The new enneanuclear nickel carbonyl anion $[Ni_9(CO)_{16}]^{2-}$ and its relationships with the $[Ni_{12}(CO)_{21}]^{4-}$ and $[Ni_6Rh_3(CO)_{17}]^{3-}$ clusters

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Dedicated to the memory of the late Luigi Venanzi in recognition of his outstanding contributions to chemistry

Abstract

The reaction of $[N(PPh_3)_2]_2[Ni_6(CO)_{12}]$ with $Cu(PPh_3)_xCl$ ($x = 1$, 2), as well as the degradation of $[N(PPh_3)_2]_2[H_2Ni_{12}(CO)_{21}]$ with PPh_3, affords the new and unstable dark orange–brown $[N(PPh_3)_2]_2[Ni_9(CO)_{16}]$·THF salt in low yields. This salt has been characterized by a CCD X-ray diffraction determination, along with IR spectroscopy and elemental analysis. The close-packed two-layer metal core geometry of the $[Ni_9(CO)_{16}]^{2-}$ dianion is directly related to that of the bimetallic $[Ni_6Rh_3(CO)_{17}]^{3-}$ trianion and may be envisioned to be formally derived from the hcp three-layer geometry of $[Ni_{12}(CO)_{21}]^{4-}$ by the substitution of one of the two outer $[Ni_3(CO)_3(\mu-CO)_3]^{2-}$ layers with a face-bridging carbonyl group. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The donor–acceptor bonding behaviour of the $Pt_3L_3(\mu\text{-}CO)_3$ (L = trisubstituted phosphine) has been thoroughly exploited experimentally by the late Luigi Venanzi from the initial observation that $Pt_3(PPh_3)_3(\mu\text{-}CO)_3$ changed colour by exposure to mercury vapour [1]. This discovery gave the start to the synthesis and characterization of a wide series of compounds in which $Pt_3L_3(\mu\text{-}CO)_3$ behaves as a conventional σ-donor and weak π-acceptor ligand [2]. As a result, there are now known half-sandwich cationic $[Pt_3L_3(\mu\text{-}CO)_3(\mu_3\text{-}ML)]^+$ (M = Cu, Ag, Au) [2,3], neutral $[Pt_3L_3(\mu\text{-}CO)_3(\mu_3\text{-}MX_n)]$ (X = Cl, Br, I; $n = 1$, M = Cu, Ag, Au; $n = 2$, M = Zn, Cd; $n = 3$, M = In) [4], bicapped $[Pt_3L_3(\mu\text{-}CO)_3(\mu_3\text{-}HgX)_2]$ addition compounds [5], as well as sandwich $[\{Pt_3L_3(\mu\text{-}CO)_3\}_2(\mu_6\text{-}M)]^+$ (M = Cu, Ag, Au) species [3,6,7].

The donor–acceptor behaviour of the unsubstituted $M_3(CO)_3(\mu\text{-}CO)_3$ and $[M_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ (M = Ni, Pt) fragments was not investigated, probably due to the lack of suitable starting materials. Indeed, neutral fragments have never been detected. The existence of the extremely reactive $[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ dianion was mentioned several years ago [8], but the compound has been only recently characterized by LXS and NMR studies [9]. Besides, even the above studies failed in providing experimental evidence for the existence of the related $[Ni_3(CO)_3(\mu-CO)_3]^{2-}$ species [9]. Nevertheless, the existence of several anionic homo- and heterometallic Ni and Pt clusters provides support for the suggested donor-acceptor behaviour of the unsubstituted $M_3(CO)_3(\mu\text{-}CO)_3$ and $[M_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ (M = Ni, Pt) fragments. For instance, the $[M_3(CO)_3(\mu\text{-}CO)_3]_2^{2-}$ (M = Ni, Pt) [10,11] clusters have been suggested to arise by electron donation from a strong $[M_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ Lewis base to a $M_3(CO)_3(\mu\text{-}CO)_3$ moiety acting as a Lewis acid [2]. Probably the nicest illustration of the Lewis base behavior of the $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ fragment is provided by the structure of the $[Au_6Ni_{12}(CO)_{24}]^{2-}$ dianion [12,13]. Indeed,

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this compound may be readily interpreted as being formally derived from the stabilization of an Au^{6+} octahedron via interaction with four $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ donor units capping four alternate triangular faces. The existence of both $[M_2Ni_3(CO)_{16}]^{2-}$ (M = Cr, Mo, W) [14] and $[Ni_5(CO)_{12}]^{2-}$ [15] likewise suggests that the $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ fragment may also behave as a digonal donor towards two opposite pairs of $M(CO)_5$ and $Ni(CO)_3$ acceptor units, respectively.

On the other side, a comparison between the structures of the recently characterized $[Ni_6Rh_3(CO)_{17}]^{3-}$ and $[Ni_9Rh_3(CO)_{22}]^{3-}$ shows that the former may be obtained from the latter by formal substitution of a $Ni_3(CO)_3(\mu\text{-}CO)_3$ moiety with a face-bridging carbonyl ligand [16]. Such a structural relationship prefigures a tight analogy between the donor and acceptor bonding behaviour of the neutral $Ni_3(CO)_3(\mu\text{-}CO)_3$ fragment and carbon monoxide.

Looking for other examples in which $Ni_3(CO)_3(\mu\text{-}CO)_3$ or $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ fragments can function as Lewis bases, we have investigated the reaction of $Cu(PPh_3)_xCl$ (x = 1, 2) with $[Ni_6(CO)_{12}]^{2-}$, as a potential source of both above fragments. Although the original aim was not fulfilled, we isolated fortuitously in low yields a new homometallic enneanuclear nickel cluster, namely the $[Ni_9(CO)_6(\mu\text{-}CO)_9(\mu_3\text{-}CO)]^{2-}$ dianion. This close-packed nonanickel cluster, which can be formally derived from the three-layer dodecanuclear $[Ni_{12}(CO)_{21}]^{4-}$ by replacement of one of its two outer $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ layers with a face-bridging carbon monoxide group, implies a donor–acceptor bonding analogy between the charged $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ fragment and carbon monoxide.

2. Results and discussion

2.1. Synthesis of the $[Ni_9(CO)_{16}]^{2-}$ dianion

The title compound has been obtained by reaction of $[N(PPh_3)_2]_2[Ni_6(CO)_{12}]$ with $Cu(PPh_3)_xCl$ complexes (x = 1, 2) in acetone or acetonitrile solution. In all cases, the first product of the reaction is a red–brown product displaying infrared carbonyl absorptions at approximately 2000 and 1810 cm^{-1}, which could not be attributed to any of the known nickel carbonyl clusters. The above compound displays limited stability in solution even in inert conditions and decomposes upon standing to a mixture of $[Ni_6(CO)_{12}]^{2-}$, $[Ni_7(CO)_{15}]^{2-}$ and $Ni(CO)_{4-x}(PPh_3)_x$ (x = 0, 1, 2) species. Accordingly, attempted crystallizations of the filtered acetone or acetonitrile reaction solutions by a layering of n-hexane and diisopropyl ether, respectively, afforded red crystals of $[N(PPh_3)_2]_2[Ni_6(CO)_{12}]$ and colourless or pale-yellow crystals of $Ni(CO)_{4-x}(PPh_3)_x$ (x = 1, 2). Crystals of the red $[N(PPh_3)_2]_2[Ni_6(CO)_{12}]$

starting material were also obtained upon work up of the reaction solution by evaporation of the reaction solvent, washing of the residue with toluene followed by extraction of the residue in THF, and precipitation with toluene. However, examination under a microscope of the crystalline precipitate indicated clearly the presence in small amounts of dark-orange crystals displaying a shape different from that of the crystals of $[N(PPh_3)_2]_2[Ni_6(CO)_{12}]$. These have been characterized by a CCD X-ray diffraction study as the $[N(PPh_3)_2]_2[Ni_9(CO)_{16}]\cdot$THF salt containing the new $[Ni_9(CO)_{16}]^{2-}$ dianion. Mechanical separation of the crystals allowed us to establish that the $[Ni_9(CO)_{16}]^{2-}$ salt dissolved in CH_3CN solution shows infrared carbonyl absorptions at 2000 (s), 1825 (mw), 1810 (mw) and 1790 (sh) cm^{-1}. These frequencies fall at slightly lower wavenumbers than those of $[Ni_9(CO)_{18}]^{2-}$ [17,18], in accordance with an increased Ni-π*(CO) backdonation due to a decreased CO/free charge ratio. Interestingly, these absorptions are very similar to those displayed by the reaction solution before crystallization. Such a similarity suggests that $[Ni_9(CO)_{16}]^{2-}$ might be the direct, though unstable, product of the reaction between of $[N(PPh_3)_2]_2[Ni_6(CO)_{12}]$ and $Cu(PPh_3)_xCl$ (x = 1, 2). An alternative possibility that the original product could be a $[Ni_6(CO)_{12}(\mu_x\text{-}CuPPh_3)]^-$ adduct, such as exemplified by $Ru_6C(CO)_{15}(NO)(\mu_3\text{-}AuPPh_3)$ [19], $[Rh_6C(CO)_{15}(\mu_3\text{-}AuPPh_3)]^-$ [20] or $Os_6P(CO)_{18}(\mu\text{-}AuPPh_3)$ [21], seems less likely. Indeed, its absorption frequencies are too low in comparison to those of $[H_2Ni_{12}(CO)_{21}]^{2-}$ [22], which would have an identical metal-to-charge ratio; furthermore, the latter displays an inferior CO/Ni ratio of 1.75 versus that of 2 for a $[Ni_6(CO)_{12}(\mu_x\text{-}CuPPh_3)]^-$ adduct. Moreover, no Cu–Ni heterometallic cluster was known prior to a recent report on the isolation of the high-nuclearity species $[Cu_xNi_{35-x}(CO)_{40}]^{5-}$ (x = 3 or 5) [23].

Partially, in keeping with the above conclusion, the $[Ni_9(CO)_{16}]^{2-}$ dianion has also been obtained by degradation of $[N(PPh_3)_2]_2[H_2Ni_{12}(CO)_{21}]$ with PPh_3 in acetone. As above, extraction of $Ni(CO)_2(PPh_3)_2$ in toluene followed by extraction of the residue in THF affords an unstable red solution, which upon a layering of toluene separates out red crystals of $[N(PPh_3)_2]_2[Ni_6(CO)_{12}]$ and a tiny amount of dark-orange crystals of $[N(PPh_3)_2]_2[Ni_9(CO)_{16}]$.

Other attempts to obtain $[Ni_9(CO)_{16}]^{2-}$ via CO elimination from $[Ni_9(CO)_{18}]^{2-}$ (e.g. by reaction with trimethylamine oxide, UV irradiation, and thermal treatment) have been unsuccessful.

The chemical behavior of $[Ni_9(CO)_{16}]^{2-}$ is rather similar to that of $[Ni_9(CO)_{18}]^{2-}$. Indeed, as found for the latter, $[Ni_9(CO)_{16}]^{2-}$ is degraded rapidly by a carbon monoxide atmosphere to give mixtures of $[Ni_5(CO)_{12}]^{2-}$ and $Ni(CO)_4$. Moreover, its reaction

with protonic acid leads to formation of $[H_{4-n}$-$Ni_{12}(CO)_{21}]^{n-}$ ($n = 2$, 3), as reported previously also for $[Ni_9(CO)_{18}]^{2-}$.
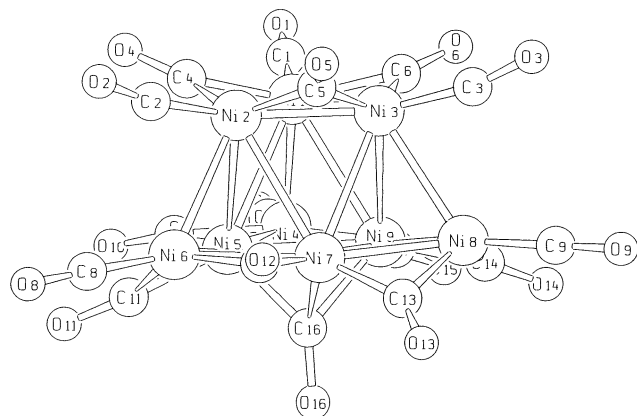

Fig. 1. The structure of $[Ni_9(CO)_{16}]^{2-}$ dianion.

Table 1
Bond distances (Å) in the $[Ni_9(CO)_6(\mu\text{-}CO)_9(\mu_3\text{-}CO)]^{2-}$ dianion

Ni1–Ni2	2.393(2)	Ni8–Ni9	2.449(2)
Ni1–Ni4	2.625(2)	Ni1–Ni3	2.391(2)
Ni1–Ni9	2.785(2)	Ni1–Ni5	2.776(2)
Ni2–Ni6	2.619(2)	Ni2–Ni3	2.398(2)
Ni2–Ni7	2.769(2)	Ni2–Ni5	2.722(2)
Ni3–Ni9	2.716(2)	Ni3–Ni8	2.586(2)
Ni4–Ni5	2.417(2)	Ni3–Ni7	2.720(2)
Ni5–Ni6	2.431(2)	Ni4–Ni9	2.426(2)
Ni5–Ni9	2.569(2)	Ni5–Ni7	2.530(2)
Ni7–Ni8	2.424(2)	Ni6–Ni7	2.429(2)
Ni1–C1	1.716(13)	Ni7–Ni9	2.580(2)
Ni1–C4	1.890(13)	Ni1–C6	1.873(12)
Ni2–C4	1.875(12)	Ni2–C2	1.781(11)
Ni3–C3	1.724(12)	Ni2–C5	1.894(13)
Ni3–C5	1.894(12)	Ni3–C6	1.858(11)
Ni4–C7	1.789(14)	Ni4–C10'	1.72(2)
Ni4–C10	1.94(3)	Ni4–C15	1.861(12)
Ni5–C10	1.87(3)	Ni5–C11'	1.77(2)
Ni5–C11	1.92(3)	Ni5–C16	1.912(11)
Ni6–C8	1.733(12)	Ni5–C10'	1.97(2)
Ni6–C12	1.848(18)	Ni6–C12'	1.81(4)
Ni6–C11	1.92(3)	Ni6–C11'	1.92(2)
Ni7–C13	1.834(12)	Ni7–C12	1.747(18)
Ni7–C12'	2.05(6)	Ni7–C16	1.994(11)
Ni8–C14	1.897(12)	Ni8–C9	1.686(12)
Ni9–C14	1.788(13)	Ni8–C13	1.921(13)
Ni9–C16	2.027(12)	Ni9–C15	1.839(10)
O1–C1	1.178(12)	O2–C2	1.145(11)
O3–C3	1.165(12)	O4–C4	1.181(11)
O5–C5	1.201(13)	O6–C6	1.204(11)
O7–C7	1.137(13)	O8–C8	1.148(12)
O9–C9	1.174(11)	O10–C10	1.212(18)
O10'–C10'	1.222(16)	O11–C11	1.206(17)
O11'–C11'	1.219(16)	O12–C12	1.256(15)
O12'–C12'	1.24(2)	O13–C13	1.166(11)
O14–C14	1.184(12)	O15–C15	1.186(11)
O16–C16	1.237(11)		

2.2. Molecular structure of the $[Ni_9(CO)_{16}]^{2-}$ dianion

The unit cell of $[N(PPh_3)_2]_2[Ni_9(CO)_{16}]$. THF contains two cluster dianions, four $[N(PPh_3)_2]^+$ cations and two solvated THF molecules (separated by normal van der Waals contacts) with one formula species being crystallographically independent. A view of the $[Ni_9(CO)_{16}]^{2-}$ dianion is given in Fig. 1 and the most relevant bond contacts are collected in Table 1. The two-layer metal framework of $[Ni_9(CO)_{16}]^{2-}$ is identical to that displayed by the electronically equivalent $[Ni_6Rh_3(CO)_{17}]^{3-}$ trianion [16] and is formally constructed via the condensation of a planar Ni_6 ν_2-triangle (average Ni–Ni$_{inner}$ 2.560 and Ni–Ni$_{outer}$ 2.429 Å) with a Ni_3 triangular moiety (Ni–Ni$_{av}$ 2.394 Å), to give a Ni_6 trigonal antiprism that is face-capped by three Ni atoms on alternate lateral triangular faces. The interlayer Ni–Ni bond contacts may be divided under pseudo-C_{3v} symmetry into two sets: six inner ones of length 2.75 Å (av) giving rise to the trigonal antiprism and three outer ones of length 2.61 Å (av) connecting the corners of the Ni_6 ν_2-triangle with the Ni_3 ν_2-triangle. To our knowledge, the only other species displaying a related two-layer metal framework is the bimetallic $[Ag_6Fe_3(CO)_{12}(PPh_2)_3CH]$ cluster [24]. All remaining enneanuclear metal carbonyl clusters display three-layer metal frameworks based on face-sharing bioctahedra (e.g. $[Rh_9(CO)_{19}]^{3-}$ [25], $[Ir_9(CO)_{20}]^{3-}$ [26], $[HIr_9(CO)_{19}]^{4-}$ [27], $[Ni_6Ir_3(CO)_{17}]^{3-}$ [28] and $[PtRh_8(CO)_{19}]^{2-}$ [29]), face-sharing trigonal prisms (e.g. $[Pt_9(CO)_{18}]^{2-}$ [9]), face-sharing trigonal prism and antiprism (e.g. $[Ni_9(CO)_{18}]^{2-}$ [18]) or capped square antiprism as $[Rh_9P(CO)_{21}]^{2-}$ [30].

The metal framework of $[Ni_9(CO)_{16}]^{2-}$ implies three additional Ni–Ni interactions with respect to the face-sharing trigonal prism and antiprism of $[Ni_9(CO)_{18}]^{2-}$. A change in the geometry of the metallic framework with an increase in the number of M–M interactions upon a decrease of the number of cluster valence electrons and/or M–CO interactions is already documented by several pairs of clusters having the same nuclearity: e.g. $Os_6(CO)_{18}$–$Os_6(CO)_{21}$ (as exemplified by the structure of $Os_6(CO)_{17}\{P(OMe)_3\}_4$) [31,32], $[Rh_{14}(CO)_{25}]^{4-}$–$[Rh_{14}(CO)_{26}]^{2-}$ [33,34] and $[Rh_{15}(CO)_{27}]^{3-}$–$[Rh_{15}(CO)_{30}]^{3-}$ [35,36]. It is worth noting that $[Ni_9(CO)_{16}]^{2-}$ is electronically equivalent not only with the tricapped octahedral $[Ni_6Rh_3(CO)_{17}]^{3-}$ but also with the face-sharing bioctahedral $[Ir_9(CO)_{20}]^{3-}$ and $[Ni_6Ir_3(CO)_{17}]^{3-}$. Both metal geometries feature the same number of M–M interactions. The adoption by $[Ni_6Rh_3(CO)_{17}]^{3-}$ of a tricapped octahedral rather than a face-sharing bi-octahedral geometry was attributed to the fact that a Rh_3 triangle often displays a greater flexibility than an Ir_3 triangle in accomodating face-bridging carbonyl ligands. In the case of $[Ni_9(CO)_{16}]^{2-}$ it also seems likely that a two- rather than a three-layer
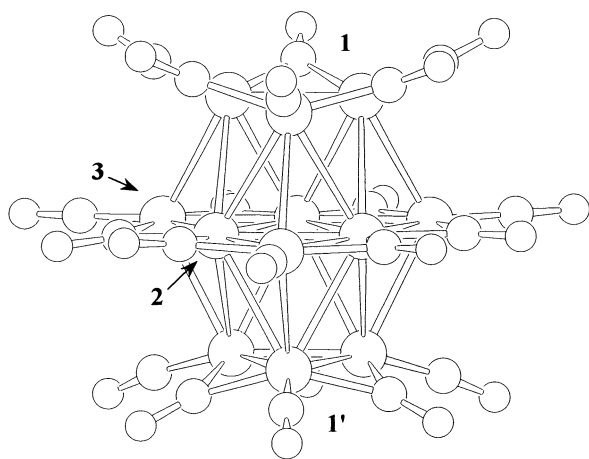
Fig. 2. The structure of $[Ni_{12}(CO)_{21}]^{4-}$ [38] and the adopted numbering scheme for the nickel atoms.

Table 2
Average Ni–Ni distances in $[Ni_{12}(CO)_{21}]^{4-}$ and $[Ni_9(CO)_{16}]^{2-}$

	$[Ni_{12}(CO)_{21}]^{4-}$	$[Ni_9(CO)_{16}]^{2-}$
Reference	[38]	this work
1–1	2.42	2.39
1–2	2.78	2.75
1–3	2.76	2.61
2–2	2.68	2.56
2–3	2.43	2.43
1^Δ–2^Δ	2.35	2.35

For atom numbering see Fig. 2. 1^Δ–2^Δ stands for the distance between the centroids of atoms 1 and 2.

metal geometry could better relieve steric pressures among interlayer carbonyl groups at the observed short Ni–Ni distances (vide infra).

The carbonyl stereochemistry of $[Ni_9(CO)_{16}]^{2-}$ comprises six terminal groups (Ni–C_{av} = 1.74, C–O_{av} = 1.16 Å), nine edge-bridging carbonyls spanning the three Ni–Ni bonds of the top Ni_3 triangle and the six Ni–Ni bonds of the Ni_6 ν_2-triangle (Ni–C_{av} = 1.87, C–O_{av} = 1.21 Å), and one face-bridging carbonyl ligand capping the inner Ni_3 triangle of the Ni_6 ν_2-triangle (Ni–C_{av} = 1.98, C–O = 1.237(11) Å). Three carbonyl groups, viz. C(10)–O(10), C(11)–O(11) and C(12)–O(12), spanning three consecutive edges of the Ni_6 hexaring are disordered and have been refined in two different orientations. These two different orientations probably represent two alternative possibilities to lengthen the otherwise too short intralayer C···C nonbonding contacts by tilting the carbonyl groups alternatively above and below the Ni_6 ν_2-triangle. Analogous alternate tilting of the CO ligands has previously been observed in the related $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ (n = 2, 3) [37,38] and was clearly detectable by ^{13}C CP MAS NMR [38].

The major difference between the structure of $[Ni_9(CO)_{16}]^{2-}$ and $[Ni_6Rh_3(CO)_{17}]^{3-}$ is the presence in the Ni_6Rh_3 trianion of one additional face-bridging carbonyl group capping the top Ni_3 face; moreover, the three carbonyl groups spanning the Ni–Ni bonds of the top Ni_3 face are bent inward (rather than outward) toward the second metal layer and become triply bridging by binding with a third Rh atom.

2.3. Comparison between the structures of $[Ni_9(CO)_{16}]^{2-}$ and $[Ni_{12}(CO)_{21}]^{4-}$ and bonding implications

From a formal point of view, the structure of $[Ni_9(CO)_{16}]^{2-}$ can be derived from that of $[Ni_{12}(CO)_{21}]^{4-}$ [39], sketched in Fig. 2, by substitution of a $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ moiety with a face-bridging carbonyl group. To support this derivation, in Table 2 we report the average Ni–Ni distances between geometrically equivalent Ni atoms of $[Ni_{12}(CO)_{21}]^{4-}$ and $[Ni_9(CO)_{16}]^{2-}$, according to the numbering in Fig. 2. Such a comparison points out the constancy of the 2–3 bonds and the distance between the centroids of atoms 1 and 2 and a barely significant shortening (0.03 Å) of the 1–1 and 1–2 connectivities in $[Ni_9(CO)_{16}]^{2-}$ with respect to those in $[Ni_{12}(CO)_{21}]^{4-}$. The major differences are found in the 1–3 and 2–2 Ni–Ni distances, which are more than 0.1 Å shorter in the former than in the latter. However, the shortening of the interlayer 1–3 distance in $[Ni_9(CO)_{16}]^{2-}$ clearly arises from the tilting upward of atoms 3, whereas the shortening of the 2–2 bonding connectivities of the inner Ni_3 triangle of the Ni_6 ν_2-triangle may probably be ascribed to the presence of the capping carbonyl group. The above comparison does not reveal markedly significant differences in corresponding molecular parameters between the two compounds (other than the above-mentioned 1–3 and 2–2 Ni–Ni distances) and lends further support to the view that the $[Ni_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ moiety in $[Ni_{12}(CO)_{21}]^{4-}$ may be considered as a two-electron donor like CO.

As pointed out by Hoffmann and coworkers 16 years ago [40,41], the isolobal relationships between a C_{2v} d^{10} $Ni(CO)_2$ fragment, a C_{2v} d^8 $Fe(CO)_4$ and CO formally correlate among them several clusters and cluster fragments. For instance, the planar D_{3h} $Ni_3(CO)_3\{(\mu\text{-}Ni(CO)_2\}_3$, as well as the $Ni_6(CO)_3(\mu\text{-}CO)_6$ fragment present in $[Ni_{12}(CO)_{21}]^{4-}$ and $[Ni_9(CO)_{16}]^{2-}$, can be related both to the $[Pt_3(CO)_3\{\mu\text{-}Fe(CO)_4\}_3]^{n-}$ (n = 0–2) cluster [42,43] and the $M_3(CO)_3(\mu\text{-}CO)_3$ (M = Ni, Pt) fragments, as well as the $[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$ dianion. [9] In keeping with this suggestion, EH calculations with CACAO [44] on a $Ni_6(CO)_3(\mu-CO)_6$ moiety show that its HOMO, LUMO and SLUMO of a_2', a_2'' and a_1' symmetry, respectively, are closely related to the corresponding frontier MOs of a $Ni_3(CO)_3\{(\mu\text{-}$

Ni(CO)$_2$}$_3$ isomeric moiety and a Ni$_3$(CO)$_3$(μ-CO)$_3$ fragment, as obtained from both the extended Hückel [40,45,46] and Fenske–Hall [13] calculations. The major difference is represented by an inversion in energy between the σ-type LUMO and the π-type SLUMO. These two frontier empty orbitals of the Ni$_6$(CO)$_3$(μ-CO)$_6$ moiety are of appropriate symmetry to interact with the HOMO of a carbon monoxide group in a face-bridging fashion and a [Ni$_3$(CO)$_3$(μ-CO)$_3$]$^{2-}$ fragment, respectively. Examination of the molecular orbital diagram of [Ni$_9$(CO)$_{16}$]$^{2-}$ is essentially in agreement with the above oversimplified interpretation arising from sequential FMO interactions.

3. Experimental

All reactions including sample manipulations were carried out using standard Schlenk techniques under nitrogen and in dried solvents. The [Ni$_6$(CO)$_{12}$]$^{2-}$ and

Table 3
Crystal data and structure refinement for [N(PPh$_3$)$_2$]$_2$[Ni$_9$-(CO)$_{16}$]·THF

Empirical formula	C$_{92}$H$_{71}$N$_2$Ni$_9$O$_{17}$P$_4$
Formula weight	2128.78
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	13.9442(10)
b (Å)	14.7530(13)
c (Å)	25.175(2)
α (°)	78.074(4)
β (°)	78.992(4)
γ (°)	63.688(4)
V (Å^3)	4513.0(6)
Z	2
D_{calc} (Mg m^{-3})	1.567
λ (Mo–K$_\alpha$)/(Å)	0.71073
Absorption coefficient (mm^{-1})	1.970
$F(000)$	2170
Crystal size (mm)	0.20 × 0.15 × 0.10
θ Range for data collection (°)	2.66–26.99
Index ranges	$-15 \leq h \leq 17$, $-18 \leq k \leq 18$, $-32 \leq l \leq 32$
Reflections collected	43877
Independent reflections	19673 [$R_{int} = 0.2013$]
Completeness to theta = 26.99°	99.9%
Absorption correction	empirical
Max. and min. transmission	0.8273 and 0.6940
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	19673/35/1053
Goodness-of-fit on F^2	0.671
Final R indices [$I > 2\sigma(I)$][a,b]	$R_1 = 0.0606$, $wR_2 = 0.0904$
Largest difference peak and hole (e Å^{-3})	0.611 and -0.426

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

[H$_2$Ni$_{12}$(CO)$_{21}$]$^{2-}$ salts have been prepared according to the literature [47,22]. Analysis of Ni was performed by atomic absorption on a Pye–Unicam instrument. Infrared spectra were recorded on a Perkin–Elmer 1605 interferometer using CaF$_2$ cells. Proton NMR spectra have been recorded on a Varian Gemini 300 MHz instrument.

3.1. Synthesis of [N(PPh$_3$)$_2$]$_2$[Ni$_9$(CO)$_{16}$]·THF from [N(PPh$_3$)$_2$]$_2$[Ni$_6$(CO)$_{12}$]

[N(PPh$_3$)$_2$]$_2$[Ni$_6$(CO)$_{12}$] (3.08 g, 1.74 mmol) was dissolved in anhydrous CH$_3$CN (50 ml) in a 250-ml flask under a nitrogen atmosphere. A solution of Cu(PPh$_3$)Cl (0.63 g, 1.74 mmol) in anhydrous CH$_3$CN (30 ml) was added in portions under stirring over a period of 2 h. The resulting red–brown suspension was filtered, and the solution was evaporated to dryness. The brown residue was washed with toluene (30 ml) and methanol (20 ml), and extracted with THF (50 ml). The THF solution was concentrated to approximately 30 ml and precipitated by diffusion of toluene (50 ml). The resulting red crystalline precipitate mainly consisted of crystals of the starting [N(PPh$_3$)$_2$]$_2$[Ni$_6$(CO)$_{12}$] as confirmed by IR and unit cell measurements. A few dark orange–brown crystals displayed a different morphology. These were separated mechanically under a microscope and characterized as the new [N(PPh$_3$)$_2$]$_2$[Ni$_9$(CO)$_{16}$]·THF salt. *Anal.* Found: C, 52.92; H 3.31; N, 1.38; Ni, 24.01. Calc. for [N(PPh$_3$)$_2$]$_2$[Ni$_9$(CO)$_{16}$]·THF: C, 52.44; H, 3.20; N, 1.32; Ni, 24.87%.

3.2. Synthesis of [N(PPh$_3$)$_2$]$_2$[Ni$_9$(CO)$_{16}$] from [N(PPh$_3$)$_2$]$_2$[H$_2$Ni$_{12}$(CO)$_{21}$]

[N(PPh$_3$)$_2$]$_2$[H$_2$Ni$_{12}$(CO)$_{21}$] (3.10 g, 1.3 mmol) was dissolved in anhydrous acetone (40 ml) in a 250-ml flask under a nitrogen atmosphere. A solution of PPh$_3$ (2.04 g, 7.8 mmol) in anhydrous acetone (30 ml) was added in portions under stirring over a period of 6 h. The resulting red–brown suspension was filtered, and the solution was evaporated to dryness. The brown residue was washed with toluene (20 ml) and extracted in THF (30 ml). Precipitation by diffusion of toluene (50 ml) gave a red crystalline precipitate mainly composed of crystals of [N(PPh$_3$)$_2$]$_2$[Ni$_6$(CO)$_{12}$]. A few darker crystals were mechanically separated under a microscope and characterized as the new [N(PPh$_3$)$_2$]$_2$[Ni$_9$(CO)$_{16}$]·THF salt by infrared spectra.

3.3. X-ray data collection and structure determination of [N(PPh$_3$)$_2$]$_2$[Ni$_9$(CO)$_{16}$]·THF

A summary of the crystallographic data and structure refinement is reported in Table 3. Data collection for [N(PPh$_3$)$_2$]$_2$[Ni$_9$(CO)$_{16}$]·THF was performed at room

temperature on a crystal of approximate $0.20 \times 0.15 \times 0.10$ mm dimensions via a Bruker SMART 2000 diffractometer equipped with a CCD detector and with the generator operated at 50 kV and 40 mA. Cell parameters and orientation matrix were obtained from least-squares refinement on the reflections, measured in three different sets of 15 frames each, in the range $0 < \theta < 25°$. A full sphere of intensity data was obtained (ω scan method); 2100 frames (20 s per frame; $\Delta\omega = 0.3°$) were collected; the first 100 frames were recollected in order to monitor crystal decay, which was not observed; an absorption correction was applied (SADABS) [48]. The structure was solved by direct methods (SIR-97 [49]) and refined with full-matrix-block least squares (SHELX-97 [50]) on the basis of 3843 independent reflections with $I > 2\sigma(I)$; anisotropic temperature factors were assigned to all non-hydrogen atoms with the exception of disordered ones which were refined isotropically. Hydrogen positions were set geometrically. Distance and anisotropic displacement parameter restraints were used for three edge-bridging carbonyl groups of the ν_2 Ni_6 triangle that were disordered in two orientations in the refinement.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 167131 for $[N(PPh_3)_2]_2[Ni_9(CO)_{16}]\cdot THF$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@aadc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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