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Bimetallic Co–Ni carbide clusters: synthesis and crystal structure of the $[Co_2Ni_{10}(CO)_{20}C]^{2-}$ and $[Co_3Ni_9(CO)_{20}C]^{2-}$ dianions *

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Abstract

The synthesis, chemical behavior and single crystal X ray structure of two new Co–Ni bimetallic carbide clusters, namely $[Co_2Ni_{10}(CO)_{20}C]^{2-}$ and $[Co_3Ni_9(CO)_{20}C]^{2-}$, are reported. The first complex was isolated in ca. 30% yield among the products of the reaction of $Co_3(CO)_9CCl$ with $[Ni_6(CO)_{12}]^{2-}$, while the second was obtained quantitatively by reaction with protonic acids of the previously reported $[Co_3Ni_9(CO)_{20}C]^{3-}$. The two compounds are isostructural and show a metal frame which can be regarded as derived by distortion of a tetra-capped triangulated dodecahedron of D_{2d} symmetry; the statistical (Co and Ni atoms being undistinguishable) idealized symmetry of the metal frame is only D_2 owing to progressive deformations toward a tetra-capped tetragonal antiprismatic geometry, which are probably related to the steric requirements of the interstitial carbide atom.

Introduction

The synthesis and structure of some homometallic nickel mono-carbide clusters, e.g. $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$ [1], and bimetallic Co–Ni carbide clusters, e.g. $[Co_3Ni_9(CO)_{20}C]^{3-}$ [2], has been reported. In all these compounds the carbide atom is interstitially lodged in a more or less regular square-antiprismatic cavity of metal atoms. This is by no means exceptional, since such a stereochemistry was previously documented both in interstitial metal carbide alloys, e.g. $Cr_{23}C_6$ [3],

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* Dedicated to Prof. Luigi Sacconi.

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and in molecular carbonyl clusters, e.g. $[Co_8(CO)_{18}C]^{2-}$ [4]. However, the structure of $[Ni_9(CO)_{17}C]^{2-}$, [1], as well as those of other interstitial clusters such as $[Co_9(CO)_{21}Si]^{2-}$, [5] $[Rh_9(CO)_{21}P]^{2-}$, [6] $[Rh_{10}(CO)_{22}E]^{3-}$ (E = P, As) [7,8], and $[Rh_{10}(CO)_{22}S]^{2-}$ [9], suggests that in cluster chemistry the capping of a square antiprism preferentially occurs at the two square faces. In this regard the solid state structure of $[Co_3Ni_9(CO)_{20}C]^{3-}$ was unique in showing triangular, rather than square, faces capped by the four additional atoms [2]. Moreover, all the attempts to uncap the above structure invariably led to decomposition. It was, therefore, of some interest to re-investigate the chemistry of bimetallic Co–Ni mono-carbide clusters in order to gain more understanding of the above structural oddity.

We report here the synthesis and chemical behaviour of two new Co–Ni carbide clusters, namely $[Co_2Ni_{10}(CO)_{20}C]^{2-}$ (I) and $[Co_3Ni_9(CO)_{20}C]^{2-}$ (II). Although their structures are closely related to that previously observed for $[Co_3Ni_9(CO)_{20}C]^{3-}$ (III), small differences in some molecular parameters justify an alternative description that offers a possible rationale for the stereochemistry of the metal frame.

Results and discussion

1. Synthesis and chemical behaviour of $[Co_2Ni_{10}(CO)_{20}C]^{2-}$ *(I)*

It has been reported that addition of $[Co_3(CO)_9CCl]$ to $[NEt_4]_2[Ni_6(CO)_{12}]$ (1/2 molar ratio) in tetrahydrofuran (thf) solution and under nitrogen gives III, according to stoichiometry (eq. 1) [2].

$$2\,[Ni_6(CO)_{12}]^{2-} + Co_3(CO)_9CCl \rightarrow [Co_3Ni_9(CO)_{20}C]^{3-} + Cl^- + 3\,Ni(CO)_4 + CO \qquad (1)$$

However, other by-products, among which small amounts of $[Co(CO)_4]^-$, were always obtained, and the yield of III never exceeded 50–60% of that calculated from the formal stoichiometry (eq. 1) [2]. A re-investigation of the above reaction enabled the synthesis of the new bimetallic Co–Ni carbide derivative I, which is obtained along with III owing to the concurrent reaction (eq. 2).

$$2\,[Ni_6(CO)_{12}]^{2-} + Co_3(CO)_9CCl \rightarrow [Co_2Ni_{10}(CO)_{20}C]^{2-} + [Co(CO)_4]^- + 2Ni(CO)_4 + Cl^- + CO \qquad (2)$$

A more appropriate formal equation of the reaction of $Co_3(CO)_9CCl$ with $[Ni_6(CO)_{12}]^{2-}$ is thus represented by the overall stoichiometry (eq. 3).

$$4\,[Ni_6(CO)_{12}]^{2-} + 2\,Co_3(CO)_9CCl \rightarrow [Co_2Ni_{10}(CO)_{20}C]^{2-} + [Co_3Ni_9(CO)_{20}C]^{3-} + 2\,Cl^- + [Co(CO)_4]^- + 5\,Ni(CO)_4 + 2\,CO \qquad (3)$$

It was possible to demonstrate the presence in the reaction mixture of a roughly 1/1 ratio of I and III owing to differential solubilities of their tetraethylammonium salts in methanol. Thus when the reaction mixture obtained according to equation 3 was evaporated to dryness and the residue extracted with methanol, the dark brown solution obtained contained I and $[Co(CO)_4]^-$ salts, the residue consisted of the corresponding salts of III. I was precipitated in a fairly pure state from the

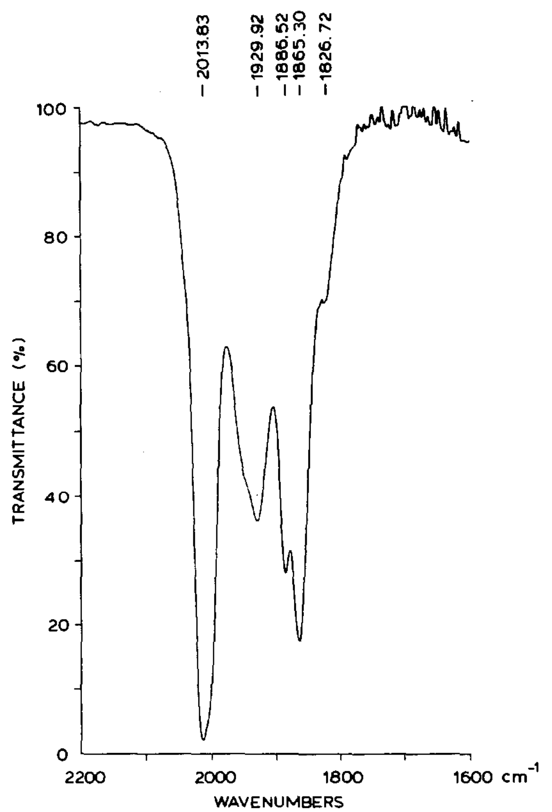

Fig. 1. Infrared spectrum in the carbonyl stretching region for $[Co_2Ni_{10}(CO)_{20}C]^{2-}$ (I) in thf.

methanol solution by addition either of an excess of NEt_4Cl or halides of bulkier cations such as PPh_4^+ or PPN^+ (PPN^+ = bis(triphenylphosphine)imminium cation), and water. Initial attempts to crystallize these salts by slow diffusion of a precipitating solvent, e.g. cyclohexane, into their thf solutions were unsuccessful owing to partial conversion of I into III and other, unidentified species. For instance, as also shown in separate experiments, I reacts slowly in acetone solution with $[Co(CO)_4]^-$ to give the previously mentioned but still uncharacterized green anion (ν(CO) at 1995(vs) and 1830(m) cm^{-1}) [2].

Since I is not protonated by protonic acids, it was possible to carry out the crystallization from thf solutions acidified with CF_3COOH by slow diffusion of cyclohexane. Yields in I are in the range 30–35% based on equation 3. The infrared spectrum of crystalline $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$ dissolved in thf shows absorption bands in the carbonyl stretching region at 2014(s), 1930(m), 1886(ms), 1865(ms), and 1827(sh) cm^{-1}, and a pattern closely related to that of III (see Fig. 1). Elemental analysis of the crystals shows a PPh_4^+/Co/Ni ratio very close to the expected 1/1/5 ratio.

Most salts of I, e.g. NEt_4^+, NBu_4^+, PPh_4^+, are soluble in many organic polar solvents, including thf and acetone and insoluble in hydrocarbons and water. Once purified, I is more stable in these solvents. In contrast complex transformations were observed on dissolution of I in other solvents such as CH_3CN or dimethylsulfoxide (DMSO): these result in the rapid appearance of new IR bands at 1995, 1955, 1875, 1850 cm^{-1}, which are not attributable to any of the known Co–Ni carbide species. The lability of a bimetallic Co–Ni carbonyl cluster in basic solvents is not unexpected in view of the instability toward disproportionation of several homometallic cobalt clusters [10]; furthermore we recently observed that $[Co_6Ni_2(CO)_{16}C_2]^{2-}$ [11] in acetonitrile undergoes a ready carbonyl-substitution reaction, to give $[Co_6Ni_2(CO)_{14}(CH_3CN)_2C_2]^{2-}$ [12].

2. *Synthesis and chemical behaviour of the* $[Co_3Ni_9(CO)_{20}C]^{2-}$ *(II) dianion*

In contrast to the isoelectronic dianion I, the trianion III readily reacts with protonic acids. The product of the reaction depends greatly on the solvent used. Thus, in acetonitrile a very complicated transformation occurs, with formation of $Ni(CO)_4$ and $[Co(CO)_4]^-$ and other unidentified products, whereas in acetone the reaction takes the much simpler course represented by equation 4:

$$\underset{\text{(III)}}{[Co_3Ni_9(CO)_{20}C]^{3-}} + H^+ \rightarrow \underset{\text{(II)}}{[Co_3Ni_9(CO)_{20}C]^{2-}} + \tfrac{1}{2}\,H_2 \qquad (4)$$

The resulting dianion II is not further protonated, and does not undergo further transformation even in the presence of a large excess of acids. In contrast, other oxidizing agents such as I_2, Fe^{3+} and Cu^+ are much less selective. When the reaction mixture is evaporated to dryness and the residue dissolved in methanol, addition of bulkier cation halides in excess (PPh_4^+, PPN^+, NEt_4^+) produces precipitates of the corresponding salts of II in a fairly pure microcristalline state. Yields become almost quantitative if water is also added. As for I, II in thf or acetone solution is more stable under the acidic conditions obtained by addition of small amounts of CF_3COOH. Under these experimental conditions, it was possible to grow crystals of the PPh_4^+ salt of II with little decomposition. The infrared spectrum of crystals of $[PPh_4]_2[Co_3Ni_9(CO)_{20}C]$ in thf solution (see Fig. 2) is only slightly different from that of the corresponding $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$, and shows infrared carbonyl absorptions at 2016(vs), 1930(sh), 1907(ms), 1880(ms), 1865(sh) cm^{-1}. No proton signal was found in the NMR spectrum from δ -50 to 40 ppm except for those due to the cations, which appeared as broad signals. The odd electron formulation of II was confirmed by the observation of a strong and broad ESR signal with a g factor of 2.03. Other reported examples of carbonyl high-nuclearity clusters with an odd electron formulation include the $[Co_6(CO)_{14}C]^-$ [13], $[Co_{13}(CO)_{24}C_2]^{4-}$ [14], $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ [15], $[Rh_{12}(CO)_{24}C_2]^{3-}$ [16], carbide clusters, as well as $[Co_9(CO)_{21}Si]^{2-}$ [5], $[Fe_3Pt_3(CO)_{15}]^-$ [17], and $[Ni_6Rh_5(CO)_{21}H_x]^{3-}$ [18].

In keeping with their identical metal/free charge ratios, the corresponding salts of I and II show very similar solubilities and stabilities in organic solvents. In DMSO, for example, II is rapidly converted into III. Like III [2], both I and II are completely and readily degraded by carbon monoxide (25 ° C, 1 atm) to a mixture of $[Co(CO)_4]^-$ and $Ni(CO)_4$; the fate of the carbide atom has not been established.

3. *X-Ray structure of* $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$ *and* $[PPh_4]_2[Co_3Ni_9(CO)_{20}C]$

The crystals of $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$ and $[PPh_4]_2[Co_3Ni_9(CO)_{20}C]$ are strictly isomorphous, with only small differences in the unit cell parameters (see

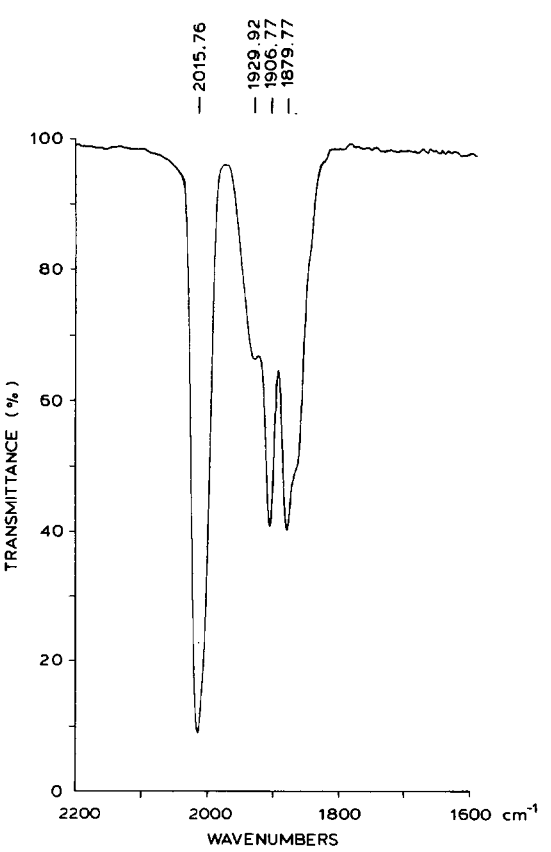

Fig. 2. Infrared spectrum in the carbonyl stretching region for $[Co_3Ni_9(CO)_{20}C]^{2-}$ (II) in thf.

Experimental). The crystals of both salts are made up of discrete $[PPh_4]^+$ and $[Co_2Ni_{10}(CO)_{20}C]^{2-}$, or $[Co_3Ni_9(CO)_{20}C]^{2-}$ ions. Positional parameters are listed in Tables 1 and 2, respectively; selected bond distances and angles for both dianions are listed in Table 3.

The structures of dianions I and II are very similar (and closely related to that of the trianion III [2]) and so an ORTEP drawing is shown only for I (see Fig. 3). For ease of comparison, in Fig. 3 and in Tables 1–3 the atoms are labeled in the same way as the corresponding atoms of III. The metal framework of both I and II can, in keeping with the description previously given for III, be regarded as based on a tetragonal antiprism of metal atoms, which is tetra-capped on two alternate pairs of adjacent triangular faces so to give rise to a metal frame of statistical idealized D_2 symmetry. In neither anion can the cobalt and nickel atoms be distinguished (see Experimental), but the stereochemistry of the four capping atoms suggests their labelling as nickel atoms, since it is identical to that of the corresponding atoms of III and is that usually adopted by nickel atoms capping a triangular face (see for instance $[Fe_3Ni(CO)_{12}H]^-$ [19] and $[Ni_{12}(CO)_{16}C_2]^{4-}$ [20]).

Major deviations from the above description arise because the two tetragonal faces are more accurately described as two fused triangular faces with a rather long

(Continued on p. 247)

TABLE 1

ATOMIC COORDINATES FOR $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$ WITH ESTIMATED STANDAR DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	$B(Å^2)$ [a]
Ni(1)	−0.05458(8)	0.5113(1)	0.35586(7)	3.94(4)
Ni(2)	−0.11650(8)	0.6349(1)	0.24581(8)	3.72(4)
Ni(3)	0.19323(8)	0.5662(1)	0.25928(8)	4.29(5)
Ni(4)	0.11851(8)	0.3812(1)	0.20408(7)	4.07(4)
M(1)	0.00136(8)	0.6250(1)	0.31321(7)	2.79(4)
M(2)	0.10333(7)	0.6297(1)	0.29226(7)	3.07(4)
M(3)	0.13339(7)	0.4567(1)	0.29717(7)	3.06(4)
M(4)	0.04984(7)	0.4625(1)	0.34160(6)	2.99(4)
M(5)	−0.06754(7)	0.4816(1)	0.25470(7)	2.56(4)
M(6)	−0.02770(8)	0.6081(1)	0.20194(7)	3.09(4)
M(7)	0.07423(8)	0.5409(1)	0.19651(7)	3.28(4)
M(8)	0.01566(7)	0.4046(1)	0.22685(7)	2.95(4)
P(1)	0.6175(2)	0.5021(3)	0.4143(2)	3.66(9)
P(2)	0.3383(2)	0.5299(3)	0.0089(2)	3.70(9)
O(1)	0.0966(5)	0.7676(7)	0.3730(4)	5.6(2)*
O(2)	0.1680(5)	0.3560(7)	0.4055(4)	5.9(3)*
O(3)	−0.1186(5)	0.3381(7)	0.1673(4)	5.9(3)*
O(4)	0.0004(5)	0.6623(7)	0.1001(4)	6.0(3)*
O(5)	0.1991(5)	0.7722(8)	0.2957(4)	6.6(3)*
O(6)	0.0427(5)	0.3846(8)	0.4467(5)	7.5(3)*
O(7)	−0.1406(5)	0.7119(8)	0.1235(5)	7.4(3)*
O(8)	0.0290(5)	0.2123(7)	0.2034(4)	5.3(2)*
O(9)	0.0104(6)	0.6641(9)	0.4306(5)	8.1(3)*
O(10)	0.2626(5)	0.5175(7)	0.3806(4)	5.7(2)*
O(11)	−0.2108(5)	0.4918(7)	0.1837(4)	5.9(3)*
O(12)	0.0301(4)	0.4408(7)	0.0877(4)	5.0(2)*
O(13)	−0.0519(5)	0.8092(7)	0.2857(4)	5.6(2)*
O(14)	0.2203(5)	0.2981(8)	0.3055(5)	7.2(3)*
O(15)	−0.1202(5)	0.3385(8)	0.3070(5)	7.1(3)*
O(16)	0.1548(5)	0.6430(7)	0.1439(4)	6.3(3)*
O(17)	−0.1321(6)	0.4932(9)	0.4308(5)	9.1(4)*
O(18)	−0.2367(5)	0.7441(7)	0.2233(4)	5.6(2)*
O(19)	0.3260(6)	0.5882(9)	0.2548(5)	9.1(4)*
O(20)	0.1520(6)	0.2448(9)	0.1354(5)	8.5(3)*
C	0.0348(5)	0.5288(8)	0.2647(5)	2.2(2)*
C(1)	0.0777(6)	0.7018(9)	0.3420(5)	3.9(3)*
C(2)	0.1336(6)	0.402(1)	0.3670(6)	4.2(3)*
C(3)	−0.0767(6)	0.3867(9)	0.2011(5)	3.7(3)*
C(4)	0.0120(6)	0.623(1)	0.1465(6)	4.2(3)*
C(5)	0.1681(7)	0.706(1)	0.2934(6)	5.2(4)*
C(6)	0.0378(7)	0.425(1)	0.4045(6)	5.4(4)*
C(7)	−0.0986(7)	0.672(1)	0.1608(6)	5.3(4)*
C(8)	0.0313(7)	0.291(1)	0.2107(6)	4.4(3)*
C(9)	−0.0047(7)	0.626(1)	0.3862(6)	5.0(3)*
C(10)	0.2164(6)	0.5145(9)	0.3356(6)	4.1(3)*
C(11)	−0.1561(6)	0.5176(9)	0.2140(6)	4.0(3)*
C(12)	0.0581(6)	0.4549(9)	0.1384(5)	3.7(3)*
C(13)	−0.0515(7)	0.728(1)	0.2860(6)	4.5(3)*
C(14)	0.1787(7)	0.352(1)	0.2803(6)	4.9(3)*
C(15)	−0.0943(7)	0.410(1)	0.3042(6)	4.4(3)*
C(16)	0.1424(7)	0.601(1)	0.1795(6)	4.6(3)*

TABLE 1 (continued)

Atom	x	y	z	$B(\text{Å}^2)$ [a]
C(17)	−0.1013(8)	0.502(1)	0.3999(7)	6.4(4)*
C(18)	−0.1894(7)	0.699(1)	0.2331(6)	4.5(3)*
C(19)	0.2733(8)	0.582(1)	0.2578(7)	6.6(4)*
C(20)	0.1421(8)	0.302(1)	0.1624(7)	6.0(4)*
C(111)	0.5343(7)	0.460(1)	0.3838(6)	4.4(3)*
C(112)	0.5136(8)	0.417(1)	0.3314(7)	5.4(4)*
C(113)	0.4464(9)	0.378(1)	0.3064(8)	7.9(5)*
C(114)	0.4056(9)	0.383(1)	0.3375(8)	7.5(5)*
C(115)	0.4244(9)	0.423(1)	0.3886(8)	7.7(5)*
C(116)	0.4897(9)	0.463(1)	0.4143(8)	7.5(5)*
C(121)	0.6168(7)	0.605(1)	0.4541(6)	4.2(3)*
C(122)	0.6692(7)	0.626(1)	0.5058(6)	4.1(3)*
C(123)	0.6676(8)	0.706(1)	0.5356(7)	5.7(4)*
C(124)	0.6152(9)	0.765(1)	0.5152(8)	6.7(5)*
C(125)	0.5609(9)	0.746(1)	0.4645(8)	7.3(5)*
C(126)	0.5615(8)	0.666(1)	0.4348(7)	5.9(4)*
C(131)	0.6488(6)	0.5259(9)	0.3580(5)	2.8(3)*
C(132)	0.6745(7)	0.453(1)	0.3325(6)	4.6(3)*
C(133)	0.6931(8)	0.472(1)	0.2867(7)	6.3(4)*
C(134)	0.6892(8)	0.561(1)	0.2653(7)	6.1(4)*
C(135)	0.6637(8)	0.631(1)	0.2886(7)	5.9(4)*
C(136)	0.6449(7)	0.616(1)	0.3351(6)	4.0(3)*
C(141)	0.6724(7)	0.416(1)	0.4623(6)	4.2(3)*
C(142)	0.7401(7)	0.425(1)	0.4794(6)	5.0(4)*
C(143)	0.7831(8)	0.358(1)	0.5165(7)	5.7(4)*
C(144)	0.7526(8)	0.289(1)	0.5338(7)	6.5(4)*
C(145)	0.6882(8)	0.277(1)	0.5169(7)	6.4(4)*
C(146)	0.6418(8)	0.343(1)	0.4799(7)	5.7(4)*
C(211)	0.3641(6)	0.427(1)	−0.0178(6)	3.6(3)*
C(212)	0.4329(8)	0.411(1)	−0.0031(7)	5.7(4)*
C(213)	0.4542(8)	0.330(1)	−0.0256(7)	6.1(4)*
C(214)	0.4049(8)	0.276(1)	−0.0602(7)	6.3(4)*
C(215)	0.3395(9)	0.290(1)	−0.0756(8)	6.9(5)*
C(216)	0.3183(7)	0.367(1)	−0.0521(6)	5.2(4)*
C(221)	0.3334(6)	0.623(1)	−0.0412(6)	3.8(3)*
C(222)	0.3615(7)	0.610(1)	−0.0832(7)	5.4(4)*
C(223)	0.3561(9)	0.685(1)	−0.1211(8)	7.4(5)*
C(224)	0.3290(9)	0.764(1)	−0.1136(8)	7.2(5)*
C(225)	0.3031(9)	0.776(1)	−0.0719(8)	7.2(5)*
C(226)	0.3025(8)	0.703(1)	−0.0367(7)	6.1(4)*
C(231)	0.2551(6)	0.514(1)	0.0097(6)	4.0(3)*
C(232)	0.2465(7)	0.486(1)	0.0620(6)	4.9(4)*
C(233)	0.1802(8)	0.470(1)	0.0585(7)	6.1(4)*
C(234)	0.1293(8)	0.480(1)	0.0096(7)	6.8(5)*
C(235)	0.1343(8)	0.506(1)	−0.0405(7)	5.8(4)*
C(236)	0.1991(8)	0.526(1)	−0.0399(7)	5.8(4)*
C(241)	0.4000(7)	0.557(1)	0.0782(6)	4.8(4)*
C(242)	0.4139(8)	0.648(1)	0.0955(7)	5.8(4)*
C(243)	0.462(1)	0.671(2)	0.1516(9)	8.8(6)*
C(244)	0.489(1)	0.599(2)	0.1891(9)	9.1(6)*
C(245)	0.472(1)	0.509(2)	0.1751(9)	8.9(6)*
C(246)	0.4280(9)	0.490(1)	0.1188(8)	7.5(5)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
$\frac{4}{3}(a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)\times B_{1,2} + ac(\cos\beta)\times B_{1,3} + bc(\cos\alpha)\times B_{2,3})$.

TABLE 2

ATOMIC COORDINATES FOR $[PPh_4]_2[Co_3Ni_9(CO)_{20}C]$ WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	$B(Å^2)$
Ni(1)	−0.05053(7)	0.5076(1)	0.36072(6)	3.92(4)
Ni(2)	−0.11669(6)	0.6380(1)	0.24321(6)	3.57(3)
Ni(3)	0.19309(6)	0.5683(1)	0.25962(6)	4.03(4)
Ni(4)	0.11672(7)	0.3792(1)	0.20433(6)	4.00(4)
M(1)	0.00033(6)	0.6265(1)	0.31504(6)	3.26(3)
M(2)	0.10259(6)	0.62863(9)	0.29263(5)	2.95(3)
M(3)	0.13425(6)	0.4559(1)	0.29766(5)	3.04(3)
M(4)	0.05030(6)	0.46289(9)	0.34206(5)	2.78(3)
M(5)	−0.06999(6)	0.48132(9)	0.25635(6)	3.12(3)
M(6)	−0.02698(6)	0.60644(9)	0.20310(5)	2.95(3)
M(7)	0.07465(6)	0.5401(1)	0.19647(6)	3.20(3)
M(8)	0.01500(6)	0.40605(9)	0.22820(5)	2.84(3)
P(1)	0.6175(1)	0.5010(2)	0.4142(1)	3.44(7)
P(2)	0.3376(1)	0.5329(2)	0.0091(1)	3.51(7)
O(1)	0.0966(4)	0.7686(6)	0.3724(3)	5.5(2)*
O(2)	0.1692(4)	0.3614(6)	0.4076(3)	5.7(2)*
O(3)	−0.1182(4)	0.3363(6)	0.1704(3)	5.3(2)*
O(4)	−0.0005(4)	0.6594(6)	0.1004(3)	5.3(2)*
O(5)	0.1987(4)	0.7711(6)	0.2966(4)	6.6(2)*
O(6)	0.0435(4)	0.3783(7)	0.4458(4)	6.9(2)*
O(7)	−0.1383(4)	0.7113(7)	0.1239(4)	7.0(2)*
O(8)	0.0267(4)	0.2136(6)	0.2026(3)	5.1(2)*
O(9)	0.0193(5)	0.6604(7)	0.4360(4)	7.8(3)*
O(10)	0.2643(4)	0.5161(6)	0.3799(3)	5.6(2)*
O(11)	−0.2105(4)	0.4947(6)	0.1805(3)	5.3(2)*
O(12)	0.0310(4)	0.4396(5)	0.0876(3)	4.7(2)*
O(13)	−0.0513(4)	0.8117(6)	0.2867(3)	5.0(2)*
O(14)	0.2163(5)	0.2930(7)	0.3067(4)	8.0(3)*
O(15)	−0.1204(4)	0.3366(6)	0.3091(4)	6.0(2)*
O(16)	0.1534(4)	0.6464(6)	0.1440(3)	5.7(2)*
O(17)	−0.1275(5)	0.4902(8)	0.4358(4)	8.8(3)*
O(18)	−0.2378(4)	0.7455(6)	0.2221(3)	5.8(2)*
O(19)	0.3255(5)	0.5898(8)	0.2553(4)	8.7(3)*
O(20)	0.1516(3)	0.2434(7)	0.1365(4)	7.9(3)*
C	0.0356(4)	0.5276(6)	0.2662(4)	2.3(2)*
C(1)	0.0783(5)	0.7035(8)	0.3409(4)	3.9(2)*
C(2)	0.1347(5)	0.4054(8)	0.3673(4)	3.8(2)*
C(3)	−0.0773(5)	0.3863(8)	0.2036(4)	3.7(2)*
C(4)	0.0104(5)	0.6203(8)	0.1461(5)	4.1(2)*
C(5)	0.1684(6)	0.7037(8)	0.2926(5)	4.7(3)*
C(6)	0.0351(6)	0.4210(9)	0.4047(5)	4.8(3)*
C(7)	−0.0987(6)	0.6719(9)	0.1624(5)	5.2(3)*
C(8)	0.0310(5)	0.2925(8)	0.2106(5)	4.0(2)*
C(9)	0.0010(6)	0.6235(9)	0.3897(5)	5.4(3)*
C(10)	0.2174(5)	0.5118(8)	0.3355(4)	3.8(2)*
C(11)	−0.1567(5)	0.5166(8)	0.2133(4)	3.9(2)*
C(12)	0.0583(5)	0.4554(7)	0.1379(4)	3.4(2)*
C(13)	−0.0508(5)	0.7303(8)	0.2871(4)	3.6(2)*
C(14)	0.1762(6)	0.3488(9)	0.2825(5)	5.4(3)*
C(15)	−0.0952(5)	0.4066(8)	0.3042(5)	4.1(2)*
C(16)	0.1410(6)	0.6029(8)	0.1786(5)	4.5(3)*

TABLE 2 (continued)

Atom	x	y	z	B(Å^2)
C(17)	−0.0966(7)	0.498(1)	0.4046(6)	6.2(3)*
C(18)	−0.1892(5)	0.7011(8)	0.2315(5)	4.0(2)*
C(19)	0.2725(6)	0.5830(9)	0.2576(5)	5.6(3)*
C(20)	0.1405(6)	0.3012(9)	0.1631(5)	5.0(3)*
C(111)	0.5322(5)	0.4584(8)	0.3829(5)	4.0(3)*
C(112)	0.5124(6)	0.415(1)	0.3291(5)	5.5(3)*
C(113)	0.4474(8)	0.379(1)	0.3060(7)	7.8(4)*
C(114)	0.4063(7)	0.381(1)	0.3365(6)	7.3(4)*
C(115)	0.4241(8)	0.422(1)	0.3875(7)	7.9(4)*
C(116)	0.4890(7)	0.462(1)	0.4128(6)	6.5(4)*
C(121)	0.6158(6)	0.6051(8)	0.4539(5)	4.2(3)*
C(122)	0.6692(6)	0.6258(8)	0.5046(5)	4.4(3)*
C(123)	0.6662(6)	0.7060(9)	0.5347(5)	5.3(3)*
C(124)	0.6133(7)	0.764(1)	0.5134(6)	6.4(3)*
C(125)	0.5388(8)	0.742(1)	0.4641(6)	7.7(4)*
C(126)	0.5601(7)	0.662(1)	0.4339(6)	6.0(3)*
C(131)	0.6487(5)	0.5258(7)	0.3579(4)	3.1(2)*
C(132)	0.6760(6)	0.4534(9)	0.3345(5)	5.1(3)*
C(133)	0.6962(7)	0.473(1)	0.2885(6)	6.1(3)*
C(134)	0.6912(6)	0.5610(9)	0.2663(5)	5.7(3)*
C(135)	0.6644(6)	0.6287(9)	0.2887(5)	5.6(3)*
C(136)	0.6444(5)	0.6129(8)	0.3345(5)	4.1(3)*
C(141)	0.6706(5)	0.4146(8)	0.4612(4)	3.7(2)*
C(142)	0.7393(6)	0.4248(9)	0.4798(5)	5.4(3)*
C(143)	0.7812(7)	0.358(1)	0.5175(6)	6.2(3)*
C(144)	0.7512(7)	0.286(1)	0.5341(6)	6.3(3)*
C(145)	0.6843(6)	0.277(1)	0.5160(6)	5.9(3)*
C(146)	0.6420(6)	0.3421(9)	0.4798(5)	5.0(3)*
C(211)	0.3637(5)	0.4315(8)	−0.0168(5)	3.6(2)*
C(212)	0.4315(7)	0.413(1)	−0.0029(6)	6.2(3)*
C(213)	0.4535(7)	0.332(1)	−0.0247(6)	6.7(4)*
C(214)	0.4055(7)	0.278(1)	−0.0605(6)	6.5(4)*
C(215)	0.3393(7)	0.294(1)	−0.0749(6)	6.7(4)*
C(216)	0.3181(6)	0.370(1)	−0.0520(5)	5.7(3)*
C(221)	0.3334(5)	0.6254(8)	−0.0412(5)	4.0(3)*
C(222)	0.3611(6)	0.614(1)	−0.0829(5)	5.8(3)*
C(223)	0.3572(7)	0.690(1)	−0.1207(6)	7.5(4)*
C(224)	0.3299(8)	0.767(1)	−0.1123(7)	8.1(4)*
C(225)	0.3038(7)	0.781(1)	−0.0710(6)	7.2(4)*
C(226)	0.3046(7)	0.707(1)	−0.0354(6)	5.8(3)*
C(231)	0.2551(5)	0.5175(8)	0.0108(5)	3.9(2)*
C(232)	0.2452(6)	0.4886(9)	0.0623(5)	5.2(3)*
C(233)	0.1793(6)	0.472(1)	0.0577(6)	5.7(3)*
C(234)	0.1276(7)	0.483(1)	0.0086(6)	6.4(4)*
C(235)	0.1336(7)	0.510(1)	−0.0413(6)	5.8(3)*
C(236)	0.1995(6)	0.5291(9)	−0.0402(5)	5.3(3)*
C(241)	0.3982(5)	0.5612(8)	0.0800(5)	4.0(3)*
C(242)	0.4147(6)	0.6511(9)	0.0959(5)	5.4(3)*
C(243)	0.4614(7)	0.672(1)	0.1520(6)	7.3(4)*
C(244)	0.4878(8)	0.600(1)	0.1901(7)	8.1(4)*
C(245)	0.4700(8)	0.512(1)	0.1738(7)	8.6(5)*
C(246)	0.4256(7)	0.492(1)	0.1183(6)	6.7(4)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
$\frac{4}{3}\times(a^2B_{1,1}+b^2B_{2,2}+c^2B_{3,3}+ab(\cos\gamma)\times B_{1,2}+ac(\cos\beta)\times B_{1,3}+bc(\cos\alpha)\times B_{2,3}$.

TABLE 3

SELECTED BOND DISTANCES (Å) AND GNALES (°) IN I AND II

	I	II		I	II
M(1)–M(2)	2.409(2)	2.428(2)	M(5)–C(11)	1.854(11)	1.831(9)
M(1)–M(4)	2.566(2)	2.590(2)	M(5)–C(15)	1.845(12)	1.823(10)
M(1)–M(5)	2.647(2)	2.683(2)	M(6)–C(4)	1.867(12)	1.859(10)
M(1)–M(6)	2.595(2)	2.621(2)	M(6)–C(7)	1.745(13)	1.764(11)
M(1)–Ni(1)	2.484(2)	2.511(2)	M(7)–C(4)	1.872(11)	1.877(9)
M(1)–Ni(2)	2.449(2)	2.475(2)	M(7)–C(12)	1.835(11)	1.832(9)
M(2)–M(3)	2.583(2)	2.589(2)	M(7)–C(16)	1.869(12)	1.862(10)
M(2)–M(6)	2.874(2)	2.848(1)	M(8)–C(3)	1.847(11)	1.849(9)
M(2)–M(7)	2.560(2)	2.569(2)	M(8)–C(8)	1.764(12)	1.771(10)
M(2)–Ni(3)	2.514(2)	2.503(2)	Ni(1)–C(6)	2.266(13)	2.153(10)
M(3)–M(4)	2.409(2)	2.410(1)	Ni(1)–C(9)	1.965(13)	1.992(11)
M(3)–M(7)	2.635(2)	2.649(1)	Ni(1)–C(15)	1.923(12)	2.007(9)
M(3)–M(8)	2.579(2)	2.589(1)	Ni(1)–C(17)	1.726(15)	1.706(12)
M(3)–Ni(3)	2.429(2)	2.442(2)	Ni(2)–C(7)	2.330(13)	2.218(10)
M(3)–Ni(4)	2.459(2)	2.460(2)	Ni(2)–C(11)	1.932(11)	1.980(9)
M(4)–M(5)	2.639(2)	2.668(1)	Ni(2)–C(13)	1.925(12)	1.955(9)
M(4)–M(8)	2.782(2)	2.754(1)	Ni(2)–C(18)	1.733(12)	1.724(9)
M(4)–Ni(1)	2.477(2)	2.437(2)	Ni(3)–C(5)	2.337(13)	2.264(10)
M(5)–M(6)	2.569(2)	2.596(2)	Ni(3)–C(10)	1.915(11)	1.932(9)
M(5)–M(8)	2.398(2)	2.418(1)	Ni(3)–C(16)	1.932(12)	1.963(10)
M(5)–Ni(1)	2.447(2)	2.482(2)	Ni(3)–C(19)	1.733(15)	1.721(11)
M(5)–Ni(2)	2.432(2)	2.456(2)	Ni(4)–C(8)	2.328(12)	2.263(9)
M(6)–M(7)	2.426(2)	2.423(2)	Ni(4)–C(12)	1.972(11)	1.990(8)
M(6)–Ni(2)	2.530(2)	2.488(2)	Ni(4)–C(14)	1.892(12)	1.930(11)
M(7)–M(8)	2.590(2)	2.595(2)	Ni(4)–C(20)	1.731(15)	1.717(11)
M(7)–Ni(3)	2.460(2)	2.461(1)			
M(7)–Ni(4)	2.483(2)	2.486(2)	C(1)–O(1)	1.197(12)	1.196(9)
M(8)–Ni(4)	2.475(2)	2.468(2)	C(2)–O(2)	1.176(12)	1.184(9)
			C(3)–O(3)	1.199(11)	1.197(9)
M(1)–C	2.126(9)	2.176(7)	C(4)–O(4)	1.218(12)	1.207(10)
M(2)–C	2.001(9)	1.981(7)	C(5)–O(5)	1.151(13)	1.155(10)
M(3)–C	2.212(9)	2.221(7)	C(6)–O(6)	1.167(13)	1.146(10)
M(4)–C	2.046(9)	2.013(7)	C(7)–O(7)	1.170(13)	1.164(10)
M(5)–C	2.209(9)	2.267(7)	C(8)–O(8)	1.147(12)	1.162(10)
M(6)–C	1.994(9)	1.997(7)	C(9)–O(9)	1.165(13)	1.192(11)
M(7)–C	2.146(9)	2.172(7)	C(10)–O(10)	1.183(11)	1.183(9)
M(8)–C	2.001(9)	1.972(7)	C(11)–O(11)	1.189(11)	1.175(9)
M(1)–C(1)	1.880(11)	1.905(9)	C(12)–O(12)	1.189(11)	1.185(9)
M(1)–C(9)	1.853(13)	1.834(11)	C(13)–O(13)	1.181(12)	1.183(9)
M(1)–C(13)	1.840(12)	1.839(9)	C(14)–O(14)	1.174(13)	1.170(11)
M(2)–C(1)	1.842(11)	1.818(9)	C(15)–O(15)	1.191(13)	1.175(10)
M(2)–C(5)	1.762(13)	1.775(10)	C(16)–O(16)	1.177(12)	1.166(10)
M(3)–C(2)	1.893(12)	1.864(9)	C(17)–O(17)	1.182(15)	1.186(12)
M(3)–C(10)	1.867(11)	1.856(9)	C(18)–O(18)	1.152(12)	1.167(10)
M(3)–C(14)	1.926(13)	1.897(11)	C(19)–O(19)	1.153(15)	1.149(11)
M(4)–C(2)	1.872(11)	1.865(9)	C(20)–O(20)	1.137(15)	1.141(11)
M(4)–C(6)	1.751(13)	1.793(10)			
M(5)–C(3)	1.869(11)	1.863(9)			
M(2)–M(1)–M(4)	77.41(6)	75.74(5)	M(3)–C(10)–Ni(3)	79.9(4)	80.2(3)
M(1)–M(2)–M(3)	100.88(6)	102.42(5)	M(3)–C(10)–O(10)	142.7(9)	144.4(8)
M(2)–M(3)–M(4)	77.07(6)	76.05(5)	Ni(3)–C(10)–O(10)	137.2(9)	135.3(7)
M(1)–M(4)–M(3)	101.37(6)	102.90(5)	M(5)–C(11)–Ni(2)	79.9(4)	80.2(3)

TABLE 3 (continued)

	I	II		I	II
M(6)–M(5)–M(8)	76.77(6)	74.60(5)	M(5)–C(11)–O(11)	144.7(9)	147.2(8)
M(5)–M(6)–M(7)	102.07(6)	104.01(5)	Ni(2)–C(11)–O(11)	135.4(9)	132.4(7)
M(6)–M(7)–M(8)	75.88(6)	74.57(5)	M(7)–C(12)–Ni(4)	81.3(4)	81.0(3)
M(5)–M(8)–M(7)	102.25(7)	104.15(5)	M(7)–C(12)–O(12)	144.8(9)	146.5(7)
			Ni(4)–C(12)–O(12)	133.9(9)	132.4(7)
M(1)–C(1)–M(2)	80.6(5)	81.4(4)	M(1)–C(13)–Ni(2)	81.1(5)	81.3(4)
M(1)–C(1)–O(1)	139.1(9)	135.9(7)	M(1)–C(13)–O(13)	144.7(1.0)	145.6(7)
M(2)–C(1)–O(1)	140.0(9)	142.8(8)	Ni(2)–C(13)–O(13)	134.0(9)	132.8(7)
M(3)–C(2)–M(4)	79.6(5)	81.4(4)	M(3)–C(14)–Ni(4)	80.1(5)	80.0(4)
M(3)–C(2)–O(2)	140.1(1.0)	141.3(8)	M(3)–C(14)–O(14)	138.6(1.0)	140.7(9)
M(4)–C(2)–O(2)	140.3(1.0)	138.4(8)	Ni(4)–C(14)–O(14)	141.1(1.1)	139.3(9)
M(5)–C(3)–M(8)	80.4(4)	81.3(4)	M(5)–C(15)–Ni(1)	81.0(5)	80.6(4)
M(5)–C(3)–O(3)	141.5(9)	141.3(7)	M(5)–C(15)–O(15)	142.3(1.0)	146.4(8)
M(8)–C(3)–O(3)	138.1(9)	137.4(7)	Ni(1)–C(15)–O(15)	136.7(1.0)	132.9(8)
M(6)–C(4)–M(7)	80.9(5)	80.9(4)	M(7)–C(16)–Ni(3)	80.7(5)	80.0(4)
M(6)–C(4)–O(4)	139.0(9)	140.1(7)	M(7)–C(16)–O(16)	144.7(1.0)	146.2(8)
M(7)–C(4)–O(4)	140.0(1.0)	139.0(8)	Ni(3)–C(16)–O(16)	134.6(1.0)	133.6(8)
M(2)–C(5)–Ni(3)	74.1(5)	75.5(4)			
M(2)–C(5)–O(5)	162.7(1.2)	159.3(9)	Ni(1)–C(17)–O(17)	177.5(1.3)	178.3(1.1)
Ni(3)–C(5)–O(5)	122.5(1)	125.0(8)	Ni(2)–C(18)–O(18)	176.7(1.2)	177.6(9)
M(4)–C(6)–Ni(1)	74.9(5)	75.6(4)	Ni(3)–C(19)–O(19)	176.2(1.4)	177.7(1.1)
M(4)–C(6)–O(6)	162.7(1.2)	158.0(9)	Ni(4)–C(20)–O(20)	172.5(1.3)	172.8(1.0)
Ni(1)–C(6)–O(6)	121.6(1.0)	126.2(8)			
M(6)–C(7)–Ni(2)	75.2(5)	76.4(4)			
M(6)–C(7)–O(7)	164.8(1.2)	161.2(9)			
Ni(2)–C(7)–O(7)	119.6(1.0)	122.0(8)			
M(8)–C(8)–Ni(4)	73.0(4)	74.3(3)			
M(8)–C(8)–O(8)	164.5(1.1)	161.9(8)			
Ni(4)–C(8)–O(8)	122.5(9)	123.7(7)			
M(1)–C(9)–Ni(1)	81.1(5)	81.9(4)			
M(1)–C(9)–O(9)	145.6(1.1)	133.8(8)			
Ni(1)–C(9)–O(9)	133.3(1.1)	131.9(9)			

common edge (M(2)–M(4) and M(6)–M(8)), which on the average has a length of 3.10 Å in I and one of 3.06 Å in II. Moreover the two fused triangles are not coplanar, the average dihedral angle being ca. 163° in I and 164° in II. These deformations, which were present in III but less pronounced, permit an alternate description of the metal framework of both I and II; as shown schematically in Fig. 4, the metal skeleton can be regarded as derived from a "wing-to-hinge" condensation of two slightly bent edge-sharing bi-tetrahedra, which permits encapsulation of the carbon atom. A perfectly orthogonal condensation of the two units would result in a central D_{2d} triangulated dodecahedral moiety, subsequently referred to as Wells' bis-disphenoid [21], similar to that found in boranes (see later). In both II, I, and III, the angle for this condensation falls increasingly below 90° (the angles are 83.9° for II, 83,7° for I, and 78.2° for III). As a result the metal skeletons show only an idealized D_2 symmetry, and progressively approach a tetragonal antiprismatic geometry. A triangulated dodecahedral geometry is commonly found in boranes, e.g. $[B_8H_8]^{2-}$ and B_8Cl_8 [22,23], and metalloboranes, e.g. $B_4H_4[MCp]_4$ (M = Co, Ni; Cp = cyclopentadiene) [24,25]; in contrast, it is rather

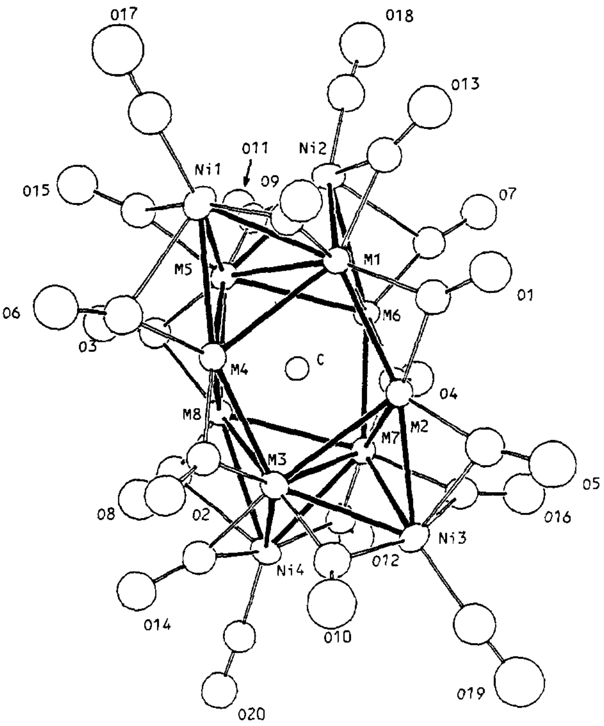

Fig. 3. ORTEP drawing of the $[Co_2Ni_{10}(CO)_{20}C]^{2-}$ (I) dianion.

unusual in metal clusters, and to our knowledge the only reported example is $Cu_8(dppp)_4H_8$ (dppp = bis(diphenylphosphinepropane)) [26].

The most significant mean M–M and M–C interatomic distances of compounds I–III are shown in Table 4. The major (although still fairly small) variations are in

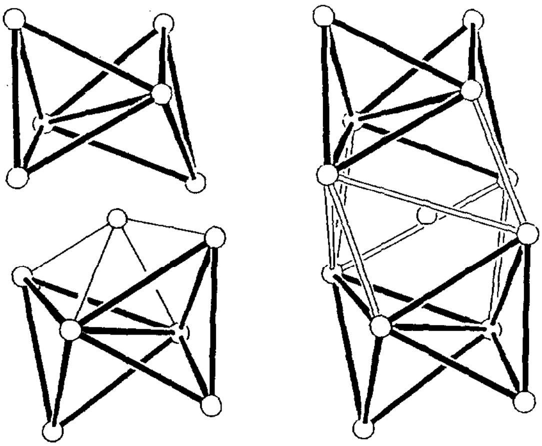

Fig. 4. Orthogonal "wing-to-hinge" condensation of two edge-sharing bis-tetrahedral M_6 moieties giving rise to a tetracapped D_2 triangulated dodecahedral frame encapsulating a carbide atom.

Table 4

Selected mean interatomic distances (Å) in I–III [a]

	I	II	III
Ni–M (12)	2.467	2.472	2.465
$M-M_{\text{spanned by Ni}}$ (8)	2.583	2.602	2.581
$M-M_{\text{spanned by 2 Ni}}$ (2)	2.639	2.668	2.660
$M-M_{\text{spanned by CO}}$ (4)	2.408	2.420	2.415
$M-M_{\text{unspanned}}$ (2)	2.824	2.802	2.715
M...M [b] (2)	3.098	3.061	3.221
$M-C_{\text{flattened tetrahedron}}$ (4)	2.008	1.991	2.016
$M-C_{\text{elongated tetrahedron}}$ (4)	2.170	2.207	2.165

[a] The figures in parentheses denote the number of averaged distances. [b] The short diagonals of the two tetragonal faces of Fig. 3.

the longer sets of interatomic distances and in the coordination of the carbide atom. An average lenghtening of ca. 0.1 Å in the M(2)–M(6) and M(4)–M(8) bond distances ($M-M_{\text{unspanned}}$ in Table 4) on going from III to I and II is paralleled by a 0.12–0.16 Å average shortening of the two diagonals of the tetragonal faces, which is formally in keeping with the condensation scheme shown in Fig. 4. The alternative bis-disphenoidal description is also supported by the stereochemistry of the carbide atom, which in both I and II shows a bis-tetrahedral coordination arising from a set of shorter contacts with the "wing" atoms (which define a flattened tetrahedron with respect to the C_2 axis) and a slightly longer set with the "hinge" atoms (which individuate an elongated tetrahedron); indeed, the triangulated dodecahedron, as the bis-disphenoid name suggests, can be also regarded as resulting from the interpenetration of two D_{2d}-distorted tetrahedra [21,27].

The limiting experimental radius of the carbon atom is 0.72, 0.70 and 0.73 Å, respectively in I, II and III. It is noteworthy that a "regular" Δ-dodecahedron (viz. made up by equilateral triangles) [28] with an edge of 2.58 Å (corresponding to the average M–M distance in compounds I–III), while maximizing M–M interactions, would provide an unsuitable ellipsoidal cavity, with semi-axes of ca. 0.46 and 1.11 Å. On the other hand, both a regular square-antiprism of the same edge-length and a Wells' bis-disphenoid having 2.58 Å as shorter M–M contact (Wells' bis-disphenoid has two different types of edge lengths but a single centre-to-vertex distance) [21] would provide rather large spherical cavities, with radii of ca. 0.83 and 0.86 Å, respectively. It thus seems conceivable that the actual metal geometries found in I, II and III, which are intermediate between those of a bis-disphenoid and a tetragonal antiprism, are the result of a compromise between the need to provide effective M–M contacts and that to meet both the steric requirements of the interstitial carbide atom and its preference for a tetrahedral coordination. A bis-tetrahedral coordination of the carbide atom has been observed previously in $[Co_8(CO)_{18}C]^{2-}$ [4], but is not found in $[Ni_8(CO)_{16}C]^{2-}$ [1].

As shown in Fig. 3, the carbonyl stereochemistry comprises four terminal CO groups bonded to the four nickel caps, and sixteen edge bridging ligands. Of these, the four spanning the four uncapped edges of the tetragonal faces are symmetrical, whereas the remaining twelve, spanning the edges of the four caps, show various degrees of asymmetry. Those labelled 5–8 are so unsymmetrical ($M-C_{av}$ 1.756 and $Ni-C_{av}$ 2.315 Å in I and $M-C_{av}$ 1.776 and $Ni-C_{av}$ 2.225 Å in II), that they may also be described as terminal ligands of the "wing" atoms interacting very weakly with the nickel caps. The stereochemistry of the carbonyl groups of I and II is strictly comparable to that in III, [2] whereas individual parameters apparently reflect the lower free negative charge.

It seemed likely that the formal condensation scheme shown in Fig. 4 might also have some chemical implications. It seemed conceivable that a one-to-one condensation between $Co_3(CO)_9CCl$ and $[Ni_6(CO)_{12}]^{2-}$ could give rise to an unstable intermediate species; for instance one related to that depicted at the top right-hand side of Fig. 4 which has an exposed carbide atom, such as present in $[Fe_4(CO)_{12}C]^{2-}$ [29]; this could subsequently behave as a "template" for a second incoming $[Ni_6(CO)_{12}]^{2-}$ molecule. However, all the attempts to isolate this suggested intermediate species, for instance using inverse addition, involving addition of solutions of $[Ni_6(CO)_{12}]^{2-}$ to $Co_3(CO)_9CCl$, were unsuccessful, and resulted in a new and more convenient synthesis of the known $[Co_6Ni_2(CO)_{16}C_2]^{2-}$ dianion [11,12].

Experimental

All operations were carried out under nitrogen in anhydrous solvents. Infrared spectra were recorded with a Perkin–Elmer 457 grating spectrophotometer or a Nicolet interferometer using CaF_2 cells. Elemental analyses were obtained as described previously [30], $[Ni_6(CO)_{12}]^{2-}$ [30], $Co_3(CO)_9CCl$ [31], and III [2] were synthesized by published methods.

1. Synthesis of $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$

$[N(C_2H_5)_4]_2[Ni_6(CO)_{12}]$ (1.62 g, 1.71 mmol) was suspended in anhydrous tetrahydrofuran (30 ml) and a solution of $Co_3(CO)_9CCl$ (0.412 g, 0.86 mmol) in thf (20 ml) was added dropwise with stirring during 1 h. The resulting red-brown suspension was evaporated to dryness in vacuum. The residue was stirred with methanol (50 ml) and crude $[N(C_2H_5)_4]_3[Co_3Ni_9(CO)_{20}C]$ was filtered off, leaving a solution containing only salts of $[Co(CO)_4]^-$ and $[Co_2Ni_{10}(CO)_{20}C]^{2-}$. Addition of PPh_4Cl (0.5 g) to this solution with stirring resulted in almost quantitative precipitation of flakes of $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$, while the $[Co(CO)_4]^-$ salts were mainly left in solution. The precipitate was filtered off, washed twice with isopropyl alcohol, and dried in vacuo. Yield 0.6 g (35% based on the starting $Co_3(CO)_9CCl$). Well-shaped crystals suitable for X-ray determination were grown by dissolving this precipitate in thf (30 ml) acidified with CF_3COOH (100 μl) and inducing slow diffusion of cyclohexane (40 ml) into the solution. Found $[PPh_4]^+$, 34.23; Co, 6.11; Ni, 29.87; Co/Ni 1/4.89. $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$ calcd.: $[PPh_4]^+$, 34.70; Co, 6.03; Ni, 30.02%. The compound is soluble in acetone and thf, sparingly soluble in alcohols, and insoluble in non polar solvents such as toluene or n-heptane.

2. Synthesis of $[PPh_4]_2[Co_3Ni_9(CO)_{20}C]$

Aqueous H_3PO_4 (ca. 48%) was added dropwise to a solution of $[N(C_2H_5)_4]_3[Co_3Ni_9(CO)_{20}C]$ (0.6 g) in acetone (25 ml) in a 100 ml flask. The solution being monitored by IR spectroscopy during the addition. After addition of ca. 4 ml of acid, the solution only showed carbonyl absorptions due to $[Co_3Ni_9(CO)_{20}C]^{2-}$. The solution was dried in vacuo and the residue dissolved in methanol (30 ml). Addition with stirring of PPh_4Cl (0.5 g) produced a precipitate of

$[PPh_4]_2[Co_3Ni_9(CO)_{20}C]$, which was filtered off, washed with water then with isopropyl alcohol, and dried in vacuo. Yield 0.55 g (ca. 78%). It was recrystallized by diffusion of cyclohexane into a solution in acidified thf, as described for $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$. Found: $[PPh_4]^+$, 34.31; Co, 9.10; Ni, 26.84; Co/Ni 1/2.95. $[PPh_4]_2[Co_3Ni_9(CO)_{20}C]$ calcd.: $[PPh_4]^+$, 34.69; Co, 9.04; Ni, 27.02%.

3. *X-Ray intensity measurements*

Crystal data for $[PPh_4]_2[Co_2Ni_{10}(CO)_{20}C]$ (I): $C_{69}Co_2H_{40}Ni_{10}O_{20}P_2$, monoclinic, space group $P2_1/n$ (no. 14) from systematic absences, M 1956.0 amu, a 21.273(3), b 14.514(5), c 24.684(5) Å, β 111.63(1)°, U 7084.3 Å^3, D_c 1.834 g cm^{-3} for $Z = 4$, μ(Mo-K_α) 31.8 cm^{-1}. Crystal data for $[PPh_4]_2[Co_3Ni_9(CO)_{20}C]$ (II): $C_{69}Co_3H_{40}Ni_9O_{20}P_2$ M 1956.2 amu, monoclinic, space group $P2_1/n$, (no. 14), a 21.233(4), b 14,531(11), c 24,652(6) Å, β 111.42(1)°, U 7080.6 Å^3, D_c 1.835 g cm^{-3} for $Z = 4$, μ(Mo-K_α) 31.4 cm^{-1}.

The unit cell parameters were obtained from a least-squares refinement of the 2ϑ values, for 25 reflections in the range $16 < 2\vartheta < 24°$.

Crystals of maximum dimensions 0.50 × 0.30 × 0.35 mm, were mounted on an Enraf-Nonius CAD 4 diffractometer. Intensities were measured for 12443 reflections in the range $6 < 2\vartheta < 46°$ for I and 11098 in the range $6 < 2\vartheta < 45°$ for II, corresponding to the $\pm h$ $+k$ $+l$ quadrant. Scan parameters were: for I scan width $1.1 + 0.35$ tg ϑ and maximum count time 40 s; for II scan width $1.0 + 0.35$ tg ϑ and maximum count time 40 s. Periodical monitoring of three reflections in each set revealed an average linear decay of the diffracted intensity which reached a maximum of ca. 5 and 7% by the end of data collection for I and II, respectively. Structure factors were computed by application of Lorentz-polarisation-, decay-, and absorption-corrections. The last correction was evaluated by the empirical PSI scan method, involving monitoring of the diffracted intensity of reflections with χ value close to 90°. Minimum transmission factors were 0.728 for I and 0.598 for II. Averaging of equivalent reflections resulted in a total of 4646 reflections with $|F^2| > 3\sigma(F^2)$ for I and 4967 for II, for use in the structure solution and refinement.

4. *Structure solution and refinement*

The structures were solved by direct methods using MULTAN. In both cases the E-maps from the best set showed twelve peaks of similar height, which at this stage were all refined as Ni atoms. The subsequent iterative application of difference Fourier syntheses and full-matrix least-squares refinement revealed the whole structure. In the final stages of refinement the Co-Ni disorder within the inner dodecahedral moiety was treated as described in ref. 2. The anomalous dispersions of Ni and Co were taken into account in their real and imaginary components. Final weights were given by $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{1/2}/Lp$ and $A = 0.040$, and this gave a fairly constant distribution of $w(F_o - k|F_c|)^2$ as a function of F_o. The final agreement indices were $R = 0.056$ and $R' = 0.065$ for I and $R = 0.048$ and $R' = 0.058$ for II, where $R' = [\Sigma w(F_o - t|F_c|)^2/\Sigma wF_o^2]^{1/2}$. The hydrogen atoms of the cations were introduced in their calculated positions (d(C–H) 0.95 Å) and not refined. They were assigned a 7.5 Å^2 B-factor, slightly higher than the refined factors for the carbon atoms of the cations. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [32].

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 [33]. The details of the structure are shown in Tables 1–3 and Fig. 3. Lists of hydrogen atom coordinates and observed and calculated structure factors are available from the authors.

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