

Hetero-Bimetallic Ni-Rh Carbido Carbonyl Clusters: Synthesis, Structure and ^{13}C NMR of $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$, $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$ and $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$

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The reaction of $[\text{Ni}_9\text{C}(\text{CO})_{17}]^{2-}$ (**1**) with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (**2**) results in the formation of the new hetero-bimetallic $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ (**3**) and $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$ (**4**) clusters, which have been separated by differential solubility. Degradation of **3** under a carbon monoxide atmosphere leads to the formation of the first bis-acetylide Ni-Rh cluster, i.e. $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$ (**5**). These new compounds have been characterised by X-ray crystallography, elemental analysis, ESI-MS, IR and ^{13}C NMR spectroscopy (on ^{13}C -carbido-en-

riched samples). The ^{13}C NMR spectra indicate that **3** exists as a mixture of two isomers in a 4:1 ratio, as also inferable from partial Ni/Rh disorder in the solid-state structure. More interestingly, coordination of Rh atoms to the interstitial carbido atom seems to be very effective in shortening its longitudinal relaxation time (T_1) by ca. two orders of magnitude compared to homometallic Ni carbido clusters.

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1. Introduction

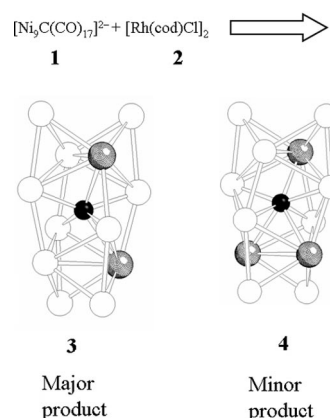
Despite the fact that the chemistry of homo-metallic Ni and Rh carbido carbonyl clusters has been extensively investigated,^[1–4] no report has appeared on hetero-bimetallic Ni-Rh carbido carbonyl clusters. This should be contrasted with the very rich chemistry of homoleptic Ni-Rh carbonyl clusters which comprises species such as $[\text{NiRh}_6(\text{CO})_{16}]^{2-}$,^[5] $[\text{Ni}_6\text{Rh}_5(\text{CO})_{21}]^{3-}$,^[6] $[\text{Ni}_{10}\text{Rh}(\text{CO})_{19}]^{3-}$,^[7] $[\text{Ni}_9\text{Rh}_3(\text{CO})_{22}]^{3-}$,^[7] $[\text{Ni}_6\text{Rh}_3(\text{CO})_{17}]^{3-}$,^[7] $[\text{NiRh}_{13}(\text{CO})_{25}]^{5-}$,^[8] $[\text{Ni}_2\text{Rh}_{12}(\text{CO})_{25}]^{4-}$,^[8] $[\text{Ni}_5\text{Rh}_9(\text{CO})_{25}]^{n-}$,^[8] $[\text{NiRh}_5(\text{CO})_{14}]^{3-}$ and $[\text{NiRh}_{14}(\text{CO})_{28}]^{4-}$.^[9] At the same time, several hetero-bimetallic Ni-Co carbide and acetylide carbonyl clusters are known, e.g. $[\text{Co}_2\text{Ni}_{10}\text{C}(\text{CO})_{20}]^{2-}$,^[10] $[\text{Co}_3\text{Ni}_9\text{C}(\text{CO})_{20}]^{2-}$,^[10] $[\text{Co}_3\text{Ni}_9\text{C}(\text{CO})_{20}]^{3-}$,^[11] $[\text{Co}_3\text{Ni}_7\text{C}_2(\text{CO})_{15}]^{3-}$,^[12] $[\text{Co}_3\text{Ni}_7\text{C}_2(\text{CO})_{16}]^{2-}$,^[13] $[\text{Co}_6\text{Ni}_2\text{C}_2(\text{CO})_{16}]^{2-}$.^[14]

Bimetallic and hetero-metallic clusters often display rather different properties than the analogous homo-metallic species, and can more easily reach higher nuclearities.^[15–17] Moreover, they can be useful precursors for the preparation of bimetallic, hetero-metallic or hetero-bimetallic metal nanoparticles.^[18–21] Thus, we became interested in filling the above gap, and herein we report on the first examples of hetero-bimetallic Ni-Rh carbide and bis-acetylide carbonyl clusters, i.e. $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ (**3**), $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$ (**4**), and $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$ (**5**).

2. Results and Discussion

2.1 Synthesis and Spectroscopic Characterisation of $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ (**3**), $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$ (**4**), and $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$ (**5**)

The hetero-bimetallic Ni-Rh carbide cluster $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ (**3**), was obtained by reacting $[\text{Ni}_9\text{C}(\text{CO})_{17}]^{2-}$ (**1**), with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (**2**), in THF in a ca. 2:1 molar ratio (Scheme 1). Different tetrasubstituted ammonium $[\text{NR}_4] = \text{NMe}_4$, NEt_4 , NBu_4 , $\text{NMe}_3\text{CH}_2\text{Ph}$ salts of the dianion **3** have been isolated by reacting the corresponding $[\text{NR}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]^{2-}$ starting material. These $[\text{NR}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ salts are recovered in good yields by removal of the solvent under reduced pressure, washing of the residue with water and toluene in order to remove some Ni^{II} salts and excess **2**, and extraction in THF. After complete extraction



Scheme 1.

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of **3** in THF, a small amount of a dark precipitate composed by the $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$, **4**, by-product remains, which is soluble in acetone or acetonitrile. Crystals suitable for X-ray analysis of $[\text{NBu}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$ and $[\text{NEt}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]$ have been obtained from THF/*n*-hexane and acetone/2-propanol mixtures, respectively. Both cluster anions have been characterised by X-ray crystallography (see next section) and elemental analysis, as well as ESI-MS, IR and ^{13}C NMR spectroscopy (on ^{13}C -carbido-enriched samples).

In agreement with the minor anionic charge, **3** shows infrared carbonyl absorptions at higher frequencies [$\nu(\text{CO})$ in acetone at 2021 (s), 1929 (w) and 1877 (m) cm^{-1}] in comparison to **4** [$\nu(\text{CO})$ in acetone at 1993 (s) and 1840 (ms) cm^{-1}]. The ESI-MS of a CH_2Cl_2 solution obtained by dissolving solid $[\text{NEt}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$ displays a main feature (relative intensities are given in parentheses) centred at m/z 681 (100) due to the intact $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ (M^{2-}) dianion, as well as minor sets of peaks centred at m/z 668 (20), 655 (5) and 1495 (25) which are attributable to the $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{19}]^{2-}$ ($[\text{M} - \text{CO}]^{2-}$) and $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{18}]^{2-}$ ($[\text{M} - 2\text{CO}]^{2-}$) ions, and the $\{[\text{NEt}_4][\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]\}^-$ ion pair, respectively.

Conversely, ESI-MS analyses on $[\text{NEt}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]$ dissolved in acetonitrile are more complicated, probably because of its minor stability toward partial decarbonylation. Thus, the ESI-MS spectrum displays the most intense features (relative intensities are given in parentheses) centred at m/z 690 (100) and 676 (65), which are due to the partially decarbonylated species $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{19}]^{2-}$ ($[\text{M} - \text{CO}]^{2-}$) and $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{18}]^{2-}$ ($[\text{M} - 2\text{CO}]^{2-}$), respectively (partial oxidation of the tri-anion occurs during ionisation as often encountered in similar species). The intact molecular ion is only disclosed by a much weaker signal at m/z 705 (10) ($[\text{M}]^{2-}$). Other sets of signals centred at m/z 769 (55), 756 (50), 742 (20) and 885 (40) are attributable to the $\{[\text{NEt}_4][\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]\}^{2-}$, $\{[\text{NEt}_4][\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{19}]\}^{2-}$, $\{[\text{NEt}_4][\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{18}]\}^{2-}$ and $\{[\text{NEt}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{19}]\}^{2-}$ ion pairs.

As a major conclusion, the ESI-MS analyses on both **3** and **4** confirm the molecular composition indicated by elemental analysis and, in particular, their Ni/Rh contents (10:2 and 9:3, respectively). Furthermore, they unambiguously show that the Ni/Rh disorder found in the crystal structures (see next section) is uniquely a position and not a composition disorder.

In order to further elucidate the above mentioned positional Ni/Rh disorder, both species have been investigated by ^{13}C NMR on samples selectively-enriched with ^{13}C at the carbide atom. These have been obtained by first preparing $[\text{Ni}_9^{13}\text{C}(\text{CO})_{17}]^{2-}$, ^{13}C -**1**, by reaction of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$, **6**, with $^{13}\text{CCl}_4$, and, then, by reacting the former with **2** as described above. In this way, both $[\text{Ni}_{10}\text{Rh}_2^{13}\text{C}(\text{CO})_{20}]^{2-}$, ^{13}C -**3**, (major product) and $[\text{Ni}_9\text{Rh}_3^{13}\text{C}(\text{CO})_{20}]^{3-}$, ^{13}C -**4**, (minor product) have been obtained. Their ^{13}C NMR spectra have been recorded at room temperature in $[\text{D}_6]\text{acetone}$ at 9.4 Tesla (Figure 1) and the longitudinal relaxation time T_1 measured under the same experimental conditions by

means of the inversion/recovery pulse sequence. In keeping with the site Ni/Rh disorder ascertained in the solid state, the **3** dianion exhibits two very close triplets at $\delta = 362.9$ ($^1J_{\text{C-Rh}} = 11.5$ Hz) and 363.7 ($^1J_{\text{C-Rh}} = 9.1$ Hz) ppm in a ca. 4:1 ratio.

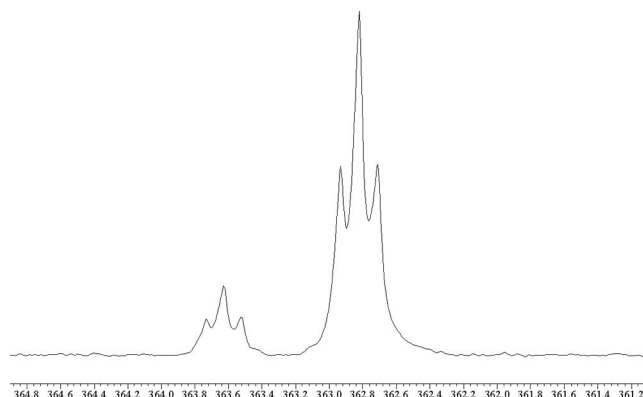


Figure 1. ^{13}C NMR spectrum in $[\text{D}_6]\text{acetone}$ at 298 K of the two isomers of $[\text{Ni}_{10}\text{Rh}_2^{13}\text{C}(\text{CO})_{20}]^{2-}$, ^{13}C -**3**.

The two resonances display very similar T_1 (6.5 ± 0.3 s and 6.3 ± 0.5 s, respectively). This spectrum may be accounted for by the presence in solution of two isomeric forms of **3** [A (most abundant) and B (least abundant); see Figure 2] which differ in the location of the two Rh atoms respect to the central carbide. Such an attribution is based on the following considerations and experimental facts. First of all, the X-ray single-crystal structure determination shows Ni/Rh partial disorder involving the four metal positions located on the outer edges of the tetra-capped bis-disphenoid encapsulating the eight-coordinate carbido atom. Therefore, one isomer (A) contains one Rh atom on each of the two edges, whereas in the second isomer (B) both Rh atoms are located on the same edge. In both isomers the carbide atom is located in a very similar environment composed by 6 Ni and 2 Rh atoms, and the resulting ^{13}C resonances should be a triplet in both cases, as experimentally found.

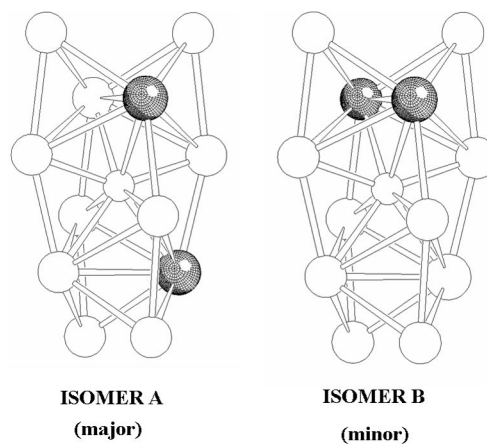


Figure 2. The two isomers of $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ (**3**) (only the metal framework and the interstitial carbide atom are drawn). A:B isomer ratio is ca. 4 according to ^{13}C NMR in solution.

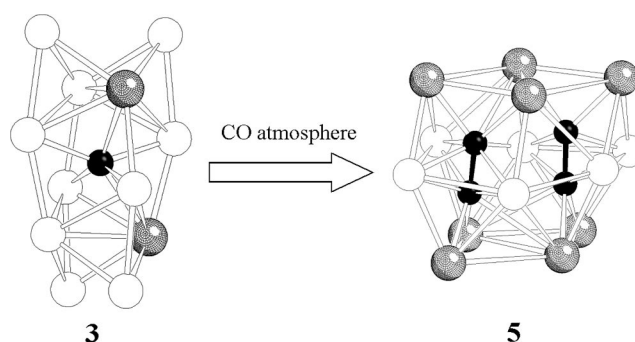
Random distribution of the two Rh atoms over those four sites would lead to a 2:1 ratio between A and B. On the basis of the ^{13}C NMR spectrum, it seems like that the major isomer (A) is actually twice more frequent than predicted by a random distribution, resulting in a 4:1 ratio for A:B. This fact could be a consequence of the different contribution to energy minimisation of the metal bonds in the two isomers. Indeed, conversion of A into B requires substitution of two Ni–Rh interactions with one Ni–Ni and one Rh–Rh bond. It is likely that this process is unfavourable because the energy of a heteroatomic Ni–Rh bond (according to Pauling) is expected to be slightly greater than the average energy of a Ni–Ni and a Rh–Rh bond. Of course, ^{13}C NMR is not able to unambiguously discriminate between the two isomers, and assignment of A as the major species is only based on the above thermodynamic considerations and on the fact that A would be the prevailing species also in the case of perfect randomisation. Moreover, also interpretation of the disorder model found in the solid state (see next section) indicates A as the prevailing species within the crystal structure.

Finally, it is noteworthy that the longitudinal relaxation times T_1 of both isomers are extremely shorter than that of the homometallic Ni carbonyl precursor $[\text{Ni}_9^{13}\text{C}(\text{CO})_{17}]^{2-}$ (T_1 212 s), but slightly longer than those of homometallic Rh carbides, e.g. $[\text{Rh}_6^{13}\text{C}(\text{CO})_{15}]^{2-}$ (T_1 1.15 s) and $[\text{Rh}_6^{13}\text{C}(\text{CO})_{13}]^{2-}$ (T_1 = 1.58 s).^[22] Notice that all data have been constantly measured at 9.4 Tesla and 298 K, since T_1 is field- and temperature-dependent.

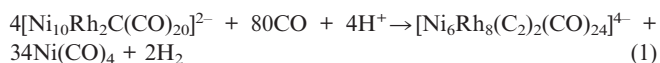
The $[\text{Ni}_9\text{Rh}_3^{13}\text{C}(\text{CO})_{20}]^{3-}$ trianion (^{13}C -4) exhibits, in contrast, a single carbide resonance at δ = 378.3 ppm split into a quartet ($J_{\text{C-Rh}}$ = 9.6 Hz), due to coupling of ^{13}C with three equivalent Rh atoms, which are disordered over the same two edges of the inner triangulated dodecahedron, as inferable from the X-ray structure (only one isomer is possible in this case). The presence of a third Rh atom in the coordination sphere of the interstitial carbide atom slightly shortens the relaxation time T_1 (3.4 ± 0.6 s). Considering the whole series of clusters $[\text{Ni}_9^{13}\text{C}(\text{CO})_{17}]^{2-}$, $[\text{Ni}_{10}\text{Rh}_2^{13}\text{C}(\text{CO})_{20}]^{2-}$, $[\text{Ni}_9\text{Rh}_3^{13}\text{C}(\text{CO})_{20}]^{3-}$, $[\text{Rh}_6^{13}\text{C}(\text{CO})_{15}]^{2-}$ and $[\text{Rh}_6^{13}\text{C}(\text{CO})_{13}]^{2-}$, it is evident that the longitudinal relaxation time T_1 is exceedingly long in the absence of any Rh atom, whereas relaxation becomes much more effective as some Rh atom is introduced in the coordination sphere of the interstitial carbide atom to the point to observe a rate enhancement of two order of magnitude. Moreover, further shortening of T_1 occurs upon increasing the amount of Rh atoms which naturally occurs as a single isotope with nuclear spin 1/2 (^{103}Rh).

The reaction of **3** with stoichiometric amounts of oxidising agents, such as I_2 and Ag^+ , results in the formation of a new species, which displays $\nu(\text{CO})$ at higher frequencies, i.e. 2038 (s) and 1868 (m) cm^{-1} ; this is likely to be the $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^-$ mono-anion. Its rapid decomposition has so far hindered any further characterisation. Conversely, the reduction of the di-anion with Na/naphthalene in THF results in a complex mixture of yet uncharacterised products.

The dianion **3** is not stable under CO atmosphere (Scheme 2) and, its carbonylation reaction in CH_2Cl_2 leads to progressive change of the colour of its solution from red-brown to pale green owing to formation of Ni^{2+} complexes and $\text{Ni}(\text{CO})_4$ and separation of a waxy brown precipitate. The waxy precipitate is soluble in CH_3CN and has been crystallised by slow diffusion of a mixture of *n*-hexane/diisopropyl ether. This new compound has been shown to consist in the new bis-acetylide $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$ anion, **5**. Formally, its formation is due to reaction (1). The protons required by stoichiometry (1) are likely due to the unavoidable presence of HCl impurities in anhydrous CH_2Cl_2 .



Scheme 2.



The tetra-anion **5** displays infrared carbonyl absorptions at 1989 (s) and 1803 (m) cm^{-1} . The ESI-MS spectrum of the $[\text{NEt}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]$ salt in CH_3CN solution points out ready loss of CO from the molecular ion and its ion pairs. Most relevant sets of peaks are due to $\{[\text{NEt}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{22}]^{2-}\}$ (986 *m/z*), $\{[\text{NEt}_4]_2[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{21}]^{3-}\}$ (690 *m/z*), $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{22}]^{2-}$ (920 *m/z*), and $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{22}]^{3-}$ (611 *m/z*). The ^{13}C NMR spectrum of a ^{13}C -enriched sample of $[\text{Ni}_6\text{Rh}_8(^{13}\text{C}_2)_2(\text{CO})_{24}]^{4-}$, ^{13}C -5, shows only one broad resonance at δ = 365.3 ppm without any detectable fine structure. The measured relaxation time T_1 is ca. 2.1 ± 0.5 s, even if the uncertainty is relatively high due to line broadening.

2.2. Crystal Structures of $[\text{NBu}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$, $[\text{NEt}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]$ and $[\text{NEt}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}] \cdot 4\text{CH}_3\text{CN}$

The molecular structure of the di-anion **3** has been determined on its $[\text{NBu}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$ salt (Figure 3 and Table 1). The asymmetric unit contains only half of the cluster anion, since the other half is generated by a twofold axis.

Table 1. Main bond lengths for $[\text{NBu}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$, $[\text{NEt}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$ and $[\text{NEt}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-} \cdot 4\text{CH}_3\text{CN}$.

	$[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ (3)	$[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$ (4)	$[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$ (5)
Ni–Ni	2.4950(10)–3.0580(10) av. 2.76	2.4865(8)–3.286(2) av. 2.76	2.771(2)–2.8291(17) av. 2.81
Ni–M ^[a]	2.4682(8)–2.6572(9) av. 2.56	2.4928(7)–2.7056(7) av. 2.59	2.5705(11)–2.9515(16) av. 2.69
M–M ^[a]	2.7043(8)–2.7582(7) av. 2.73	2.7477(6)–2.8136(6) av. 2.79	2.8038(12)–3.2430(10) av. 3.01
Ni–C	2.037(2)–2.038(2) av. 2.04	2.025(4)–2.048(4) av. 2.04	2.063(9)–2.092(9) av. 2.08
M–C ^[a]	2.225(6)–2.268(6) av. 2.25	2.248(4)–2.298(4) av. 2.28	2.101(9)–2.9630(10) av. 2.40
C–C	–	–	1.382(19)

[a] The M positions are disordered Rh/Ni in $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ and $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$, whereas they are all Rh in $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$.

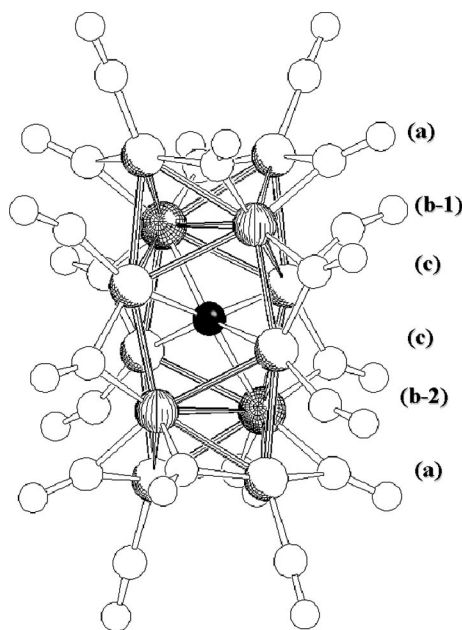


Figure 3. Molecular structure of $[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]^{2-}$ (3). The positions which are fully occupied by Ni are shadowed; hatched spheres are disordered Ni/Rh (two different hatching modes have been used in order to point out the relative 2:2 ratio); the interstitial carbide is in black. Isomer (A), according to Figure 2, is here represented. (a) Capping positions (Ni); (b-1) outer bis-disphenoid positions [Ni(1)/Rh(1)]; (b-2) outer bis-disphenoid positions [Ni(2)/Rh(2)]; (c) inner bis-disphenoid positions (Ni).

The structure of this cluster anion closely resembles that of the previously reported Ni–Co carbido clusters $[\text{Ni}_{10}\text{Co}_2\text{C}(\text{CO})_{20}]^{2-}$, $[\text{Ni}_9\text{Co}_3\text{C}(\text{CO})_{20}]^{2-}$ and $[\text{Ni}_9\text{Co}_3\text{C}(\text{CO})_{20}]^{3-}$.^[10,11] Thus, the metal framework of **3** may be described as a distorted square antiprism which is tetra-capped on two alternate pairs of adjacent triangular faces. Major deviations from this description arise from the two square faces being more accurately described as two rhombus having alternate angles of ca. 73 and 104°, resulting in a 222 (D_2) idealised symmetry. Alternatively, the metal cage of the cluster might be viewed as a distorted tetra-capped triangulated dodecahedron (bis-disphenoid). A regular triangulated dodecahedron should have D_{2d} instead of D_2 symmetry, and is often found in boranes, e.g. $[\text{B}_8\text{H}_8]^{2-}$ and

B_8Cl_8 ,^[23,24] and metallaboranes, e.g. $\text{B}_4\text{H}_4(\text{MCP})_4$ (M = Co, Ni).^[25,26]

The four capping atoms are purely Ni as the four inner positions of the dodecahedral cage. The two Rh atoms are disordered over the four outer positions of the bis-disphenoid and tetrahedrally arranged around the central carbide atom. In the absence of any preferential recognition during the assembly of the ionic lattice, the occupancy fraction of Rh in the above sites should be 0.5, both in the case of a random distribution, as well as prevalence of one isomer, as found in solution by ^{13}C NMR spectroscopy. The small difference in the refined Rh occupancy fraction between the Rh(1)/Ni(1) and Rh(2)/Ni(2) sites (0.58 vs. 0.42) determined in the crystal probably descends from the non equivalence of the Rh(1)/Ni(1)–Rh(1)/Ni(1)* and Rh(2)/Ni(2)–Rh(2)/Ni(2)* contacts (2.76 vs. 2.70 Å) which imparts some selectivity in the orientation of the dianion during its association into the ionic lattice (* refers to the symmetry generated M atom on each edge).

The 12 metal atoms in **3** can be divided into three sets consisting of four metal atoms each: a) the four capping Ni atoms; b) the four apical M atoms of the bis-disphenoid which are disordered Ni/Rh (2:2) (outer bis-disphenoid positions); c) the four inner Ni atoms of the bis-disphenoid. The metal–metal distances are quite spread [2.4682(8)–3.0580(10) Å, average 2.63 Å], if also the longest Ni–Ni contacts within the four atoms of the (c) set are considered [2.9657(9) and 3.0580(10) Å]. The exclusion of these two longer contacts results in a narrower interval [2.4682(8)–2.7583(9) Å, average 2.57 Å].

The structure of the cluster is completed by 20 carbonyl ligands, of which 4 are terminal, 4 are semi-bridging and 12 are bridging. In particular, the four capping Ni atoms [set (a)] are seven-coordinate by displaying one Ni–Ni, two Ni–M contacts and being coordinated to one terminal and two bridging CO, and displaying a longer contact to a semi-bridging carbonyl [2.215(6)–2.251(6) Å]. Conversely, the four M atoms of the (b) set [disordered Ni/Rh] display a connectivity of 10: six metal atoms, three bridging carbonyls and the interstitial carbide. This confirms the preference of the two heavier Rh atoms for the positions with higher M–M connectivity. The coordination sphere of the four inner Ni atoms [set (c)] is slightly more complicated, since

they are bonded to one bridging and one semi-bridging CO (shorter contact), the interstitial carbide and display three Ni–M and three Ni–Ni contacts. Two Ni–Ni contacts (corresponding to the longer diagonals of the rhombic faces) are rather elongated [2.9657(9) and 3.0580(10) Å] with respect to the other four metallic bonds [2.4950(10)–2.5221(8) Å] and have been omitted in Figure 3.

The molecular structure of the related trianion **4** (Figure 4 and Table 1), as determined in its $[\text{NEt}_4]_3^- [\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$ salt, is very similar to that of the dianion, for what concerns both the metal cage and the stereochemistry of the ligands. Therefore, a detailed description is avoided.

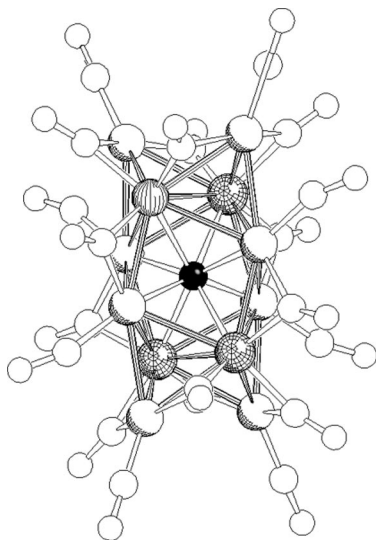


Figure 4. Molecular structure of $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{3-}$ (**4**). The positions which are fully occupied by Ni are shadowed; hatched spheres are disordered Ni/Rh (two different hatching modes have been used in order to point out the relative 1:3 ratio); the interstitial carbide is in black.

The major difference between the two is represented by the replacement of one Ni with a further Rh atom. Also in this case, the three Rh atoms are disordered over the same four sites of the inner triangulated dodecahedron. The constrained Rh occupancy fractions refined as follows: 0.93509 Rh(1)/Ni(1), 0.85178 Rh(2)/Ni(2), 0.62743 Rh(3)/Ni(3), 0.58511 Rh(4)/Ni(4) [The composition constrain is imposed following elemental and ESI-MS analyses; Ni occupancy factors are the complement at one]. Absence of preferential recognition during crystallisation should lead to identical occupancy fractions of 0.75 of the above four sites. In contrast, the Rh refined occupancy fraction of two Ni/Rh positions are slightly less than unit and the other two are slightly greater than 0.5. Once again, the refinement points out a slight degree of ion recognition during the association of the tri-anion to the crystal lattice. That probably derives from the fact that the sites containing more Rh show both M–M and M–Ni more elongated than those less populated by Rh. Only one isomer is expected as it has been experimentally confirmed by ^{13}C NMR spectroscopy.

The molecular structure of the tetra-anion **5**, as determined in its $[\text{NEt}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$ salt, is reported in Figure 5. The unit cell contains eight cluster anions [only Rh(1), Rh(2), Ni(3), Ni(4), C(1) and six CO ligands are independent; all other atoms are generated by symmetry], 32 $[\text{NEt}_4]^+$ cations (two halves are independent; all other atoms are generated by symmetry) and 32 CH_3CN molecules (on general positions).

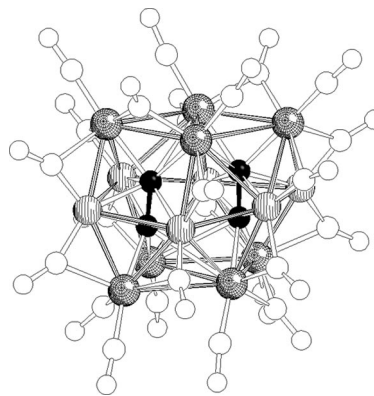


Figure 5. Molecular structure of $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]^{4-}$ (**5**) (two directions hatched spheres are Rh; one direction hatched spheres are Ni, black spheres are interstitial C atoms).

The metal framework displays 16 triangular and 4 square faces, and is perfectly ordered, being the 8 Rh atoms all located on the two external layers and the 6 Ni atoms on the central one of Figure 5. It consists of three metal layers: the two external ones comprise four Rh atoms each and can be described as two edge sharing triangles. Conversely, the central layer, comprising six Ni atoms, is essentially a hexagon elongated along a twofold axis. Two tightly bonded carbide atom pairs are encapsulated within this metal cage and their bonding contacts [C–C 1.382(19) Å; C···C between pairs 2.898(19) Å] as well as the overlap population (inferable from EHMO calculations) suggest a bond order of ca. 2. The four interstitial C atoms are completely equivalent (only one of them is, in fact, present within the asymmetric unit) and each of them displays bonding contacts to three Ni [2.063(9)–2.092(9) Å] and two Rh atoms [2.101(9)–2.137(9) Å], as well as a rather loose contact to a third rhodium atom [2.9630(10) Å].

Several Co, Ni and Co–Ni carbonyl clusters containing one interstitial C_2 moiety displaying a short C–C contact are known, i.e. $[\text{Co}_9\text{C}_2(\text{CO})_{19}]^{2-}$,^[27] $[\text{Ni}_{10}\text{C}_2(\text{CO})_{15}]^{2-}$,^[28] $[\text{Ni}_{11}\text{C}_2(\text{CO})_{15}]^{4-}$,^[29] $[\text{Ni}_{12}\text{C}_2(\text{CO})_{16}]^{4-}$,^[29] $[\text{Co}_6\text{Ni}_2\text{C}_2(\text{CO})_{16}]^{2-}$,^[10] $[\text{Co}_3\text{Ni}_2\text{C}_2(\text{CO})_{15}]^{3-}$,^[11] $[\text{Co}_3\text{Ni}_2\text{C}_2(\text{CO})_{16}]^{2-}$,^[12] as well as species containing two, i.e. $[\text{Ni}_{16}(\text{C}_2)_2(\text{CO})_{23}]^{4-}$ ^[30] and also four acetylide units, i.e. $[\text{HNi}_{25}(\text{C}_2)_4(\text{CO})_{32}]^{3-}$ and $[\text{Ni}_{22}(\text{C}_2)_4(\text{CO})_{28}\text{Cl}]^{3-}$.^[31]

The structure of the cluster is completed by 24 CO ligands, 8 terminal on each Rh atoms, 12 semi-bridging on the Rh–Ni edges, and 4 bridging the Rh–Rh edges. The 12 metal atoms show rather different environments. The four Rh atoms at the vertices of the external triangular faces display a coordination number of 9, being bonded to two Rh and two Ni atoms, four CO ligands and one C atom of

one C₂ unit. The coordination number of the other four Rh atoms (located on the hinge of the top and bottom edge sharing triangles) can be considered 9 or 10, displaying bonding contacts to 3 Rh, 2 Ni and 3 CO ligands, as well as a short [2.137(9) Å] and a longer [2.9630(10) Å] contact to the two interstitial C₂ units. The six Ni atoms can be divided into two sets, the first comprising the two Ni atoms along the twofold elongation axis, and the second consisting on the remaining four nickels. The two Ni atoms of the first set are eight-coordinate, being bonded to two Rh and two Ni atoms, two CO ligands and one C₂ unit. The remaining four Ni atoms are nine-coordinate, displaying short contacts to three Rh and two Ni atoms, 2 CO ligands and one C₂ unit.

3. Conclusions

The first examples of hetero-bimetallic Ni–Rh carbide and bis-acetylide carbonyl clusters, i.e. [Ni₁₀Rh₂C(CO)₂₀]²⁻ (**3**), [Ni₉Rh₃C(CO)₂₀]³⁻ (**4**), and [Ni₆Rh₈(C₂)₂(CO)₂₄]⁴⁻ (**5**) have been reported and fully characterised. This study evidences analogies but also interesting differences between Ni–Rh and Ni–Co carbide carbonyl clusters. In fact, the two mono-carbido species **3** and **4** are strictly related to similar Ni–Co carbido clusters, whereas a bis-acetylide Ni–Co tetra-anion analogous to **5** is not known. It seems, therefore, possible that the nuclearity of these clusters could be further increased.

The relative location of the Ni and Rh atoms within the metal cage seems to be the result of a subtle balance of the M–M, M–C and M–CO bonding environments, as previously found in other bimetallic and hetero-bimetallic species.^[3,32]

The possibility of preparing ¹³C-enriched species offered the chance to study the spectroscopic behaviour of interstitial carbido atoms and gain more information about any eventual metal disorder. First of all, these studies have clearly demonstrated the existence of two isomeric forms of the dianion **3**. Moreover, inspection of the data present in the literature points out that homometallic Ni-cages are not effective in enabling the relaxation of the interstitial carbide atoms. In contrast, it is now demonstrated that the presence of two or three spin 1/2 Rh atoms in the metal cage enormously increases the relaxation rates, which become comparable to those of homometallic Rh clusters. That fuelled interest in bimetallic Ni–Rh carbonyl clusters containing interstitial C₂ moieties. A preliminary search ended in the isolation of **5**, which displays two equivalent acetylide moieties. The chemical shift of the carbon atoms of the C₂ moieties of **5** turned out to be very similar to that of the carbide atoms of **3** and **4**. Further studies are undergoing in order to better understand the effect of different metal atoms on the longitudinal relaxation time of interstitial carbide and acetylide groups, as well as other spectroscopic features. It would be, for instance, of interest to prepare metal clusters containing tightly bonded non-equivalent C atoms, to eventually detect any direct ¹J_{C–C} in interstitial acetylide units.

Finally, joined crystallographic, ESI-MS and ¹³C NMR studies on **3** and **4** have demonstrated that the Ni/Rh disorder found in their crystal structures is uniquely a position and not a composition disorder. This suggests that X-ray crystallography alone is sometime not sufficient in order to clearly elucidate the nature of bimetallic clusters. Some degree of ion recognition during crystallisation of [NBu₄]₂[Ni₁₀Rh₂C(CO)₂₀] and [NEt₄]₃[Ni₉Rh₃C(CO)₂₀] has also been evidenced.

Experimental Section

General Procedures: All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and in dried solvents. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. The [NR₄]₂[Ni₉C(CO)₁₇] [NR₄ = NMe₄, NEt₄, NBu₄]^[33] and [Rh(cod)Cl]₂ (**2**)^[34] complexes have been prepared according to the literature. Analysis of Ni and Rh were performed by atomic absorption on a Pye-Unicam instrument. Elemental analyses (C, H, N) were obtained with a ThermoQuest FlashEA 1112NC instrument. IR spectra were recorded on a Perkin–Elmer SpectrumOne interferometer in CaF₂ cells. ESI mass spectra were recorded on a Waters Micro-mass ZQ4000 instrument. All NMR measurements were performed on Varian Inova 600 and Mercury Plus 400 instruments. ¹³C was referenced to TMS. Relaxation times T₁ were obtained at 9.4 Tesla by using the inversion/recovery pulse sequence.^[35] Structure drawings have been performed with SCHAKAL99.^[36] EHMO calculations have been carried out with CACAO.^[37]

Synthesis of [NBu₄]₂[Ni₁₀Rh₂C(CO)₂₀] (3**):** Complex **2** (0.37 g, 0.75 mmol) was added in portions to a solution of [NBu₄]₂[Ni₉C(CO)₁₇] (1.02 g, 0.68 mmol) in THF (20 mL). After stirring for 3 h, the solvent was removed in vacuo and the residue washed with water (2 × 30 mL) and toluene (2 × 30 mL), dried under reduced pressure and extracted in THF (20 mL). Precipitation by slow diffusion of *n*-hexane (40 mL) gave a dark-brown crystalline precipitate composed of crystals of [NBu₄]₂[Ni₁₀Rh₂C(CO)₂₀] (yield 0.61 g, 53.9% based on Ni) suitable for X-ray analysis. The compound is soluble in CH₂Cl₂, THF, acetone and CH₃CN.

Other salts of the same cluster, i.e. [NR₄]₂[Ni₁₀Rh₂C(CO)₂₀] [NR₄ = NMe₄, NEt₄, NMe₃CH₂Ph] can be obtained by using the same procedure and replacing [NBu₄]₂[Ni₉C(CO)₁₇] with other [NR₄]₂[Ni₉C(CO)₁₇] salts. Similarly, ¹³C-enriched samples [NR₄]₂[Ni₁₀Rh₂¹³C(CO)₂₀] were prepared from [NR₄]₂[Ni₉¹³C(CO)₁₇].

C₅₃H₇₂N₂Ni₁₀O₂₀Rh₂ (1850.05): calcd. C 34.41, H 3.92, N 1.51, Ni 31.73, Rh 11.13; found C 34.59, H 4.05, N 1.28, Ni 31.52, Rh 11.02. IR (CH₂Cl₂, 293 K): ν(CO) = 2027 (s), 1921 (w), 1871 cm⁻¹ (m). IR (THF, 293 K): ν(CO) = 2020 (s), 1925 (w), 1876 cm⁻¹ (m). IR (acetone, 293 K): ν(CO) = 2021(s), 1929 (w), 1877 cm⁻¹ (m). ESI-MS (CH₂Cl₂, on [NEt₄]₂[Ni₁₀Rh₂C(CO)₂₀]): ES-*m/z* (relative intensity in parentheses): 1495 (25) {[Ni₁₀Rh₂C(CO)₂₀][NEt₄]}⁻; 681 (100) [Ni₁₀Rh₂C(CO)₂₀]²⁻; 668 (20) [Ni₁₀Rh₂C(CO)₁₉]²⁻; 655 (5) [Ni₁₀Rh₂C(CO)₁₈]²⁻. ¹³C NMR ([D₆]acetone on [NEt₄]₂[Ni₁₀Rh₂¹³C(CO)₂₀]): δ = 362.9 (t, ¹J_{C–Rh} = 11.5 Hz, T₁ = 6.5 ± 0.3 s; isomer A), 363.7 ppm (t, ¹J_{C–Rh} = 9.1 Hz, T₁ = 6.3 ± 0.5 s; isomer B); isomer ratio A:B = 4:1.

Synthesis of [NEt₄]₃[Ni₉Rh₃C(CO)₂₀] (4**):** This compound was obtained as a minor side-product during the synthesis of [NEt₄]₂[Ni₁₀Rh₂C(CO)₂₀] and separated on the basis of the different solubility. Complex **2** (0.62 g, 1.26 mmol) was added in portions to a

solution of $[\text{NET}_4]_2[\text{Ni}_9\text{C}(\text{CO})_{17}]$ (1.55 g, 1.21 mmol) in THF (30 mL). After stirring overnight, the solvent was removed in vacuo and the residue washed with water (2×30 mL) and toluene (2×30 mL), and dried under reduced pressure. The main product of the reaction, i.e. $[\text{NET}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$, was extracted from the solid in THF (2×20 mL), leaving a residue completely soluble in acetone (15 mL). Precipitation from the latter solution by slow diffusion of isopropyl alcohol (30 mL) gave a dark-brown crystalline precipitate composed of crystals of $[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]$ (yield 70 mg, 3.2% based on Ni) suitable for X-ray analysis. The compound is soluble in acetone and CH_3CN .

$\text{C}_{45}\text{H}_{60}\text{N}_3\text{Ni}_9\text{O}_{20}\text{Rh}_3$ (1800.08): calcd. C 30.03, H 3.36, N 2.33, Ni 29.35, Rh 17.15; found C 30.21, H 3.12, N 2.44, Ni 29.19, Rh 17.06. IR (acetone, 293 K): $\nu(\text{CO}) = 1993$ (s), 1840 cm^{-1} (ms). IR (CH_3CN , 293 K): $\nu(\text{CO}) = 1994$ (s), 1838 cm^{-1} (ms). ESI-MS (CH_3CN , on $[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]$): ES- m/z (relative intensity in parentheses): 885 (40) $\{[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{19}]^{2-}\}^-$; 769 (55) $\{[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{2-}\}^-$; 756 (50) $\{[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{19}]^{2-}\}^-$; 742 (20) $\{[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{18}]^{2-}\}^-$; 705 (10) $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]^{2-}$; 690 (100) $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{19}]^{2-}$; 676 (65) $[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{18}]^{2-}$. ^{13}C NMR ($[\text{D}_6]\text{acetone}$): $\delta = 378.3$ ppm (q, $^1J_{\text{C-Rh}} = 9.6$ Hz, $T_1 = 3.4 \pm 0.6$ s).

Synthesis of $[\text{NET}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]\cdot 4\text{CH}_3\text{CN}$: This compound was obtained by degradation under CO atmosphere of $[\text{NET}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$ in CH_2Cl_2 . Complex $[\text{NET}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$ (0.45 g, 0.35 mmol) was dissolved in CH_2Cl_2 (20 mL) under CO atmosphere and stirred at room temperature for 3 h, until an oily brown precipitate formed and the solution became bright green for the presence on Ni^{2+} complexes; $\text{Ni}(\text{CO})_4$ was also detected in solution at this stage by IR spectroscopy. Then the solvent was removed in vacuo and the residue washed with water (2×20 mL), toluene (2×20 mL) and THF (2×20 mL). Finally, the target prod-

uct was extracted in CH_3CN (20 mL) and precipitation by slow diffusion of *n*-hexane (5 mL) and diisopropyl ether (40 mL) gave a dark-brown crystalline precipitate composed of crystals of $[\text{NET}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]\cdot 4\text{CH}_3\text{CN}$ (yield 0.194 g, 12.9% based on Ni, 85.9% based on Rh) suitable for X-ray analysis. The compound is soluble in acetone and CH_3CN .

$\text{C}_{68}\text{H}_{92}\text{N}_8\text{Ni}_6\text{O}_{24}\text{Rh}_8$ (2581.04): calcd. C 31.64, H 3.59, N 4.34, Ni 13.64, Rh 31.90; found C 31.47, H 3.74, N 4.09, Ni 13.71, Rh 32.08. IR (acetone, 293 K) $\nu(\text{CO})$: 1984(s), 1835(br) cm^{-1} . IR (CH_3CN , 293 K) $\nu(\text{CO})$: 1984 (s), 1803 (m) cm^{-1} . ESI-MS (CH_3CN , on $[\text{NET}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]$): ES- m/z : 986 $\{[\text{NET}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{22}]^{2-}\}^-$; 920 $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{22}]^{2-}$; 690 $\{[\text{NET}_4]_2[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{21}]^{3-}\}^-$; 611 $[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{22}]^{3-}$. ^{13}C NMR ($[\text{D}_6]\text{acetone}$): $\delta = 365.3$ ppm (br., $T_1 = 2.1 \pm 0.5$ s).

X-ray Crystallographic Study: Crystal data and collection details for $[\text{NBu}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$, $[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]$ and $[\text{NET}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]\cdot 4\text{CH}_3\text{CN}$ are reported in Table 2. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo- K_α radiation. Data were corrected for Lorentz polarisation and absorption effects (empirical absorption correction SADABS).^[38] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 .^[39] Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated.

$[\text{NBu}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$: The unit cell contains four cluster anions (located on a 2 axis; only half of a molecule in the asymmetric unit) and eight $[\text{NBu}_4]^+$ cations (on general positions; one cation in the asymmetric unit). The positions occupied by M(1) and M(2) are disordered Rh and Ni. Dummy atom constrains (instructions

Table 2. Crystal data and collection details for $[\text{NBu}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$, $[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]$ and $[\text{NET}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]\cdot 4\text{CH}_3\text{CN}$.

	$[\text{NBu}_4]_2[\text{Ni}_{10}\text{Rh}_2\text{C}(\text{CO})_{20}]$	$[\text{NET}_4]_3[\text{Ni}_9\text{Rh}_3\text{C}(\text{CO})_{20}]$	$[\text{NET}_4]_4[\text{Ni}_6\text{Rh}_8(\text{C}_2)_2(\text{CO})_{24}]\cdot 4\text{CH}_3\text{CN}$
Formula	$\text{C}_{53}\text{H}_{72}\text{N}_2\text{Ni}_{10}\text{O}_{20}\text{Rh}_2$	$\text{C}_{45}\text{H}_{60}\text{N}_3\text{Ni}_9\text{O}_{20}\text{Rh}_3$	$\text{C}_{68}\text{H}_{92}\text{N}_8\text{Ni}_6\text{O}_{24}\text{Rh}_8$
<i>F</i> _w	1850.05	1800.08	2581.04
<i>T</i> [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>F</i> ddd
<i>a</i> [Å]	24.688(2)	12.6927(12)	14.4248(14)
<i>b</i> [Å]	11.5843(9)	12.5377(12)	22.944(2)
<i>c</i> [Å]	25.519(2)	38.232(4)	51.483(5)
β [°]	111.3990(10)	98.9620(10)	90
Cell volume [Å ³]	6795.3(9)	6009.8(10)	17039(3)
<i>Z</i>	4	4	8
<i>D</i> _c [g cm ⁻³]	1.808	1.989	2.0127
μ [mm ⁻¹]	3.239	3.618	2.870
<i>F</i> (000)	3763	3592	10208
Crystal size [mm]	0.21 × 0.16 × 0.12	0.22 × 0.15 × 0.12	0.21 × 0.15 × 0.12
θ limits [°]	1.71–28.00	1.62–27.00	1.58–28.00
Index ranges	–32 ≤ <i>h</i> ≤ 32 –15 ≤ <i>k</i> ≤ 15 –32 ≤ <i>l</i> ≤ 32	–16 ≤ <i>h</i> ≤ 16 –16 ≤ <i>k</i> ≤ 16 –48 ≤ <i>l</i> ≤ 48	–19 ≤ <i>h</i> ≤ 18 –29 ≤ <i>k</i> ≤ 30 –67 ≤ <i>l</i> ≤ 68
Reflections collected	38604	65568	46851
Independent reflections	8091 [<i>R</i> _{int} = 0.0566]	13110 [<i>R</i> _{int} = 0.0342]	5128 [<i>R</i> _{int} = 0.0240]
% Completeness to θ maximum	98.7	100.0	99.6
Data/restraints/parameters	8091/145/397	13110/242/725	5128/81/243
Goodness on fit on <i>F</i> ²	1.030	1.023	1.219
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0466	0.0366	0.0585
<i>wR</i> ₂ (all data)	0.1196	0.1009	0.1880
Largest diff. peak and hole [e Å ⁻³]	1.121/–0.445	1.004/–0.662	0.860/–0.682

EXYZ and EADP in SHELXL) were used during refinement for these positions, and a free variable was assigned to each position. The overall composition of the cluster was constrained to be in the ratio Rh:Ni = 2:10 on the basis of ESI-MS analyses. The constrained free variable refined as follows: 0.58167 Rh(1), 0.41818 Rh(2) [Ni occupancy factors are the complement at one of each free variable]. Similar *U* restraints were applied to the C (s.u. 0.01) and O (s.u. 0.005) atoms. Restraints to bond lengths were applied as follow: 1.44 Å (s.u. 0.01) for C–N and 1.53 Å (s.u. 0.01) for C–C in [NBu₄]⁺.

[NEt₄]₃[Ni₆Rh₃C(CO)₂₀]: The unit cell contains four cluster anions and twelve [NEt₄]⁺ cations (all on general positions). The positions occupied by M(1), M(2), M(3) and M(4) are disordered Rh and Ni. Dummy atom constrains (instructions EXYZ and EADP in SHELXL) were used during refinement for these positions, and a free variable was assigned to each position. The overall composition of the cluster was constrained to be in the ratio Rh/Ni = 3:9 on the basis of analytical data and ESI-MS results. The constrained free variable refined as follows: 0.93509 Rh(1), 0.85178 Rh(2), 0.62743 Rh(3), 0.58511 Rh(4) [Ni occupancy factors are the complement at one of each free variable]. Similar *U* restraints (s.u. 0.001) were applied to the C and O atoms. Restraints to bond lengths were applied as follow: 1.47 Å (s.u. 0.01) for C–N and 1.53 Å (s.u. 0.01) for C–C in [NEt₄]⁺. Similar geometries were imposed to the three independent [NEt₄]⁺ cations (instruction SAME in SHELXL).

[NEt₄]₄[Ni₆Rh₈(C₂)₂(CO)₂₄]₄CH₃CN: The unit cell contains eight cluster anions (only Rh(1), Rh(2), Ni(3), Ni(4), C(1) and six CO ligands are independent; all other atoms are generated by symmetry), 32 [NEt₄]⁺ cations (two halves are independent; all other atoms are generated by symmetry) and 32 CH₃CN molecules (on general positions). One of the two independent [NEt₄]⁺ cations is disordered over two positions. Therefore, its atomic positions were split and refined using one occupancy parameter per disordered group. Similar *U* restraints were applied to the C (s.u. 0.001) and O atoms. Restraints to bond lengths were applied as follows: 1.47 Å (s.u. 0.01) for C–N and 1.53 Å (s.u. 0.01) for C–C in [NEt₄]⁺; 1.14 Å (s.u. 0.01) for C–N and 1.41 Å (s.u. 0.01) for C–C in CH₃CN.

CCDC-715236 (for [NBu₄]₂[Ni₁₀Rh₂C(CO)₂₀]), -715235 (for [NEt₄]₃[Ni₆Rh₃C(CO)₂₀]), -715234 (for [NEt₄]₄[Ni₆Rh₈(C₂)₂(CO)₂₄]₄CH₃CN) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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