{(\eta\text{-}C_5H_5)Rh\}_3(\mu_3\text{-}H)(\mu_3\text{-}C_5H_5)]$,[5] $[\{(CO)_3M\}_3(\mu_3\text{-}C_6H_6)]$ (M = Ru, Os),[6] $[\{(CO)_2Ru\}_3(\mu_3\text{-}SBu^t)(\mu_3\text{-}C_7H_7)]$[7] and $[\{(CO)Ni\}_3\{\mu_3\text{-}(CF_3)_2C_2\}(\mu_3\text{-}C_8H_8)]$.[8] In such complexes, the C_nH_n ligand bonds to a triangular array of three metal atoms, which may even be part of a larger cluster moiety. This coordination geometry is frequently related to the adsorption states of the corresponding hydrocarbons on atomically flat (single crystal) metal surfaces.[9] Similar adsorbates are key intermediates in the industrially enormously important catalytic hydrocarbon reforming processes.[10] Curiously, although heteronuclear cluster complexes are quite commonplace, to our knowledge only one compound has been reported with a facial coordination of a cyclic conjugated unsaturated hydrocarbon to a cluster face comprised of two different types of metal atoms, *viz.* an Ru_2Pt face in $[Ru_6Pt_3(CO)_{18}\{\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5(CH_2)_2Ph\}(\mu_3\text{-}H)_4]$ **1**.[11] Our prime interest in such species comes from the well known fact that metal alloys and supported bimetallic clusters can have catalytic properties which may be vastly different from those of the pure metals.[12] Complexes such as **1** may be important stepping stones on the way towards an understanding of some of the factors which control how these catalysts work on the molecular level. Recently we reported on the simple one-pot synthesis of the complexes $[Co_4(CO)_6(\mu_3\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ **2** and $[Co_4(CO)_6(\mu_3\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$ **3**, starting from the binary carbonyl $[Co_4(CO)_{12}]$ and cycloheptatriene or cyclooctatetraene, respectively.[13] The products **2** and **3** provide a convenient entrance to large families of tri- and tetra-nuclear cluster complexes with facial C_7H_7 and C_8H_8 ligands.[3,13] Here, we report the synthesis and characterisation of a cluster complex containing a C_8H_8 ligand in the facial coordination mode to a Co_2Ni metal triangle. This is the first example of facial C_8H_8 coordination to a heterometallic face of a cluster, and only the second throughout the whole series $M_m(\mu_3\text{-}C_nH_n)$ (n = 5–8).

Reaction of the tetranuclear complex $[(\eta\text{-}C_5H_5)NiCo_3(CO)_9]$ **4** with an excess of cyclooctatetraene in refluxing *n*-heptane gave a dark red microcrystalline precipitate in 25% yield. The presence of a face-capping C_8H_8 ligand in this product was indicated by the NMR spectra.† However, no resonances were observed for a cyclopentadienyl ligand. The IR spectrum‡ indicated terminal and bridging carbonyl ligands; the large number of bands in the ν_{CO} region pointed to a rather low molecular symmetry. The structure of the product was eventually determined by a single crystal X-ray structure analysis.§ The molecular structure, $[M_3(CO)_6(\mu_3\text{-}C_8H_8)]$, is shown in Fig. 1, together with selected bond parameters. Unfortunately, the identity of the metal atoms M (cobalt or nickel) could not be determined unambiguously from the diffraction data.

The observed diamagnetism of the complex requires the composition of either $[Co_2Ni(CO)_6(C_8H_8)]$ or $[Ni_3(CO)_6(C_8H_8)]$. XPS analysis of a sample film deposited from solution on a gold foil gave the atomic ratio Co : Ni = 2 : 1. The isotope pattern starting with *m/z* 448 of the peak due to the molecular ion in the field desorption mass spectrum is also only consistent with the formulation $[Co_2Ni(CO)_6(\mu_3\text{-}C_8H_8)]$ **5**. The novel complex **5** is isoelectronic with its anionic tricobalt analog, $[Co_3(CO)_6(\mu_3\text{-}C_8H_8)]^-$ **6**, which was obtained in high yield by reductive degradation of **3**.[3]

The mean metal metal separation in **5** is 2.514 Å, shorter than in the tricobalt complex **6** (2.528 Å[14]). An even shorter mean metal metal distance (2.438 Å) was found in $[NiCo_2(\mu_2\text{-}CO)_3(PMe_3)_6]$, where D_{3h} symmetry is imposed on the molecule by the lattice symmetry (Co and Ni atoms are necessarily disordered).[15] This contraction of the metal triangles can be attributed to the effect of exchanging a cobalt for the smaller nickel atom. In both **5** and **6**, the lengths of the three individual metal metal bonds differ only by a maximum of 0.02 Å. In the only two structurally characterised cluster complexes with triangular Co_2Ni faces comprised of equally substituted apices disorder of the metals was found, indicating a close similarity of Co–Co and Co–Ni bonds.[15,16] For **5**, we cannot completely rule out some static disorder of the metal triangle, but there are no unusual shapes or orientations of the anisotropic displacement ellipsoids, and all the peaks in the Fourier synthesis are well defined.

The bridging C_8H_8 ligand attains an $\eta^2:\eta^3:\eta^3$ coordination mode with respect to the metal triangle. The carbocyclic ring is non-planar and approaches a chair conformation (Fig. 2). Carbon–carbon bond lengths within the $\mu_3\text{-}C_8H_8$ vary barely significantly within the range 1.396(8)–1.434(8) Å. The ligand

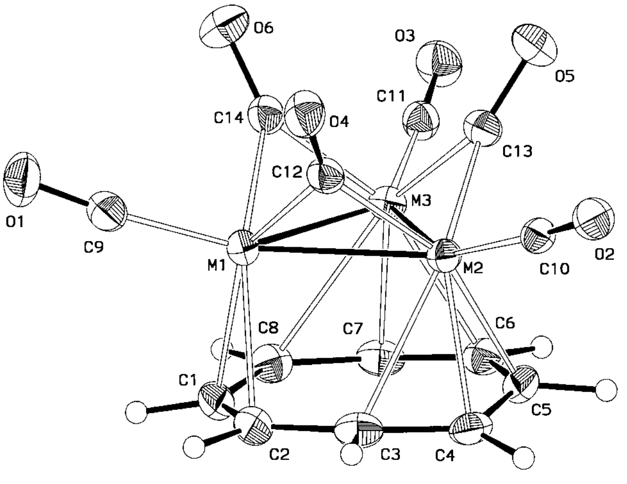

Fig. 1 Molecular structure of $[Co_2Ni(CO)_6(\mu_3\text{-}C_8H_8)]$ **5**. Selected bond lengths (Å) and angles (°): M1–M2 2.512(1), M1–M3 2.503(1), M2–M3 2.526(1), M1–C1 2.118(5), M1–C2 2.140(5), M2–C3 2.333(5), M2–C4 2.087(5), M2–C5 2.236(5), M3–C6 2.190(5), M3–C7 2.088(5), M3–C8 2.427(5), C1–C2 1.396(8), C1–C8 1.434(8), C2–C3 1.417(8), C3–C4 1.418(7), C4–C5 1.411(7), C5–C6 1.432(8), C6–C7 1.412(7), C7–C8 1.404(7), C2–C1–C8 133.2(5), C1–C2–C3 134.4(5), C2–C3–C4 136.5(5), C3–C4–C5 131.6(5), C5–C6–C7 134.8(5), C6–C7–C8 132.8(5), C7–C8–C1 136.5(5) (M = Co, Ni).

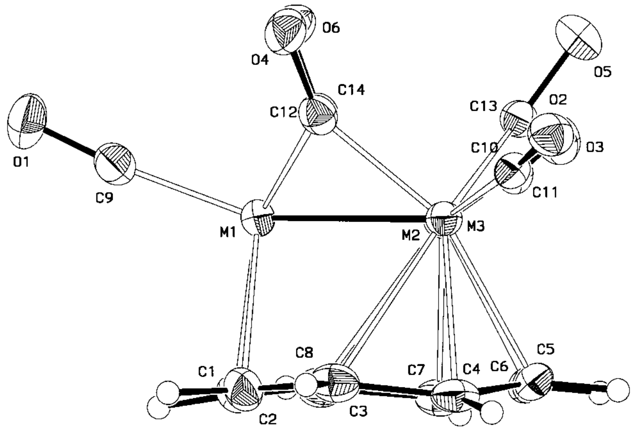

Fig. 2 Side view of **5** showing the conformation of the μ_3-C_8H_8 ring.

shell of the cluster is completed by three terminal and three edge-bridging carbonyl ligands. In solution, both the carbonyl and C_8H_8 ligands in **5** display fluxional behaviour. Only one ^{13}C NMR resonance is observed for the six carbonyl ligands, indicating a 'merry-go-round' type exchange process which involves both the terminal and bridging CO ligands. The observation of only one ^{13}C and ^1H NMR resonance for the μ_3-C_8H_8 ring is consistent with a rapid rotation of this ligand on top of the metal triangle. A high degree of fluxionality is generally characteristic for C_8H_8 ligands capping a Co_3 cluster face.[3] Evidently, the activation barrier for this process is not appreciably increased on coordination to the Co_2Ni triangle.

During the formation of **5**, the presence of $[(\eta$-$C_5H_5)Co(CO)_2]$ **7** in the reaction mixture was observed by IR spectroscopy. It is therefore likely, that the reaction involves an intra- or inter-molecular transfer of the cyclopentadienyl ligand from the nickel to a cobalt atom, which then leaves the cluster in the form of **7**. Vahrenkamp and coworkers have previously noted a similar role of an intermolecular nickel-to-cobalt transfer of a cyclopentadienyl ligand during metal exchange reactions in tri- and tetra-nuclear cluster complexes.[17]

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Notes and references

† ^1H NMR (C_6D_6, 200 MHz) δ 3.42 (s); ^{13}C NMR (C_6D_6) δ 71.8 (C_8H_8), 185.1 (CO).

‡ IR (CH_2Cl_2) ν_{CO}/cm^{-1} 2059s, 2020vs, 2003vs, 1883vs, 1853m, 1834m.

§ *Crystal data* for $[Co_2Ni(CO)_6(\mu_3$-$\eta^2:\eta^3:\eta^3$-$C_8H_8)]\cdot C_6H_6$: $C_{20}H_{14}Co_2NiO_6$, M = 526.91, monoclinic, space group $P2_1/n$, a = 10.203(5), b = 16.674(8), c = 11.902(6), β = 101.19(2), V = 1986.3(17) Å^3, Z = 4, μ(Mo-Kα) = 2.51 mm^{-1}, T = 203 K. Crystals obtained from a benzene solution at 10 °C were found to be twinned and consisted of two interpenetrating individuals with different orientation. 4951 intensity data were collected based on the orientation matrix of the individual which gave stronger reflections. Deletion of overlapping reflections resulted in 3454 unique data ($-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 22$,$0 \leqslant l \leqslant 15$; $2\theta_{max}$ = 56°). The structure was solved by direct methods and refined by full-matrix least squares based on F^2. All metal atoms were refined as cobalt. All non-hydrogen atoms were treated anisotropic, hydrogen atoms were located from difference Fourier syntheses and refined with isotropic displacement parameters, wR_2 = 0.094 (all data), R_1 = 0.040 [2261 reflections with $F_o > 4\sigma(F_o)$], GOF = 1.035. CCDC 182/1148. See http://www.rsc.org/suppdata/cc/1999/389/ for crystallographic files in .cif format.

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