SYNTHESIS AND CHEMICAL BEHAVIOR OF THE $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ AND $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ DICARBIDE CLUSTERS; X-RAY CRYSTAL STRUCTURE OF $[PPh_4]_2[Co_3Ni_7(CO)_{16}C_2]$ *

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Summary

The synthesis and properties of the new dicarbidocarbonyl bimetallic clusters $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ (I), $[Co_3Ni_7(CO)_{16}C_2]^{3-}$ (II), and $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ (III), are described. Compound I, which is paramagnetic, has been synthesized in high yields by redox-condensation of $Co_3(CO)_9CCl$ with $[Ni_9(CO)_{17}C]^{2-}$, whereas the diamagnetic trianions II and III have been respectively obtained by reduction of I, with sodium metal in THF and sodium hydroxide in methanol. The anion I has been isolated in a crystalline state in association with several tetrasubstituted ammonium or phosphonium cations, which are characterized by elemental analysis and by a single-crystal X-ray diffraction study, of the tetraphenylphosphonium salt.

The anion I has a metal frame based on a $3,4,3-C_{2h}$ stack of metal atoms, which may be regarded as derived by condensation of two either octahedral or trigonal-prismatic moieties. The resulting deca-vertices metal polyhedron encapsulates a C_2 fragment showing a short C–C interatomic separation of 1.48 Å. The three cobalt atoms cannot be distinguished from the remaining seven nickel atoms and are probably randomly distributed over the ten vertices. The M–M distances are scattered over the range 2.34–2.80 Å, and each carbide carbon is encapsulated in a seven-vertices cage which may be described as a distorted capped trigonal prism. The carbonyl stereochemistry comprises six carbonyl groups terminally bonded to the atoms of the top and bottom triangular layers, and ten edge-bridging CO which span the ten inter-layer edges.

The structure of this decanuclear dicarbide cluster is compared with those

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reported for related species and a rationalization is offered for the variations of the metal geometry and the C–C interatomic separation.

Introduction

We recently reported the synthesis and structural characterization of the $[Co_3Ni_9(CO)_{20}C]^{3-}$ carbide cluster [1,2]. A peculiar feature of this anion was its ready and complete degradation under carbon monoxide at atmospheric pressure into a mixture of $Ni(CO)_4$ and $[Co(CO)_4]^-$. When degradation was performed under a syngas atmosphere, C_1 and C_2 hydrocarbons were detected in the gas phase. Since a dicarbide species, viz. $[Co_3Ni_7(CO)_{15}C_2]^{3-}$, was isolated in very low yields as a by-product of the synthesis of $[Co_3Ni_9(CO)_{20}C]^{3-}$ [2], it was conceivable that the C_2 fraction might originate from transient formation of dicarbide clusters during degradation of the latter. It was therefore of interest to find a reproducible and reliable synthesis for $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ and related bimetallic dicarbide clusters, in order that their chemical behaviour could be investigated.

We describe here the synthesis and chemical properties of $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ (I), $[Co_3Ni_7(CO)_{16}C_2]^{3-}$ (II), and $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ (III). The structural characterization of I as $[PPh_4]_2[Co_3Ni_7(CO)_{16}C_2]$ is also reported; a preliminary report of the structure of III has appeared [2].

Results

1. Synthesis and chemical behavior of $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ and $[Co_3Ni_7(CO)_{15}C_2]^{3-}$

In recent years several dicarbide clusters of Ru, Co, Rh and Ni have been reported, e.g. $[Ru_{10}(CO)_{24}C_2]^{2-}$ [3], $[Co_{11}(CO)_{23}C_2]^{3-}$ [4], $[Co_{13}(CO)_{24}C_2]^{4-}$ [5], $Rh_{12}(CO)_{25}C_2$ [6], $[Rh_{12}(CO)_{24}C_2]^{2-}$ [7], $[Rh_{12}(CO)_{23}C_2]^{n-}$ ($n = 3, 4$) [8] and $[Ni_{10}(CO)_{16}C_2]^{2-}$ [9]. They were synthesized by (a) thermally-induced condensation of mono-carbide species [3–5], (b) in situ redox condensation [6,7], or (c) reaction of a carbonyl anion with a suitable C_2 source, such as per-chloro-ethane or -ethene [9]. These methods have been found of little or no use in the synthesis of bimetallic Co–Ni dicarbide clusters, probably owing to the thermal and oxidation stability of the only available mono-carbide precursor, namely $[Co_3Ni_9(CO)_{20}C]^{3-}$. In addition, reaction of $[Co_4Ni_2(CO)_{14}]^{2-}$ with C_2Cl_6 mainly resulted into decomposition to $Ni(CO)_4$ and $[Co(CO)_4]^-$. However the recent synthesis of $[Co_6Ni_2(CO)_{16}C_2]^{2-}$ by redox condensation of $Co_3(CO)_9CCl$ with $[Co_3Ni_9(CO)_{20}C]^{3-}$ [10] prompted us to investigate the corresponding condensation of $Co_3(CO)_9CCl$ with the homometallic carbide precursor $[Ni_9(CO)_{17}C]^{2-}$ [11].

Slow dropwise addition of a solution of $Co_3(CO)_9CCl$ in THF to a similar solution of $[Ni_9(CO)_{17}C]^{2-}$, as its $[NEt_4]^+$ or $[NBu_4]^+$ salt, up to a $1/1$ molar ratio, gives good yields of the $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ dianion, I, according to the formal stoichiometry (eq. 1). This new (brown) anion was isolated in the solid state as its $[NEt_4]^+$, $[NBu_4]^+$, $[N(PPh_3)_2]^+$ and $[PPh_4]^+$ salts by evaporation of the solvent and
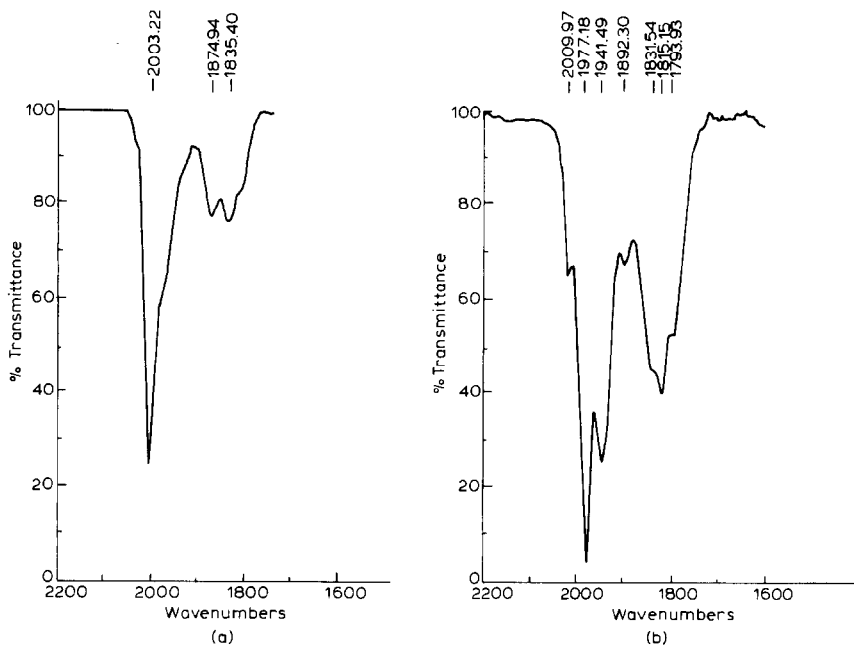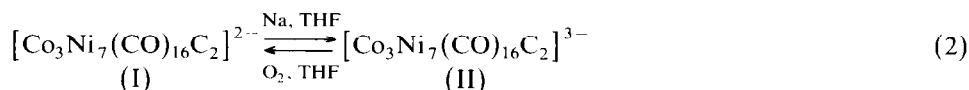
$$2[Ni_9(CO)_{17}C]^{2-} + 2\,Co_3(CO)_9CCl \rightarrow 2[Co_3Ni_7(CO)_{16}C_2]^{2-} + Ni^{2+}$$

$$+ 3\,Ni(CO)_4 + 2\,Cl^- + 8\,CO \tag{1}$$
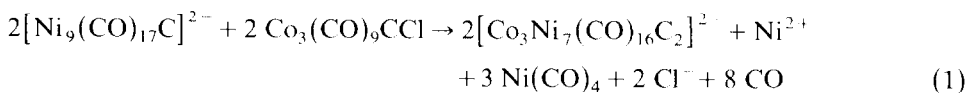
Fig. 1. Infrared spectra of (a) $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ (I) in THF and (b) $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ (III) in acetonitrile.

subsequent precipitation from methanol solution by addition of the corresponding tetrasubstituted ammonium or phosphonium halide, or by metathesis. These salts were crystallized by slow diffusion of cyclohexane into their solutions in THF. They are soluble in THF, acetone, and acetonitrile, and sparingly soluble or insoluble in the non-polar organic solvents, iso-propyl alcohol, or water. In THF solution I shows infrared carbonyl absorptions at 2003(vs), 1980(sh), 1875(s), 1835(m) and 1815(sh) cm^{-1} (see Fig. 1a). In keeping with its odd-electron formulation, compound I shows a strong ESR signal at $g = 2.05$ at room temperature, in the solid state and in solution. At liquid nitrogen temperature the signal showed some hyperfine splitting probably due to ^{59}Co, but was not sufficiently resolved to allow interpretation. Previously isolated and characterized paramagnetic carbide clusters include the $[Co_6(CO)_{14}C]^-$ mono-carbide, [12] and the $[Rh_{12}(CO)_{24}(C)_2]^{3-}$ di-carbide derivative [8]. However, I is unique in having an interstitial C_2 moiety with a short C–C interatomic separation (see next paragraph).

Attempts to oxidize I to a corresponding diamagnetic species were unsuccessful. In contrast, compound I is readily reduced both by alkali metals in THF and alkali hydroxides in methanol. On reaction with alkali metals in THF I is converted into derivative II (ν(CO) in THF at 1975vs, 1940s and 1825m cm^{-1}), according to eq. 2.

$$[Co_3Ni_7(CO)_{16}C_2]^{2-} \underset{O_2,\, THF}{\overset{Na,\, THF}{\rightleftharpoons}} [Co_3Ni_7(CO)_{16}C_2]^{3-} \qquad (2)$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$

This reaction is readily and quantitatively reversed, either with oxidizing agents and acids or by simple treatment with protic solvents such as water. This sensitivity to

protic solvents has hampered isolation of II to a pure crystalline state, and its formulation depends wholly on the spectroscopic and chemical features described.

Reduction of I with alkali hydroxides in methanol affords the different, albeit very similar, diamagnetic derivative III, according to eq. 3. Although the

$$[Co_3Ni_7(CO)_{16}C_2]^{2-} + 2\,OH^- \rightarrow [Co_3Ni_7(CO)_{15}C_2]^{3-} + HCO_3^- + \tfrac{1}{2}\,H_2 \qquad (3)$$
$$\text{(I)} \qquad\qquad\qquad\qquad\qquad \text{(III)}$$
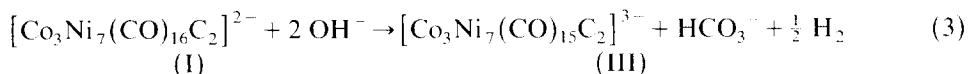
resulting trianion III shows an infrared spectrum (ν(CO) 2009w, 1977vs, 1941m, 1816m and 1791mw(sh) cm^{-1}; Fig. 1b) almost identical to that of the trianion II, it differs greatly from the latter in being stable in protic solvents. Furthermore, reaction of III with acids does not regenerate I, and gives rise to $[Co_6Ni_2(CO)_{16}C_2]^{2-}$ [10], Ni(CO)$_4$, and other unidentified products.

The tetraethylammonium salt of III was isolated as a solid, in yields up to 70%, by addition of excess [NEt$_4$]Cl to the methanol reaction solution, and subsequent crystallization from acetonitrile and diisopropyl ether. This salt of III was previously isolated in very low yields as a side-product of the synthesis of $[Co_3Ni_9(CO)_{20}C]^{3-}$ from redox condensation of $[Ni_6(CO)_{12}]^{2-}$ with Co$_3$(CO)$_9$CCl [2]. That the two products were identical, was confirmed by unit cell determination of the [NEt$_4$]$^+$ salt of tri-anion III.

Anions, I, II and III are all air sensitive in the solid state and in solution, and are readily oxidized to Ni(CO)$_4$, nickel, and cobalt carbonate. They are also extremely labile in the presence of carbon monoxide. Under an atmosphere of CO I, II and III are unreversibly degraded to a mixture of [Co(CO)$_4$]$^-$ and Ni(CO)$_4$. In the attempt to trap the C$_2$ interstitial moiety to give readily identifiable products, degradation of I and III under an atmosphere of CO and H$_2$ (1/1) was investigated; after reaction for 24 h, C$_2$ hydrocarbons and methane were detected in the gas phase, probably because of the occurrence in solution of reactions such as in eq. 4.

$$[Co_3Ni_7(CO)_{15}C_2]^{3-} + 25\,CO + 2\,H_2 \rightarrow 3[Co(CO)_4]^- + 7\,Ni(CO)_4 + C_2H_4 \qquad (4)$$
$$\text{(III)}$$
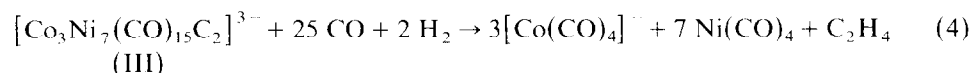
Reaction 4 is very selective and mainly gives ethylene, but anion I is less readily degraded and affords mainly methane (see Experimental). Reduction of interstitial carbide atoms with hydrogen to hydrocarbons under mild conditions is seldom observed for molecular carbide clusters [1,2,13]; it appears likely that the special reactivity of the carbide atoms of I and III may be due to progressive exposure of the carbide atoms on degradation of the metal framework with CO and subsequent elimination of hydrocarbons [14].

Attempts to confirm the presence of either I or III during degradation of $[Co_3Ni_9(CO)_{20}C]^{3-}$ with either CO + H$_2$ or CO + N$_2$, in variable mixtures, were unsuccessful; however, the results described above show that dicarbide clusters having short C–C interatomic separations produce mainly C$_2$ hydrocarbons on degradation in the presence of hydrogen.

2. X-Ray structure of [PPh$_4$]$_2$[Co$_3$Ni$_7$(CO)$_{16}$C$_2$]

The exact stoichiometry and structure of I was established by elemental analysis and a single-crystal X-ray diffraction study of the salt [PPh$_4$]$_2$[Co$_3$Ni$_7$(CO)$_{16}$C$_2$]. The crystal is composed of discrete cations and anions. An ORTEP drawing of I is shown in Fig. 2; the final positions are shown in Table 1 and the most relevant bond distances and angles of the anionic moiety are given in Table 2.

TABLE 1

TABLE OF POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	$B(\mathring{A}^2)$
Ni(1)	0.5055(1)	0.1647(1)	0.4213(2)	3.56(4)
Ni(2)	0.4718(2)	0.1882(1)	0.6349(2)	4.18(5)
Ni(3)	0.6803(2)	0.0864(1)	0.5981(2)	4.18(5)
Ni(4)	0.3442(1)	0.0746(1)	0.5319(2)	3.44(4)
Ni(5)	0.4299(1)	0.0088(1)	0.3209(2)	3.58(4)
P(1)	0.9210(3)	0.3383(3)	0.1181(2)	2.95(8)
O(1)	0.552(1)	0.3708(8)	0.421(1)	8.7(4)
O(2)	0.487(1)	0.409(1)	0.721(1)	11.7(5)
O(3)	0.804(1)	0.2584(9)	0.677(1)	8.0(4)
O(4)	0.397(1)	0.1662(9)	0.1599(9)	8.3(3)
O(5)	0.2235(9)	0.2790(9)	0.649(1)	7.3(3)
O(6)	0.491(1)	0.135(1)	0.884(1)	11.8(5)
O(7)	0.8168(9)	−0.0271(9)	0.818(1)	7.6(3)
O(8)	0.8889(8)	−0.037(1)	0.504(1)	7.8(4)
C	0.4856(9)	−0.0333(9)	0.490(1)	2.9(3)
C(1)	0.531(1)	0.291(1)	0.418(1)	5.0(4)
C(2)	0.483(1)	0.323(1)	0.692(2)	6.6(5)
C(3)	0.757(1)	0.192(1)	0.649(1)	5.4(4)
C(4)	0.428(1)	0.126(1)	0.249(1)	5.1(4)
C(5)	0.296(1)	0.210(1)	0.613(1)	4.8(4)
C(6)	0.514(2)	0.100(2)	0.791(2)	8.1(6)
C(7)	0.726(1)	−0.006(1)	0.745(1)	4.8(4)
C(8)	0.789(1)	−0.027(1)	0.508(1)	5.5(4)
C(101)	0.854(1)	0.264(1)	0.179(1)	3.5(3) ★ [a]
C(102)	0.903(1)	0.234(1)	0.296(1)	3.9(3) ★
C(103)	0.850(1)	0.177(1)	0.341(1)	5.1(3) ★
C(104)	0.748(1)	0.147(1)	0.270(1)	4.4(3) ★
C(105)	0.698(1)	0.173(1)	0.153(1)	4.6(3) ★
C(106)	0.750(1)	0.232(1)	0.108(1)	4.0(3) ★
C(107)	1.007(1)	0.2505(9)	0.015(1)	2.9(2) ★
C(108)	0.983(1)	0.154(1)	−0.043(1)	4.0(3) ★
C(109)	1.046(1)	0.093(1)	−0.127(1)	5.0(3) ★
C(110)	1.130(1)	0.128(1)	−0.152(1)	5.0(3) ★
C(111)	1.156(1)	0.223(1)	−0.093(1)	5.4(4) ★
C(112)	1.093(1)	0.285(1)	−0.005(1)	4.5(3) ★
C(113)	1.019(1)	0.4061(9)	0.242(1)	3.0(2) ★
C(114)	1.130(1)	0.346(1)	0.300(1)	4.2(3) ★
C(115)	1.204(1)	0.397(1)	0.398(1)	4.5(3) ★
C(116)	1.167(1)	0.506(1)	0.432(1)	5.2(3) ★
C(117)	1.062(1)	0.566(1)	0.377(1)	5.1(3) ★
C(118)	0.982(1)	0.518(1)	0.278(1)	3.8(3) ★
C(119)	0.800(1)	0.4370(9)	0.033(1)	2.9(2) ★
C(120)	0.800(1)	0.449(1)	−0.083(1)	4.1(3) ★
C(121)	0.705(1)	0.527(1)	−0.142(1)	5.1(3) ★
C(122)	0.619(1)	0.590(1)	−0.089(1)	5.0(3) ★
C(123)	0.621(1)	0.578(1)	0.023(1)	5.0(3) ★
C(124)	0.709(1)	0.502(1)	0.088(1)	5.0(3) ★

[a] Atoms marked ★ were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2 B_{1,1} + b^2 B_{2,2} + c^2 B_{3,3} + ab(\cos \gamma) B_{1,2} + ac(\cos \beta) B_{1,3} + bc(\cos \alpha) B_{2,3}]$.
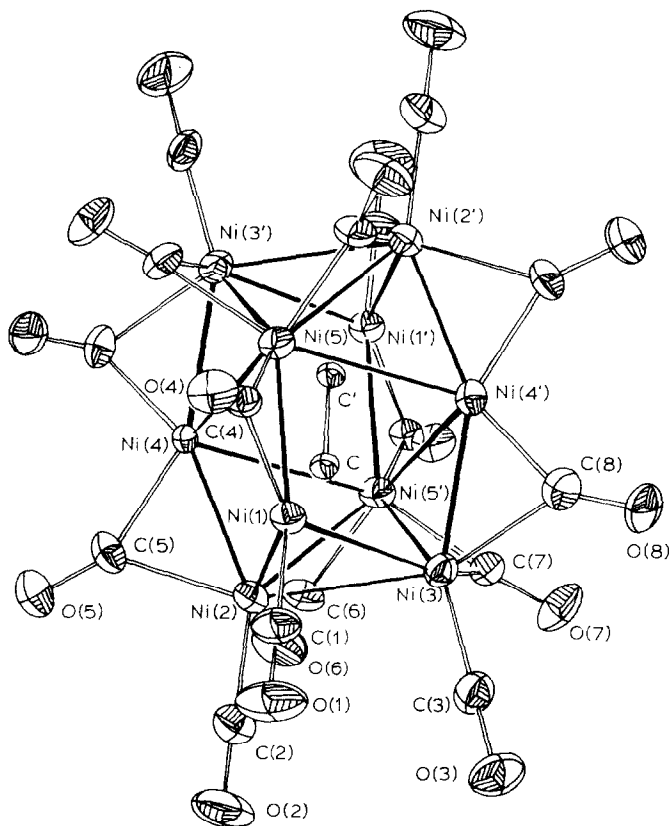
Fig. 2. ORTEP drawing of the $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ dianion (I).

As shown in Fig. 2, the metal framework of I consists of a 3,4,3 stack of metal atoms of C_{2h} idealized symmetry, and identical to that in III [2], whereas the crystallographic symmetry is only C_i. The deca-vertices metal polyhedron can be regarded as derived either from a bi-octahedron having the shared edge broken (see Scheme 1), or from distortion of two condensed trigonal prismatic moieties. These two descriptions relate the structure of I, as well as III, to those of $[Ru_{10}(CO)_{24}C_2]^{2-}$ [3] and $[Ni_{10}(CO)_{16}C_2]^{2-}$ [9].

The three cobalt atoms could not be distinguished from the seven nickel atoms neither by X-ray data nor by their stereochemistry, and are probably randomly distributed over the ten vertices. Because of this, the metal atoms are labeled only as Ni in the Tables and Fig. 1. The M–M distances are scattered over the range 2.34–2.80 Å, and may be divided in four sets: the first set, comprising six out of ten inter-layer edges (1–5, 2–4, 3–4), has a quite short mean value of 2.36 Å, and this band is spanned by bridging carbonyl groups. The remaining four inter-layer edges have a slightly longer value of 2.545 Å. The intralayer M–M distances in the top and bottom triangles show an average value of 2.58 Å, whereas the intralayer distance of the central rhombus is 2.802 Å. Four additional M–M interatomic separations (1–4) are probably too long (average 3.18 Å) to be regarded as M–M bonds.

The carbonyl groups are divided in two sets: six out of sixteen are terminally

TABLE 2

MOST SIGNIFICANT BOND DISTANCES (Å) AND ANGLES (°) IN $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ (I)

M – M

Ni(1)–Ni(2)	2.562(2)	Ni(1)–Ni(3)	2.582(2)	Ni(1)–Ni(5)	2.392(2)
Ni(2)–Ni(3)	2.589(2)	Ni(2)–Ni(4)	2.338(2)	Ni(2)–Ni(5′)	2.559(2)
Ni(3)–Ni(4′)	2.334(2)	Ni(3)–Ni(5′)	2.530(2)	Ni(4)–Ni(5)	2.802(2)
Ni(4)–Ni(5′)	2.783(2)				

$M – C_{carbide}$

Ni(1)–C	1.901(10)	Ni(2)–C	2.056(11)	Ni(3)–C	2.085(10)
Ni(4)–C′	2.082(10)	Ni(4)–C	2.089(11)	Ni(5)–C	2.114(10)
Ni(5)–C′	2.148(10)				
		C–C′	1.478(22)		

$M – CO_{terminal}$

Ni(1)–C(1)	1.762(16)	Ni(2)–C(2)	1.756(17)	Ni(3)–C(3)	1.776(17)

$M – CO_{bridging}$

Ni(1)–C(4)	1.954(14)	Ni(2)–C(5)	2.009(13)	Ni(2)–C(6)	2.187(19)
Ni(3)–C(7)	2.131(14)	Ni(3)–C(8)	1.994(17)	Ni(4)–C(5)	1.817(14)
Ni(4′)–C(8)	1.791(16)	Ni(5)–C(4)	1.866(15)	Ni(5′)–C(6)	1.816(18)
Ni(5′)–C(7)	1.819(14)				

C – O

C(1)–O(1)	1.126(15)	C(2)–O(2)	1.107(17)	C(3)–O(3)	1.112(24)
C(4)–O(4)	1.166(15)	C(5)–O(5)	1.153(14)	C(6)–O(6)	1.150(17)
C(7)–O(7)	1.162(14)	C(8)–O(8)	1.195(16)		

Angles

Ni(1)–Ni(2)–Ni(3)	60.17(6)	Ni(1)–Ni(2)–Ni(4)	81.81(7)	Ni(1)–Ni(2)–Ni(5′)	97.96(7)
Ni(1)–Ni(3)–Ni(2)	59.38(6)				
Ni(1)–Ni(5)–Ni(4)	75.97(7)	Ni(1)–Ni(5)–Ni(4′)	74.66(6)	Ni(2)–Ni(1)–Ni(3)	60.44(7)
Ni(2)–Ni(1)–Ni(5)	101.82(8)	Ni(2)–Ni(4)–Ni(5)	96.47(7)	Ni(2)–Ni(4)–Ni(5′)	59.20(6)
Ni(2)–Ni(5′)–Ni(3)	61.15(7)	Ni(2)–Ni(5′)–Ni(4′)	94.37(7)	Ni(2)–Ni(5′)–Ni(4)	51.69(6)
Ni(3)–Ni(1)–Ni(5)	102.39(7)	Ni(3)–Ni(2)–Ni(4)	106.52(8)	Ni(3)–Ni(2)–Ni(5′)	58.87(6)
Ni(3)–Ni(4′)–Ni(5′)	58.19(6)	Ni(3)–Ni(4)–Ni(5)	98.16(7)	Ni(3)–Ni(5′)–Ni(4′)	51.61(6)
Ni(3)–Ni(5)–Ni(4)	95.95(7)	Ni(4)–Ni(2)–Ni(5′)	69.10(6)	Ni(4)–Ni(5)–Ni(4′)	88.59(6)
Ni(5)–Ni(4)–Ni(5′)	91.41(6)				

bonded to the six metal atoms of the top and bottom triangular layers ($M-C_{av}$ 1.77, $C-O_{av}$ 1.12 Å). The remaining ten are edge-bridging, and span all the ten interlayer edges of the 3,4,3-C_{2h} stack. They are all unsymmetrical ($M-C_{av}$ 1.82 and 2.05, $C-O_{av}$ 1.16 Å), and show their shortest contacts with the metal atoms of the central rhombic layer which do not bear terminal carbonyl ligands.

The carbide atoms are encapsulated in two identical seven-vertices cages, which may be regarded as distorted capped trigonal prisms. The $M-C_{carbide}$ interactions are spread over the range 1.90–2.15 Å (the overall mean is 2.07 Å), which corresponds to a calculated average covalent radius for carbon of 0.80 Å. The two carbide atoms show a rather short interatomic separation of 1.48 Å. Comparably short interatomic C–C separations were previously found only in III (1.41 Å), [2] $[Co_6Ni_2(CO)_{16}C_2]^{2-}$ (1.49 Å), [10] $Rh_{12}(CO)_{25}C_2$ (1.48 Å), [6] and $[Ni_{10}(CO)_{16}C_2]^{2-}$ (1.40 Å) [9]. Comparison between the structures of I and III shows that the lengthening of the C–C interatomic separation is the major effect brought about by the presence in I of an extra valence electron, as a result of the addition of one carbonyl group to III and

A   B
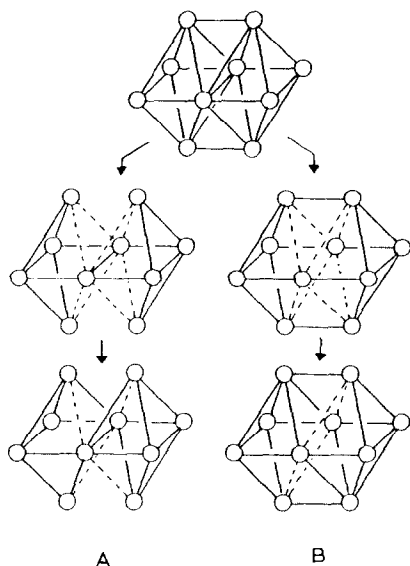
SCHEME 1

loss of a negative charge. All the other molecular parameters of the metal frame are almost identical in the two anions (maximum deviations on single bond distance and angle are less than 0.03 Å and 1°, respectively). It is, therefore, likely that the extra valence electron in I is located in a molecular orbital which has antibonding character with respect to the C–C interaction. If each interstitial carbide atom is regarded as a formal four electron donor, [15] III is isoelectronic, but not isostructural, with $[Ru_{10}(CO)_{24}(C)_2]^{2-}$, and I has one extra electron. On simple geometrical grounds the metal skeleton of both I and III may be derived from a cubic close packed (c.c.p.) bi-octahedral fragment by breaking of the inner M–M bond (path B of Scheme 1), and subsequent minimization of such a perturbation in a way similar to that (path A in Scheme 1) which may give rise to the actual metal skeleton of $[Ru_{10}(CO)_{24}C_2]^{2-}$ by rupture of two outer M–M bonds (in Scheme 1 dotted lines represent loose M–M interactions). This alternative rearrangement of I and III is in keeping with the preference for a cavity larger than octahedral of carbide atoms in both Ni and Co–Ni carbonyl carbide clusters, e.g. $[Ni_9(CO)_{17}C]^{2-}$ [11], $[Ni_{10}(CO)_{16}C_2]^{2-}$ [9], $[Co_3Ni_9(CO)_{20}C]^{3-}$ [1], and $[Co_6Ni_2(CO)_{16}C_2]^{2-}$ [10].

Discussion

EHMO calculations on a bare c.c.p. bi-octahedral cluster [16] revealed that 134 electrons are necessary in order to fill the 67 cluster valence orbitals. Owing to the structural relationships shown in Scheme 1, it is reasonable to assume 138 and 136 cluster valence electrons as the minimum requirement for arriving at the distorted frameworks of path A and B. While $[Ru_{10}(CO)_{24}C_2]^{2-}$, with two separated interstitial C^{4+} ions, formally fullfills this requirement, compound III with two separated C^{4+} ions would possess an extra pair of electrons, which may be therefore located in an orbital possessing a bonding character with respect to the C–C interaction.

Under this formalism we may consider III as enclosing an interstitial C_2^{6+} moiety with a filled σ-bonding orbital. Addition of one more valence electron should result in a C_2^{5+} moiety, with partial filling of the σ* antibonding combination and in a consequent lenghtening of the C–C interaction, as is observed on going from III to I.

This crude bonding interpretation for I and III also provides a rationalization for the instability of II; complete filling of the σ* antibonding combination by addition of one more electron could result in an intrinsic instability owing to further lengthening of the C–C interaction and weakening of the M–M interactions.

Experimental

All the operations were carried out under nitrogen in dried and deoxygenated solvents. Infrared spectra were recorded either on a Perkin–Elmer 781 grating spectrophotometer or on a Nicolet interferometer using calcium fluoride cells. GLC analyses were performed on a Perkin–Elmer Sigma 115 equipped with a silica injector or on a Carlo Erba HRGC gas chromatograph connected to a VG Micromass quadrupol mass spectrometer ESR spectra were recorded on a Varian instrument. Elemental analyses were performed as previously described [17]. $Co_3(CO)_9CCl$ [18] and salts of the $[Ni_6(CO)_{12}]^{2-}$ [17] and $[Ni_9(CO)_{17}C]^{2-}$ [11] dianions were prepared by published methods.

1. Synthesis of [N(PPh$_3$)$_2$]$_2$[Co$_3$Ni$_7$(CO)$_{16}$C$_2$]

$[NEt_4]_2[Ni_9(CO)_{17}C]$ (2.1 g) was dissolved in tetrahydrofuran (40 ml) and a solution of $Co_3(CO)_9CCl$ in THF (0.83 g in 10 ml) was added dropwise with stirring. After 2 h, the brown solution was evaporated to dryness in vacuum. The residue was dissolved in methanol, the solution was filtered, and $[N(PPh_3)_2]_2[Co_3Ni_7(CO)_{16}C_2]$ was precipitated by addition of an excess of $[N(PPh_3)_2]Cl$.

The corresponding $[PPh_4]^+$, $[NEt_4]^+$ and $[NBu_4]^+$ salts were similarly prepared. All the salts were crystallized by slow diffusion of cyclohexane into their solutions in THF. Yield of $[N(PPh_3)_2]_2[Co_3Ni_7(CO)_{16}C_2]$ 1.76 g.

Analytical data: Found: $[N(PPh_3)_2]^+$, 50.88; Co, 8.55; Ni, 20.23; $[N(PPh_3)_2]^+/$ Co/Ni 1/1.53/3.64. $[N(PPh_3)_2]_2[Co_3Ni_7(CO)_{16}C_2]$ calcd.: $[N(PPh_3)_2]^+$, 50.38; Co, 8.27; Ni, 19.24; CO, 20.98%; $[N(PPh_3)_2]^+/Co/Ni$ 1/1.5/3.5.

2. Synthesis of [NEt$_4$]$_3$[Co$_3$Ni$_7$(CO)$_{15}$C$_2$]

A solution of $[NEt_4]_2[Co_3Ni_7(CO)_{16}C_2]$ (0.62 g) in methanol (50 ml) containing 1 g of KOH was stirred for 24 h under nitrogen. $[NEt_4]_3[Co_3Ni_7(CO)_{15}C_2]$ was precipitated by addition of $[NEt_4]Cl$ (2 g), and crystallized from acetonitrile by slow diffusion of diisopropyl ether. Yield 0.54 g.

Analytical data: Found: $[NEt_4]^+$, 28.4; Co, 12.01; Ni, 28.65; $[NEt_4]^+/Co/Ni$ 1/0.97/2.39. $[NEt_4]_3[Co_3Ni_7(CO)_{15}C_2]$ calcd.: $[NEt_4]^+$, 27.49; Co, 12.43; Ni, 28.90; CO, 29.54%; $[NEt_4]^+/Ni/Co/CO$ 1/1/2.33/5.

3. Reaction of I and III with CO and H$_2$

The salt $[NEt_4]_3[Co_3Ni_7(CO)_{15}C_2]$ (0.76 g) was dissolved in CH_3CN (15 ml) in a 100 ml Schlenk tube, which was then stoppered with a serum cap. The tube was evacuated and a mixture of CO and H_2 (1/1) was admitted, which was checked by GLC. The solution was stirred for 24 h, then the gas phase was again examined by

gas chromatography, this revealed the presence of ethylene (91% of the hydro-carbons fraction), ethane (6%) and methane (3%).

An analogous experiment with $[NEt_4]_2[Co_3Ni_7(CO)_{16}C_2]$ gave the following results: methane (62%), ethylene (12%) and ethane (26%). These data were repro-ducible to within a 15%.

4. X-ray diffraction study of $[PPh_4]_2[Co_3Ni_7(CO)_{16}C_2]$

Crystal data: $C_{66}H_{40}Co_3Ni_7O_{16}P_2$, $M = 1738.8$, triclinic, space group $P1$, a 12.108(2), b 12.942(2), c 11.550(2) Å, α 102.35(2), β 107.57(2), γ 72.57(2)°, U 1631(1) Å^3, D_c 1.77 g cm^{-3} for $Z = 1$, μ(Mo-K_α) 28.4 cm^{-1}, λ(Mo-K_α) 0.71069 Å. The unit cell parameters were obtained from a least squares refinement of θ values, measured on the diffractometer, for 25 reflections in the range $17 < 2\theta < 27°$. A specimen of maximum dimensions $0.20 \times 0.30 \times 0.35$ mm was mounted on an Enraf–Nonius CAD 4 diffractometer. Intensities were measured for 5850 reflections (corresponding to the $\pm h$ $\pm k$ $+l$ quadrant in the 2θ range 6–50°) using the ω-scan technique, with a scan range of $1° + 0.35tg\theta$ and a scan speed in the range 10–3° min^{-1}. Backgrounds were counted for half the total scan time at the extreme points of the scan range. Periodical monitoring of these reflections revealed an average linear decay of the diffracted intensities of ca. 3% by the end of data collection. Structure factors were computed by application of Lorentz, polarization, decay, and absorption corrections. The latter was evaluated by the ψ-scan method, and relative transmission factors were found in the range 0.80–1. After averaging of equivalent reflections, 2236 reflections having $I > 3\sigma(I)$ were used for structure solution and refinement.

The structure was solved by direct methods, using MULTAN. The E map from the best set showed 10 peaks of similar height, which were all refined as Ni atoms. The resulting R was 0.28 and the subsequent iterative application of difference-Fourier syntheses and full matrix least-squares refinement allowed the complete structure to be revealed. In the final stage of refinement, the ten metal atoms were given an atomic scattering factor equal to $7/10 f_{Ni} + 3/10 f_{Co}$, and anisotropic thermal parameters were assigned to all the atoms of the anion. The final agreement indices were $R = 0.057$ and $R_w = 0.060$, GOF = 1.38 for 304 refined variables, where $R_w = [\Sigma w(F_0 - k \mid F_c \mid)^2 / \Sigma w F_0^2]^{1/2}$, $w = \sigma^{-2}(F_0)$, $\sigma(F_0) = \sigma(F_0^2)/2F_0$, $\sigma(F_0^2) = [\sigma^2(I) + (PI)^2]^{1/2}/Lp$; P, the ignorance factor, was 0.06. GOF = $[\Sigma w(F_0 - \mid F_c \mid)^2 / (NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables. The hydrogen atoms of cations were introduced in their calculated positions and not refined. The final difference Fourier showed no peaks exceeding 0.5 e Å^{-3}. All computations were carried out on a PDP-11/34 computer using the Enraf–Nonius structure determination package SDP (including MULTAN for direct methods and ORTEP for drawings) and the physical constants tabulated therein. Lists of thermal parameters and structure factors are available from the authors.

Acknowledgements

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