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NICKEL CARBONYL CLUSTER COMPLEXES

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CONTENTS

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1. INTRODUCTION

The discovery of $Ni(CO)_4$ in 1888, attributed to Ludwig Mond and co-workers,[1] began the search for other binary metal carbonyls. Apart from his role in the development of metal carbonyls, Mond is regarded as one of the most influential figures in the founding of the U.K.'s chemical industry.[2] As a natural progression from the simple metal carbonyls, organometallic cluster chemistry began to emerge in the early part of the 20th century with the discovery of some low-nuclearity neutral cluster complexes such as $Fe_3(CO)_{12}$. This field developed from the pioneering work of Walter Hieber[3] and Paolo Chini.[4–6] Hieber discovered neutral and anionic carbonyl cluster complexes during the 1930s–1950s, the structures of which were not known at the time. Chini and co-workers are largely responsible for the development of the chemistry and syntheses of new cluster compounds from the 1960s until Chini's untimely death in 1980. The last two decades have seen a large amount of work in the area of metal cluster chemistry, which has been reviewed.[7–11] Four main routes have thereby been established for the synthesis of carbonyl clusters: (a) thermal condensation; (b) redox condensation; (c) base-promoted carbon monoxide loss; (d) oxidative coupling of anionic species.[12] There is no doubt that advances in synthetic methods and the increasing availability of techniques used in the characterisation of transition metal cluster complexes such as X-ray diffraction, multinuclear NMR spectroscopy[13,14] and Fourier transform infrared spectroscopy have encouraged the outstanding growth in this area of inorganic chemistry.

The high nuclearity carbonyl clusters of nickel have been discussed in some detail in a review by Chini *et al.*[15] and only briefly in more recent reviews.[10,16] The formation of nickel carbonyl clusters from nickel tetracarbonyl, $Ni(CO)_4$, is in the forefront of these discussions. The discovery of new nickel cluster species has sparked interest in the application of models derived from graph-theory to metal cluster bonding in order to gain further insight into the distribution of electrons and their influence upon the shapes of these clusters.[17] Although the literature available in transition metal cluster electrochemistry has been reviewed by Lemoine,[18,19] it is apparent that there are very few data available for the clusters of nickel in the reviews and in the literature since 1988.[20–29] However, there have been significant advances not only in the identification and characterisation of a cluster which was incorrectly formulated, but also in the discovery of new high nuclearity nickel carbonyl cluster complexes which has motivated the production of the present review.

There is a large number of heterometallic nickel carbonyl clusters known today[8] that include transition elements, e.g. Ni—M where M = Pd, Pt,[30] Au,[23] Co,[31,32] Rh,[33] Ir,[34,35] Fe,[36] Cr, Mo,[37] W,[37,38] or non-transition elements,[39] e.g. M = Ge,[28,40] Sn,[40] As,[41] Sb,[22,42] Bi,[25] as heteroatoms. Nickel clusters also contain a wide range of ligands including carbonyls, phosphines, cyclopentadienyl, alkyl, alkyne, nitryl and atoms such as Cl, S, O, etc. Some of these are included in a review by Melník *et al.*[43] of the basic crystal and structural data obtained by X-ray diffraction analysis up to 1988 of nickel carbonyl compounds and their classification into monomers, oligomers and polymers. The present review is limited to the specific subgroup of homometallic nickel clusters of which carbonyls and hydrides are the only ligands. The X-ray crystal structures of these nickel complexes are described in detail in a complementary Polyhedron Report.[44] Also included in this discussion are the nickel carbonyl dimers and monomers, and those nickel carbonyl clusters with interstitial holes inside the metal framework that are occupied by smaller atoms such as carbon or hydrogen. It should be noted that some of these nickel species do not fit into Cotton's strict definition of the term "cluster" which generally refers to transition-metal complexes consisting of a framework of more than two metal atoms held together to a significant extent by metal–metal bonds and surrounded by other terminal and bridging non-metal ligands.[45] This ligand shell is essential for the chemical stabilisation of the complex and for preventing the coalescence of the metal cores to form large metallic particles; furthermore, it provides an "insulating" phase between the metal cores.[46]

In summary, we attempt to present a comprehensive review containing the known relevant syntheses, chemistry and characterisation of the neutral and anionic nickel carbonyl clusters, dimers and monomers, together with those nickel carbonyl clusters with interstitial hydrides and carbides. Some of these species have applications in homogeneous catalysis; this is discussed briefly but their full potential in this field has yet to be realised.

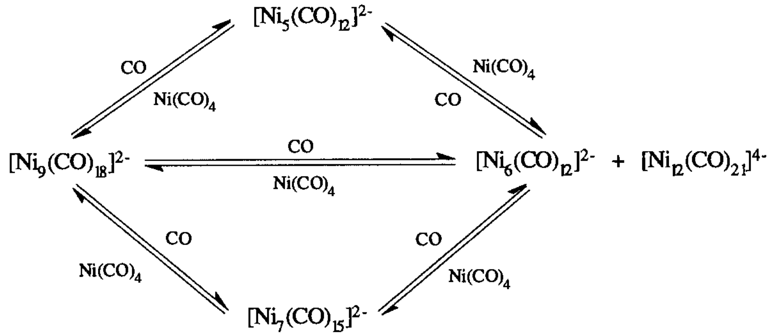
2. SYNTHESIS AND CHARACTERISATION OF NICKEL CARBONYL CLUSTERS

2.1. *Introduction*

X-ray diffraction has been an essential tool for establishing the primary structures of the nickel carbonyl clusters and for gaining definitive information concerning the structural interrelationships and bonding of the complexes. The reason for this can be understood by consideration of the variety and size of the cluster complexes and the fact that their stoichiometries cannot be unequivocally established by the usual chemical and physical methods. Infrared spectroscopy is another important and convenient technique which often provides not only the initial evidence of the existence of cluster species but also information about their structures in solution.

A number of nickel carbonyl clusters has been identified in solution, most commonly in the reduction of $Ni(CO)_4$ or in the reaction of other carbonylnickelates with various reagents. Their isolation is complicated by the large number of equilibria that exists among them and $Ni(CO)_4$ as illustrated in Scheme 1. However, there are only four nickel carbonyl clusters of the simplest type (i.e. containing carbon monoxide as the only ligand) which have been isolated and structurally characterised, namely $[Ni_5(CO)_{12}]^{2-}$, $[Ni_6(CO)_{12}]^{2-}$, $[Ni_9(CO)_{18}]^{2-}$ and $[Ni_{12}(CO)_{21}]^{4-}$. The characteristic infrared carbonyl stretching absorptions for all the known carbonylnickelates with various cations and solvents are collected in Table 1 along with the corresponding colours of their salts as solid materials. The great majority of cluster compounds are highly coloured and these clusters are no exception. Generally the colour intensities increase as the nuclearity increases. The hydride and carbide nickel carbonyl complexes are discussed in Sections 3 and 4. Variable temperature (25 to $-80°C$) ^{13}C NMR spectra of the carbonylnickelates, with the exception of $[Ni_{12}(CO)_{21}]^{4-}$ and of the nickel carbonyl hydrides (see Section 3), have been acquired in both acetone-d_6 and acetonitrile-d_3 at 25 MHz. The ^{13}C NMR shifts of the carbonyl carbon atoms are given elsewhere by Longoni *et al.*[47] and therefore are not mentioned in any detail in this review. Generally the terminal carbonyl ligands have resonances at about δ 180–210 ppm and bridging carbonyl ligands at δ 220–260 ppm, to low field of tetramethylsilane.

The involvement of carbon monoxide and $Ni(CO)_4$ in much of the chemistry makes it essential that all reactions involving these materials be carried out in a well-ventilated fume hood. A low-temperature condenser is useful in the preparations which require $Ni(CO)_4$ in order to prevent its



Scheme 1.

Table 1. Infrared carbonyl absorption frequencies of various carbonylnickelate anions and the colours of their solid salts

Anion	Colour	Cation	Solvent	ν_{CO} (cm^{-1})	Ref.
$[Ni_5(CO)_{12}]^{2-}$	brown	Li$^+$	THF	1970 s, 1920 m, 1830 w, 1790 w, 1710 mw	50
		Na$^+$, K$^+$	THF	1970 s, 1920 m, 1822 w, 1795 w, 1760 w, 1740 mw	
		$[NMe_4]^+$	THF	1965 s, 1915 m, 1810 w, sh, 1780 m, b, 1760 sh	
		[PPN]$^+$	THF	1965 s, 1915 m, 1810 w, sh, 1780 ms	
		Li$^+$, Na$^+$, K$^+$, $[NMe_4]^+$, [PPN]$^+$	DMSO^a	1965 s, 1915 m, 1805 w, sh, 1775 ms	
$[Ni_6(CO)_{12}]^{2-}$	dark red	Li$^+$	THF	1980 s, 1810 m, 1790 m, 1710 w	50
		Na$^+$, K$^+$	THF	1980 s, 1815 m, 1795 m, 1745 mw	
		$[PPh_4]^+$	THF	1975 s, 1810 m, 1780 ms	
		Na$^+$, K$^+$, $[NMe_4]^+$, $[PPh_4]^+$	DMSO^a	1975 s, 1810 m, 1780 ms	
$[Ni_7(CO)_{15}]^{2-}$	red^b	[PPN]$^+$, $[AsPh_4]^+$	MeCN	1990 s, 1940 w, 1820 sh, 1800 ms	47
$[Ni_9(CO)_{18}]^{2-}$	red	$[PPh_4]^+$	THF	2005 s, 1825 s	64
$[Ni_{12}(CO)_{21}]^{4-}$	brown	$[NMe_4]^{+c}$	MeCN^d	1980 s, 1800 s^e	66
$[HNi_2(CO)_6]^-$	colourless	[PPN]$^{+c}$	THF	2005 m, 1950 s	98
$[HNi_{12}(CO)_{21}]^{3-}$	brown	$[NMe_4]^+$, $[NBu_4]^{+f}$	MeCN^d	1990 s, 1830 s^e	66
			MeOH	2005 s, 1830 s^e	
$[H_2Ni_{12}(CO)_{21}]^{2-}$	violet	$[PPh_3CH_2Ph]^+$, $[PPh_4]^+$, [PPN]$^{+c}$	THF^d	2020 s, 1985 mw, 1865 s, 1860 s^e	66
		$[PPh_3CH_2Ph]^+$, $[PPh_4]^+$, [PPN]$^{+c}$	MeOH	2030 s, 1990 mw, 1870 s^e	

s = strong, m = medium, w = weak, ms = medium strong, mw = medium weak, b = broad, sh = shoulder, MeCN = acetonitrile, MeOH = methanol.

[a] Similar spectra have been observed in MeCN, DMF and HMPA.

[b] The $[Ni_7(CO)_{15}]^{2-}$ dianion has presumably been isolated as a red solid since it was obtained by evaporation of a red solution, however, pure crystals of this dianion have not yet been obtained for X-ray analysis.

[c] The counterions of the dianions used for the infrared measurements were not reported. However, the dianions were isolated with these particular cations[66] and so it is assumed that the same salts were used in the infrared analysis.

[d] There are only minor modifications to the carbonyl absorption frequencies on changing either the counteranion or the solvent.

[e] The frequencies given are reported to be accurate to ±5 cm^{-1}.

[f] The assumption (*c*) is made here except that the preparation of $[NBu_4]_3[HNi_{12}(CO)_{21}]$ has not been described. The stability of the $[HNi_{12}(CO)_{21}]^{3-}$ trianion may depend on the countercation. Thus, its tetrabutylammonium salt is stable in most organic solvents (such as MeCN and MeOH), while salts with other cations disproportionate on dissolution in THF.

loss due to the stripping action of the evolving carbon monoxide. The carcinogenic behaviour associated with chronic inhalation of $Ni(CO)_4$ is reflected in exposure guidelines recommended for this material.[48] Where necessary, the addition of a bubbler containing a solution of iodine or bromine between the reaction vessel and the outlet for venting gas is useful in decomposing the volatile $Ni(CO)_4$ by oxidation to the corresponding Ni^{2+} salts. (Note that the vapour pressure of $Ni(CO)_4$ at room temperature is approximately one half atmospheric pressure[49] and hence its fumes spread readily.) Since the cluster species are air sensitive both in solution and in the solid state, standard Schlenk apparatus has been used to allow the reactions to be performed under an atmosphere of nitrogen or carbon monoxide.

2.2. $[Ni_6(CO)_{12}]^{2-}$

Synthesis. Salts of $[Ni_6(CO)_{12}]^{2-}$ have been prepared by reduction of $Ni(CO)_4$ under an atmosphere of nitrogen with a variety of experimental conditions.[50] First, $Ni(CO)_4$ can be reduced by alkali metals (Li, Na, K) in tetrahydrofuran (THF) (60°C, 20 h) or boiling diethyl ether. Under these conditions, however, the reaction rates are slow. The rates can be increased by (a) raising the temperature, (b) using alkali amalgams (Na, K or Mg), or (c) by addition of anthracene, naphthalene or benzophenone to the alkali metal preparation. A second method involves reacting $Ni(CO)_4$ with saturated solutions of alkali hydroxides (NaOH or KOH) in methanol (55°C, 5 h). This reduction method is more rapid (2–3 h) in solvents such as *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). Reduction of $Ni(CO)_4$ under the above conditions gives a mixture of the hexanuclear and pentanuclear dianions, $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_5(CO)_{12}]^{2-}$ in equilibrium, and yields of the former seldom exceed 70%. However, an improved method devised by Nagaki[51] has been used to obtain large quantities and high yields of up to 80% of the $[PPh_3Me]_2[Ni_6(CO)_{12}]$ salt. The method involves a modification of the hydroxide reduction of $Ni(CO)_4$ in methanol which was originally reported by Chini *et al.*[50] Instead of adding all the $Ni(CO)_4$ at once in methanol as solvent, sodium hydroxide was stirred in wet DMSO with controlled addition of $Ni(CO)_4$ over 4–5 h. Finally, Hall and Ruff have obtained $[PPN]_2[Ni_6(CO)_{12}]$ (where $PPN^+ = N(PPh_3)_2^+$) (m.p. 194–196°C) in yields of up to 68% by reduction of $Ni(CO)_4$ with sodium tetrahydroborate ($NaBH_4$) in refluxing THF (2 h) under a nitrogen atmosphere.[38] This anion was also obtained by the reduction of $Ni(CO)_4$ with a potassium–bismuth alloy in ethylenediamine and recrystallised from acetonitrile at −20°C.[52] It should be noted that the $[Ni_6(CO)_{12}]^{2-}$ dianion is obtained by the redox condensation reactions of other carbonylnickelates (*vide infra*) with $Ni(CO)_4$ or carbon monoxide as summarised in Scheme 1. This scheme illustrates the lability of these clusters which results in their facile interconversion under mild conditions.

The formation of the $[Ni_6(CO)_{12}]^{2-}$ dianion by reaction of $Ni(CO)_4$ with alkali hydroxide in DMF[53] is schematically interesting. The final composition after 2 h is typically a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ in relative proportions which are related to the partial pressure of carbon monoxide. This can be understood by considering the existence of an equilibrium shown in eq. (1) between the pentanuclear and hexanuclear carbonyl dianions.[50]

$$[Ni_5(CO)_{12}]^{2-} + Ni(CO)_4 \rightleftharpoons [Ni_6(CO)_{12}]^{2-} + 4CO \qquad (1)$$

Under carbon monoxide (25°C, 1 atm) this equilibrium is completely shifted to the left. It is desirable, therefore, that the carbon monoxide be continuously removed from the reaction mixture in order to obtain increased yields of $[Ni_6(CO)_{12}]^{2-}$ from $Ni(CO)_4$. The reaction is stopped at 90% conversion of $Ni(CO)_4$ to avoid the formation of nickel metal and other insoluble by-products.

The reduction reaction can be thought of as occurring in two steps. The first of these steps is the formation of the pentanuclear $[Ni_5(CO)_{12}]^{2-}$ dianion as shown in eq. (2).[53]

$$5Ni(CO)_4 + 2OH^- \xrightarrow{DMF} [Ni_5(CO)_{12}]^{2-} + H_2O + CO_2 + 7CO \qquad (2)$$

This orange coloured species is then hydrolysed by the water that is produced in the first step according to eq. (3) to produce the red $[Ni_6(CO)_{12}]^{2-}$ dianion. Under neutral conditions the reaction given in eq. (3) is very rapid and addition of water to the product mixture facilitates maximum conversion to the hexanuclear dianion.

$$3[Ni_5(CO)_{12}]^{2-} + 2H_2O \xrightarrow[H_2O]{N_2} 2[Ni_6(CO)_{12}]^{2-} + H_2 + 2OH^- + 3Ni(CO)_4 \qquad (3)$$

The complete reduction process is summarised in eq. (4). It should be noted that there is no evidence for the formation of hydrogen and carbon dioxide but they are included in order to maintain the mass balance in the equation.

$$12Ni(CO)_4 + 4OH^- \xrightarrow{DMF} 2[Ni_6(CO)_{12}]^{2-} + H_2 + H_2O + 3CO_2 + 21CO \qquad (4)$$

The subsequent addition of tetramethylammonium chloride, $[NMe_4]Cl$, precipitates crystalline $[NMe_4]_2[Ni_6(CO)_{12}]$ in ~70% yield. This product is soluble in acetone, acetonitrile, DMF and DMSO, sparingly soluble in alcohols and THF and insoluble in non-polar solvents and water. It decomposes in halogenated solvents such as chloroform and dichloromethane (DCM). Salts of $[Ni_6(CO)_{12}]^{2-}$ with other counterions such as $[NEt_4]^+$, $[NMe_3CH_2Ph]^+$, $[NBu_4]^+$, or $[PPh_4]^+$ are similarly prepared in comparable yields[53] and they are generally soluble in acetone and acetonitrile and, with the exception of the $[NMe_3CH_2Ph]^+$, $[NEt_4]^+$ and $[NBu_4]^+$ salts, only sparingly soluble in THF.[50]

Characterisation. X-ray diffraction analyses of the $[Ni_6(CO)_{12}]^{2-}$ dianion as its $[NMe_4]^+$ and $[PPN]^+$ salts[52,54,55] reveal a trigonal-antiprismatic array of metal atoms formed from the dimerisation of two planar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties through direct Ni—Ni interactions generating overall $D_{3d}\text{-}\bar{3}2/m$ geometry (see Fig. 2 of ref. 44, and hereinafter all figures will be cited from this reference as PR-51 Fig. *x*). The structure is not described as an octahedral-like polyhedron simply because of the large difference of 0.4 Å between the intratriangular and intertriangular Ni—Ni distances which for a regular octahedron would be identical. The average Ni—Ni distance is 2.38 Å. It will become obvious that the $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment is a fundamental building block for the nickel carbonyl anions.

Variable temperature ^{13}C NMR experiments performed by Longoni *et al.*[47] at 25 MHz using ^{13}C-enriched (*ca* 30–40%) samples of $[NMe_4]_2[Ni_6(CO)_{12}]$ produced the following results. At −80°C a limiting slow-exchange spectrum consisting of two equally intense resonances at δ 237.0 and 196.3 ppm is observed. This is entirely consistent with the solid-state structure with an equal number of terminal and bridging carbonyl ligands. At −30°C significant broadening occurs due to the onset of terminal-bridge carbonyl exchange, while at 25°C the fast-exchange limiting spectrum has not been reached and the two resonances are completely collapsed.

The vibrational frequencies of the carbonyl stretching absorptions for the hexanickel dodecacarbonyl cluster dianion are collected in Table 1. It can be seen that these infrared absorptions vary with solvent and cation, an effect which may be attributed to ion pairing,[56–59] but no systematic study has been conducted.

A solid sample of $[NMe_4]_2[Ni_6(CO)_{12}]$ was found to be diamagnetic by magnetic susceptibility measurements made via the Faraday method.[54] Variable temperature magnetic susceptibility measurements of a solid sample of $[PPh_3Me]_2[Ni_6(CO)_{12}]$ were carried out in a magnetic field of 40 kG.[60] Unlike the magnetic data obtained for the higher nuclearity carbonyl clusters of nickel discussed in later sections, the magnetic data for the $[Ni_6(CO)_{12}]^{2-}$ dianion are not temperature dependent in the range ~0–298 K and the dianion exhibits the expected diamagnetism.

2.3. $[Ni_5(CO)_{12}]^{2-}$

Synthesis. The $[Ni_5(CO)_{12}]^{2-}$ dianion is prepared under a nitrogen atmosphere by the reduction of $Ni(CO)_4$ with alkali metals and anthracene in THF,[50] the reaction being identical to the preparation of $[Ni_6(CO)_{12}]^{2-}$, as both dianions are produced in solution according to the equilibrium in eq. (1). The difference, however, occurs in the work-up and subsequent isolation of the $[Ni_5(CO)_{12}]^{2-}$ salts which require anhydrous conditions and an atmosphere of carbon monoxide. The highly labile pentanuclear dianion readily converts to the more stable hexanuclear dianion in the presence of water as shown in eq. (3). Under the anhydrous conditions maintained by the use of alkali metals, however, the conversion shown in eq. (5) is generally complete after addition of a slight excess of sodium naphthalide [*ca* 0.5 mol per mole of $Ni(CO)_4$].

$$5Ni(CO)_4 + 2NaC_{10}H_8 \xrightarrow[THF]{N_2} [Ni_5(CO)_{12}]^{2-} + 2Na^+ + 8CO + 2C_{10}H_8 \qquad (5)$$

Further addition of the reducing agent only results in the formation of a more reduced anionic species as indicated by its solution infrared spectrum, and pure samples of this latter species have not yet been isolated. The product mixture is filtered and the resulting solution is stirred under carbon monoxide (1 h) and evaporated to dryness *in vacuo*. The residue is dissolved in anhydrous methanol under carbon monoxide and an excess of tetraethylammonium chloride is added to precipitate $[NEt_4]_2[Ni_5(CO)_{12}]$. It should be noted that it is much easier to isolate $[Ni_6(CO)_{12}]^{2-}$ produced from the reduction of $Ni(CO)_4$ than it is to obtain salts of the pentanuclear dianion.

The preferred route to pure crystalline salts of the pentanickel dianion involves reacting anhydrous solutions of $[Ni_6(CO)_{12}]^{2-}$ with carbon monoxide [thereby driving the equilibrium shown in eq. (1) to the left], followed by rapid removal under vacuum of any $Ni(CO)_4$ present. Performing the reaction in this way prevents the pentanuclear dianion from converting back to the undesired hexanuclear dianion. The $[NMe_4]^+$, $[NEt_4]^+$, $[PPh_4]^+$ and $[PPN]^+$ salts of $[Ni_5(CO)_{12}]^{2-}$ have been obtained. The last salt was recrystallised by dissolution in THF saturated with carbon monoxide followed by slow diffusion of toluene. Generally these salts are soluble in acetone, acetonitrile, and THF and only sparingly soluble in 2-propanol or toluene.

Characterisation. X-Ray diffraction analysis of the bis(triphenylphosphine)iminium salt, $[PPN]_2[Ni_5(CO)_{12}]$,[61,62] reveals the geometry of the dianion as a trigonal bipyramidal cluster of nickel atoms in which a planar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment is symmetrically capped by Ni—Ni interactions of two identical apical $Ni(CO)_3$ groups (see PR-51 Fig. 1). The average Ni—Ni distance within the $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragment is 2.36 Å. The entire dianion would ideally possess a C_{3v} geometry except for the twisting of the apical carbonyl ligands by *ca* 10° relative to those on the Ni_3 fragments, a conformation which is thought to reduce steric strain. Hence, the dianion adopts an approximate C_3 geometry. The central triangular layer has been described as possessing a "Star-of-David" arrangement in which the metal triangle is randomly distributed between two centrosymmetrically related orientations.[63]

Variable temperature ^{13}C NMR experiments performed by Longoni *et al.*[47] using ^{13}C-enriched (*ca* 30–40%) samples of $[NMe_4]_2[Ni_5(CO)_{12}]$ at both −80 and 25°C show three sharp resonances at δ 257.2, 203.5 and 197.6 ppm in the intensity ratio 1 : 2 : 1 due to the three types of carbonyl ligands (three bridging, six terminal on axial nickel atoms and three terminal on equatorial nickel atoms respectively). This is entirely consistent with the solid-state structure. Interestingly, the carbonyl ligands of the $[Ni_6(CO)_{12}]^{2-}$ dianion are fluxional on the ^{13}C timescale at room temperature, whilst those of the more reduced $[Ni_5(CO)_{12}]^{2-}$ dianion are not.

The frequencies of the infrared carbonyl stretching absorptions of the $[Ni_5(CO)_{12}]^{2-}$ dianion with various cations and in a variety of solvents are given in Table 1.

2.4. $[Ni_9(CO)_{18}]^{2-}$

Synthesis. A number of different routes lead to the formation of $[Ni_9(CO)_{18}]^{2-}$ as shown earlier in Scheme 1. For example, the $[Ni_9(CO)_{18}]^{2-}$ dianion can be prepared by a condensation reaction between $Ni(CO)_4$ and the $[Ni_6(CO)_{12}]^{2-}$ dianion in THF solution under static vacuum (45°C, 8 h).[64] The reaction is governed by the following equilibrium [eq. (6)].

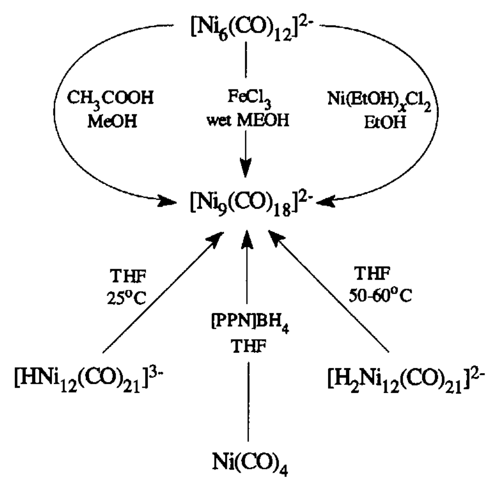
$$[Ni_6(CO)_{12}]^{2-} + 3Ni(CO)_4 \rightleftharpoons [Ni_9(CO)_{18}]^{2-} + 6CO \qquad (6)$$

Once the reaction is complete, the solution is evaporated to dryness and the residue dissolved in methanol to which excess solid trimethylbenzylammonium chloride is added to precipitate $[NMe_3(CH_2Ph)]_2[Ni_9(CO)_{18}]$. The product was obtained in ~56% yield, based on Longoni and Chini's assumption that $x \simeq 4$ in the starting material $K_2[Ni_6(CO)_{12}]\cdot xH_2O$.

The condensation equilibrium [eq. (6)] is also significant during the initial step of the reduction of $Ni(CO)_4$ with alkali metals in THF, when $Ni(CO)_4$ is still present in large excess. That is, the initially formed $[Ni_5(CO)_{12}]^{2-}$ reacts with $Ni(CO)_4$ and is converted via equilibrium (1) to $[Ni_6(CO)_{12}]^{2-}$ which then reacts further with $Ni(CO)_4$ to form $[Ni_9(CO)_{18}]^{2-}$ via equilibrium (6). Monitoring of this reaction by infrared spectroscopy has established the presence of the enneanuclear dianion during the first few hours. This cluster is then consumed, probably because of the decrease in $Ni(CO)_4$ concentration which forces both equilibria (1) and (6) to the left. The interrelationships between these carbonylnickelates is described in Scheme 1. Clearly the redox condensation method is complicated by the unfavourable position of equilibrium (6) under carbon monoxide at 25°C and by the high volatility of $Ni(CO)_4$.

The more practical preparative routes to the $[Ni_9(CO)_{18}]^{2-}$ species are summarised in Scheme 2 and most commonly involve the $[Ni_6(CO)_{12}]^{2-}$ dianion. Hall and Ruff have prepared $[PPN]_2[Ni_9(CO)_{18}]$ in yields of up to 80% by reduction of $Ni(CO)_4$ with $[PPN]BH_4$ under a nitrogen atmosphere in refluxing THF (2 h).[38] (Note that $[PPN]BH_4$ is prepared by the addition of $NaBH_4$ in cold water to a hot aqueous solution of [PPN]Cl.[38]) The solvent was removed under vacuum and the residue was dissolved in DCM containing extra [PPN]Cl. The product mixture was filtered on Celite™ and ether was added to the filtrate. Precipitation of the desired salt was achieved by standing at −10°C overnight. $[PPN]_2[Ni_9(CO)_{18}]$ was found to be soluble in acetone, THF, DCM, and acetonitrile but insoluble in ether, ethyl acetate and pentane.

An alternative preparation of $[Ni_9(CO)_{18}]^{2-}$ is via oxidation of the preformed $[Ni_6(CO)_{12}]^{2-}$ dianion with oxidizing agents such as nickel(II) chloride in ethanol,[31,64] as shown in eq. (7) giving yields of up to 62%, or iron(III) chloride in wet methanol[51,63] giving yields of up to 80%.



Scheme 2.

$$3[Ni_6(CO)_{12}]^{2-} + Ni(EtOH)_xCl_2 \xrightarrow{EtOH} 2[Ni_9(CO)_{18}]^{2-} + Ni + 2Cl^- + xEtOH \tag{7}$$

When $NiCl_2$ is used as the oxidant, the $[Ni_9(CO)_{18}]^{2-}$ dianion has been isolated as its $[NMe_3(CH_2Ph)]^+$, $[PPh_4]^+$, $[PPh_3Me]^+$, $[AsPh_4]^+$, and $[PPN]^+$ salts. These salts are generally soluble in THF, acetone, and acetonitrile, sparingly soluble in alcohol, and insoluble in water and apolar solvents such as toluene. They have been crystallised from acetone/2-propanol or THF/toluene by the slow diffusion technique. Oxidation of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ by acyl-chloride has also been reported to produce $[Ni_9(CO)_{18}]^{2-}$ as the only product but the details of this preparation and the corresponding yields are not given.[65]

The $[Ni_9(CO)_{18}]^{2-}$ dianion has been observed by infrared spectroscopy to be an intermediate [eq. (8)] in the controlled protonation of solutions of $[Ni_6(CO)_{12}]^{2-}$ in either methanol or THF.[66] The products thus generated depend on the acid concentration.

$$3[Ni_6(CO)_{12}]^{2-} + 2H^+ \longrightarrow 2[Ni_9(CO)_{18}]^{2-} + H_2 \tag{8}$$

Therefore, it is possible to obtain the $[Ni_9(CO)_{18}]^{2-}$ dianion as the main product when the reaction is carried out in methanol by careful addition of acetic acid (rather than H_3PO_4 or H_2SO_4) and by monitoring the reaction using infrared spectroscopy. Otherwise nickel carbonyl hydride clusters belonging to the $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2, 3$) group (*vide infra*) are formed.

Other alternative syntheses of $[Ni_9(CO)_{18}]^{2-}$ involve disproportionation of nickel carbonyl hydride clusters.[66] These hydride cluster anions show limited thermal stability both in solution and in the solid state. Thus the $[H_2Ni_{12}(CO)_{21}]^{2-}$ dihydride is readily converted into $[Ni_9(CO)_{18}]^{2-}$ in THF solution on warming at 50–60°C according to eq. (9).

$$4[H_2Ni_{12}(CO)_{21}]^{2-} \xrightarrow[50\text{–}60^\circ C]{THF} 4[Ni_9(CO)_{18}]^{2-} + 3Ni(CO)_4 + 9Ni + 4H_2 \tag{9}$$

The other nickel carbonyl hydride cluster in this group is the more stable $[HNi_{12}(CO)_{21}]^{3-}$ monohydride but in contrast to the dihydride, its stability may depend on the cation. For example those salts with $[NMe_4]^+$, $[PPh_4]^+$, $[AsPh_4]^+$ and $[PPN]^+$ counterions disproportionate on dissolution in THF at room temperature to $[Ni_9(CO)_{18}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ dianions according to eq. (10).

$$2[HNi_{12}(CO)_{21}]^{3-} \xrightarrow[25^\circ C]{THF} [Ni_9(CO)_{18}]^{2-} + 2[Ni_6(CO)_{12}]^{2-} + 3Ni + H_2 \tag{10}$$

This disproportionation reaction is probably induced by precipitation of elemental nickel and $[Ni_6(CO)_{12}]^{2-}$ salts which are easily removed, leaving essentially only $[Ni_9(CO)_{18}]^{2-}$ in solution.

The octadecacarbonylenneanickelate(2−) dianion is rapidly degraded by carbon monoxide (25°C, 1 atm) to $[Ni_5(CO)_{12}]^{2-}$ and $Ni(CO)_4$. The equilibrium of eq. (11) occurs with the

$$[Ni_9(CO)_{18}]^{2-} + 10CO \rightleftharpoons [Ni_5(CO)_{12}]^{2-} + 4Ni(CO)_4 \tag{11}$$

intermediate formation of $[Ni_6(CO)_{12}]^{2-}$ via equilibria given in eq. (6b) followed by (1b), the reverse of eqs (6) and (1) respectively. These equilibria are more clearly demonstrated in Scheme 1.

$$[Ni_9(CO)_{18}]^{2-} + 6CO \rightleftharpoons [Ni_6(CO)_{12}]^{2-} + 3Ni(CO)_4 \quad (6b)$$

$$[Ni_6(CO)_{12}]^{2-} + 4CO \rightleftharpoons [Ni_5(CO)_{12}]^{2-} + Ni(CO)_4 \quad (1b)$$

Characterisation. A single-crystal X-ray diffraction analysis of $[AsPh_4]_2[Ni_9(CO)_{18}]$[61,67] showed the dianion to consist of three stacked $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ layers which are orientated such that the Ni_9 core possesses a nine-vertex polyhedral conformation. The dianion has nine terminal and nine edge-bridging carbonyl ligands, none of which is bridging between adjacent triangular planes (see PR-51 Fig. 4). One of the outer triangles is essentially eclipsed by the inner triangle and the other is essentially staggered. The nine intratriangular Ni—Ni distances have a mean distance of 2.39 Å. The stereochemistry of the $[Ni_9(CO)_{18}]^{2-}$ dianion is discussed elsewhere by Nagaki *et al.*[63] in a comparative structural-bonding analysis of several nine-metal carbonyl cluster anions of the metals Pt, Ni and Rh.

Longoni *et al.*[47] report the following results from variable temperature ^{13}C NMR experiments at 25 MHz using ^{13}C-enriched (*ca* 30–40%) samples of $[AsPh_4]_2[Ni_9(CO)_{18}]$. At −80°C there are two resonances at δ 236.3 and 230.4 ppm in the intensity ratio 1 : 2 due to the bridging carbonyl ligands on the inner and outer triangles respectively. A third resonance at δ 195.2 ppm with relative intensity three is assigned to the terminal carbonyl ligands on the inner and outer triangles that are accidentally degenerate. This spectrum is consistent with a symmetrical stacking of three $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ units either in a staggered or eclipsed conformation in solution and in the solid state. At 25°C the resonance at δ 230.4 ppm disappears. A corresponding decrease in relative intensity of the terminal resonance at δ 195.2 ppm is observed, providing evidence of terminal-bridge carbonyl exchange on the outer triangle.

Elemental analysis and infrared data are both in agreement with the structural characterisation. Frequencies of the carbonyl stretching absorptions are given in Table 1.

2.5. $[Ni_{12}(CO)_{21}]^{4-}$

Synthesis. The $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion was first obtained as a by-product of the synthesis of $[Ni_6(CO)_{12}]^{2-}$ by reduction of $Ni(CO)_4$ under a nitrogen atmosphere in a saturated solution of potassium hydroxide in methanol but it was not structurally characterised at that time.[50] It was reported that longer reaction times (36–48 h) favour the formation of minor amounts of this brown anionic species along with larger quantities of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$. After methanol is removed, the residue is dissolved in water to achieve complete conversion of $[Ni_5(CO)_{12}]^{2-}$ to $[Ni_6(CO)_{12}]^{2-}$ according to eq. (3). Therefore, the product is essentially a mixture of $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_{12}(CO)_{21}]^{4-}$. The reaction can be summarised in eq. (12). (Note that eq. (2) is still valid, namely $[Ni_5(CO)_{12}]^{2-}$ is an intermediate, however less basic conditions are required.)

$$18Ni(CO)_4 + 6OH^- \xrightarrow{MeOH} [Ni_6(CO)_{12}]^{2-} + [Ni_{12}(CO)_{21}]^{4-} + 3H_2O + 3CO_2 + 36CO \quad (12)$$

Excess $Ni(CO)_4$ and methanol are removed under vacuum and the residue is suspended in water and filtered. The two cluster species can be separated due to differences in the solubilities of their salts with different sized cations. Quantitative precipitation of the $[Ni_6(CO)_{12}]^{2-}$ dianion is achieved by the addition of solid KBr and $K_2[Ni_6(CO)_{12}] \cdot xH_2O$ is removed by filtration. The $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion can be precipitated from the resulting dark brown aqueous solution only by bulkier cations such as the tetrasubstituted ammonium cations. The product was isolated and recrystallised from acetonitrile by slow diffusion of diisopropyl ether. The $[NMe_4]_4[Ni_{12}(CO)_{21}] \cdot CH_3CN$ salt has been obtained under these experimental conditions[66] only with yields of up to 5%. It is at best sparingly soluble in most organic solvents including alcohols, THF, acetone, and ethers, but is fairly soluble in acetonitrile and DMSO.

The $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion is readily protonated by acids to the corresponding mono-hydrido derivative, mentioned earlier, according to the equilibrium (13) in aqueous solution and in organic solvents.

$$[Ni_{12}(CO)_{21}]^{4-} + H^+ \rightleftharpoons [HNi_{12}(CO)_{21}]^{3-} \quad (13)$$

However, the deprotonation of the $[HNi_{12}(CO)_{21}]^{3-}$ trianion is possible only by using highly ionising solvents such as DMF or DMSO in the presence of an excess of strong bases such as potassium t-butoxide according to eq. (14). For example, a DMSO solution of potassium t-butoxide is added

$$[HNi_{12}(CO)_{21}]^{3-} + Bu^tO^- \xrightarrow{DMSO} [Ni_{12}(CO)_{21}]^{4-} + Bu^tOH \tag{14}$$

dropwise to a stirred solution of $[NMe_4]_3[HNi_{12}(CO)_{21}]$ in anhydrous DMSO until the absorptions in the carbonyl stretching region of the infrared due to the hydride cluster have disappeared. Addition of an aqueous solution of $[NMe_4]Cl$ affords a brown precipitate of $[NMe_4]_4[Ni_{12}(CO)_{21}]$. After recrystallisation in acetonitrile/ether the crude product is obtained in 18% crude yield. Although this method produces higher yields, the difficulty in subsequent purification and separation of the $[Ni_{12}(CO)_{21}]^{4-}$ salts does not make it an attractive alternative.

Infrared and ^1H NMR monitoring has shown that the $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion is rapidly degraded by carbon monoxide to the pentanuclear carbonylnickelate $[Ni_5(CO)_{12}]^{2-}$ under the mild conditions of room temperature and atmospheric pressure.

$$[Ni_{12}(CO)_{21}]^{4-} + 11CO \longrightarrow 2[Ni_5(CO)_{12}]^{2-} + 2Ni(CO)_4 \tag{15}$$

Similar results have been observed for the monohydrido and dihydrido analogues (*vide infra*). The reaction given in eq. (15) is another example of the instability of the carbonylnickelates towards carbon monoxide. This behaviour can be understood by consideration of the lower Ni—Ni bond energy as compared with the Ni—CO bond energy.[15]

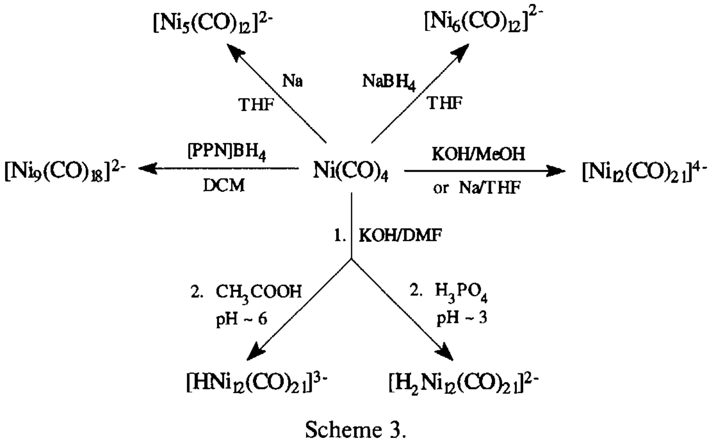
Scheme 3 provides a summary of the nickel carbonyl clusters that can be prepared directly from the reactions of $Ni(CO)_4$ with the appropriate reagents. The preparations of the hydride clusters are discussed in more detail in Section 3.

Although thermal decomposition is a common route to other higher nuclearity clusters,[15] attempts to prepare the $[Ni_{12}(CO)_{21}]^{4-}$ salts by thermally induced condensation of $[Ni_6(CO)_{12}]^{2-}$ under UV radiation and/or continuous flow of nitrogen were unsuccessful.[66] At temperatures above 120°C, it was observed that $[Ni_6(CO)_{12}]^{2-}$ completely decomposes to $Ni(CO)_4$ and nickel metal.

Characterisation. The X-ray crystal structure of $[NMe_4]_4[Ni_{12}(CO)_{21}]\cdot CH_3CN$ has been reported.[68,69] The geometry of the tetraanion can be described as a hexagonal closed packed array of metal atoms giving rise to a metal skeleton with an ideal D_{3h} symmetry[70] (see PR-51 Fig. 6). There are two octahedral and six tetrahedral cavities which have the potential for occupancy by smaller atoms such as hydrogen (namely $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ which are discussed in Section 3). However, since they are unoccupied in this species, there is a noticeable contraction in the distance between the three layers of metal atoms when compared with the protonated analogues. There are six metal atoms in the central plane which appears to have been derived from two similar triangular units with both sides of the plane being capped by the familiar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties. There are no bridging carbonyl ligands between the metal layers. Overall the tetraanion belongs to the *C*2/*c* space group. The frequencies of the infrared carbonyl stretching absorptions are collected in Table 1.

2.6. $[Ni_7(CO)_{15}]^{2-}$

Synthesis and characterisation. The heptanuclear $[Ni_7(CO)_{15}]^{2-}$ anion has been reported by Longoni *et al.*[47] To date, this dianion has not been structurally characterised and its identification is



Scheme 3.

based on spectroscopic (infrared and ^{13}C NMR) and chemical evidence alone. However, its synthesis is outlined here.

The complex $[Ni_7(CO)_{15}]^{2-}$ was obtained under a nitrogen atmosphere by the reaction of $[Ni_6(CO)_{12}]^{2-}$ in acetonitrile with a solution of $[PPN][Ni(CO)_3I]$ in acetonitrile at room temperature according to the equilibrium of eq. (16). This reaction can be monitored by infrared spectroscopy.

$$[Ni_6(CO)_{12}]^{2-} + [Ni(CO)_3I]^- \rightleftharpoons [Ni_7(CO)_{15}]^{2-} + I^- \qquad (16)$$

The carbonyl stretching absorptions attributed to $[Ni_7(CO)_{15}]^{2-}$ (Table 1) increase in intensity as those assigned to $[Ni_6(CO)_{12}]^{2-}$ decrease in intensity. The preparation of the pure heptanuclear dianion in this way is complicated by the position of equilibrium (16) which does not lie completely to the right even in the presence of excess $[Ni(CO)_3I]^-$.

The $[Ni(CO)_3I]^-$ monoanion is prepared by the displacement reaction of a carbonyl ligand in $Ni(CO)_4$ by a halide ion (namely Cl^-, Br^-, I^-) in aprotic solvents such as a 46% DMF solution in anhydrous ether at room temperature according to the equilibrium (17). The experimental details of this preparation are quite involved.[71] The halogenocarbonylnickel complexes are unstable in the pure state and therefore they must be prepared, stored and used in solution under a nitrogen atmosphere.

$$Ni(CO)_4 + [NBu_4]I \overset{\text{ether/DMF}}{\rightleftharpoons} [NBu_4][Ni(CO)_3I] + CO \qquad (17)$$

Infrared measurements have shown that the $[Ni_7(CO)_{15}]^{2-}$ dianion is an important intermediate in the condensation of $Ni(CO)_4$ with $[Ni_6(CO)_{12}]^{2-}$ to give $[Ni_9(CO)_{18}]^{2-}$,[47] [eq. (6)] as well as in the degradation of $[Ni_9(CO)_{18}]^{2-}$ by carbon monoxide to give a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $Ni(CO)_4$ [eq. (11)]. The reaction given in eq. (6) is, therefore, the result of at least two additional equilibria (18) and (19).

$$[Ni_6(CO)_{12}]^{2-} + Ni(CO)_4 \rightleftharpoons [Ni_7(CO)_{15}]^{2-} + CO \qquad (18)$$

$$[Ni_7(CO)_{15}]^{2-} + 2Ni(CO)_4 \rightleftharpoons [Ni_9(CO)_{18}]^{2-} + 5CO \qquad (19)$$

Hence, a second route to $[Ni_7(CO)_{15}]^{2-}$ is by dropwise addition of a solution of $Ni(CO)_4$ in diethyl ether to a solution of $[Ni_6(CO)_{12}]^{2-}$ at 40°C [eq. (9)]. If the reaction is followed by infrared spectroscopy this allows the subsequent isolation of a pure sample of $[Ni_7(CO)_{15}]^{2-}$ by simple evaporation of solvent before any further condensation to $[Ni_9(CO)_{18}]^{2-}$ occurs.

$[Ni_7(CO)_{15}]^{2-}$ has also been prepared by a third route which utilises the redistribution reaction given in eq. (20).[47]

$$[Ni_9(CO)_{18}]^{2-} + [Ni_5(CO)_{12}]^{2-} \longrightarrow 2[Ni_7(CO)_{15}]^{2-} \qquad (20)$$

The synthesis occurs by dissolving equimolar amounts of $[AsPh_4]_2[Ni_5(CO)_{12}]$ and $[AsPh_4]_2[Ni_9(CO)_{18}]$ in acetone at −70°C. The resulting red solution is warmed to room temperature and evaporated to dryness *in vacuo* to give $[AsPh_4]_2[Ni_7(CO)_{15}]$.

In spite of their success in obtaining the $[Ni_7(CO)_{15}]^{2-}$ dianion, Longoni and co-workers were unable to isolate crystals for X-ray analysis due to the disproportionation reaction [eq. (21)] which occurs under the conditions required for crystallisation.

$$3[Ni_7(CO)_{15}]^{2-} \rightleftharpoons [Ni_9(CO)_{18}]^{2-} + 2[Ni_6(CO)_{12}]^{2-} + 3CO \qquad (21)$$

Longoni *et al.*[47] suggest that the structure of $[Ni_7(CO)_{15}]^{2-}$ is most likely to be one which results from the capping of one of the equilateral triangles in the trigonal-antiprismatic $[Ni_6(CO)_{12}]^{2-}$ with one $Ni(CO)_3$ group. This formulation of the $[Ni_7(CO)_{15}]^{2-}$ cluster is entirely consistent with both chemical and spectroscopic studies. This formulation is electron rich (102 cluster valence electrons), and it has been suggested that the additional electrons result in the lengthening of specific Ni—Ni bonds which would account for the high reactivity of the cluster. The $^{13}C\{^1H\}$ NMR spectrum (25 MHz) at −80°C has five equally intense resonances at δ 245.4, 234.9, 198.8, 197.7 and 195.3 ppm which are attributed to $[Ni_7(CO)_{15}]^{2-}$. Between −30 and 25°C two of the five resonances disappear (δ 234.9 and 195.3 ppm) and these have been assigned to the bridging and terminal carbonyl ligands respectively on the Ni_3 triangle remote from the unique nickel by analogy with the fluxional behaviour found for the capped octahedral $[Rh_7(CO)_{16}]^{3-}$.[72]

2.7. *Preparation of other uncharacterised nickel carbonyl clusters*

There are four nickel carbonyl cluster dianions that had been reported as early as 1953 by Behrens and Lohöfer,[73] and in 1960 by Hieber and co-workers.[74] However, analysis of these species is incomplete and relies heavily on methods such as osmometry, molar conductivity studies, elemental analysis and magnetic moments. There are very few infrared data and no single crystal X-ray diffraction data reported. For this reason, and due to the instability of the clusters, the identification of the nickel species produced was difficult and therefore a full development of the chemistry of these compounds has not been possible. One of these compounds has since been identified and its formulation is different to the one initially suggested. However, the described preparations of these clusters are included for completeness. The clusters are described in terms of their original formulations, except where that has been shown to be in error.

2.7.1. A: $[Ni_2(CO)_6]^{2-}$. Hieber and co-workers report the formation of $[Ni_2(CO)_6]^{2-}$ by reaction of $Ni(CO)_4$ with relatively weak bases such as pyridine.[75] The resulting yellow solution was found to contain intermediate substitution products such as $[Ni(CO)_3py]$ (where py = pyridine) and $[Ni(CO)_2(py)_2]$ [eq. (22)] which were detected by infrared spectroscopy. Attempts to isolate these yellow products were unsuccessful due to their high solubilities in both polar and non-polar solvents. They react further with pyridine to form the hexacarbonyldinickelate complexes according to the equilibria of (23) and (24). Attempts to isolate the $[Ni_2(CO)_6]^{2-}$ dianion by concentration of the yellow solution *in vacuo* were unsuccessful as the dinickelate readily reacted with $[Ni(CO)_3py]$ accompanied by a loss of pyridine and evolution of carbon monoxide to sequentially form other carbonylnickelates claimed to be $[Ni_3(CO)_8]^{2-}$, $[Ni_4(CO)_9]^{2-}$ (*vide infra*) and finally $[Ni_5(CO)_9]^{2-}$ via the equilibria given in eqs (25)–(27). During this time the solution changed to a deep red colour followed by the eventual precipitation of $[Ni(py)_6][Ni_5(CO)_9]$ as a red–brown product. This pentanuclear cluster was stabilised by the bulky $[Ni(py)_6]^{2+}$ cation.[75]

$$Ni(CO)_4 + py \rightleftharpoons [Ni(CO)_3py] + CO \tag{22}$$

$$3[Ni(CO)_3py] + 3py \rightleftharpoons [Ni(py)_6][Ni_2(CO)_6] + 3CO \tag{23}$$

$$3[Ni(CO)_2(py)_2] \rightleftharpoons [Ni(py)_6][Ni_2(CO)_6] \tag{24}$$

$$[Ni_2(CO)_6]^{2-} + [Ni(CO)_3py] \rightleftharpoons [Ni_3(CO)_8]^{2-} + py + CO \tag{25}$$

$$[Ni_3(CO)_8]^{2-} + [Ni(CO)_3py] \rightleftharpoons [Ni_4(CO)_9]^{2-} + py + 2CO \tag{26}$$

$$[Ni_4(CO)_9]^{2-} + [Ni(CO)_3py] \rightleftharpoons [Ni_5(CO)_9]^{2-} + py + 3CO \tag{27}$$

Similar compounds were obtained when $Ni(CO)_4$ is mixed with other nitrogen Lewis bases such as morpholine, γ-picoline or piperidine, whereas the use of the stronger base, ethylenediamine, produced only the supposed $[Ni_4(CO)_9]^{2-}$ dianion (*vide infra*). In all the above $Ni(CO)_4$/base systems, carbon monoxide evolution was observed and yellow solutions were generated except when the base was morpholine in which case an olive green solution resulted.[75]

An increase in the basicity of the $Ni(CO)_4$/py system by the addition of KOH in methanol with stirring for 1–2 h at 40°C under an inert atmosphere resulted in a deep red solution containing the potassium salt of the $[Ni_2(CO)_6]^{2-}$ dianion as shown in eq. (28).

$$[Nipy_6][Ni_2(CO)_6] + 2KOH \xrightarrow{MeOH} Ni(OH)_2 + 6py + K_2[Ni_2(CO)_6] \tag{28}$$

Attempts to isolate complex salts of the dinickelate by filtration followed by the addition of $[Ni(phen)_3]Cl_2$, $[Fe(phen)_3]Cl_2$ (where phen = 1,10-phenanthroline) or 1,10-phenanthroline to the filtrate were unsuccessful[75] since $[Ni_2(CO)_6]^{2-}$ is a strong reducing agent and reduces bulky cations such as $[Ni(phen)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ with the formation of the substitution products given in eqs (29) and (30).

$$[Ni(phen)_3]^{2+} + [Ni_2(CO)_6]^{2-} \longrightarrow 3[Ni(CO)_2phen] \tag{29}$$

$$[Fe(phen)_3]^{2+} + [Ni_2(CO)_6]^{2-} \longrightarrow 2[Ni(CO)_2phen] + Fe + 2CO + phen \tag{30}$$

The red crystalline product in both reactions was characterised by infrared spectroscopy and found to be $[Ni(CO)_2phen]$ (ν_{CO} in acetone in 1981 s and 1903 vs cm^{-1} and in benzene at 1981 s and 1907 vs cm^{-1}). This red product was reported to have been isolated earlier and formulated as either $[Ni(CO)_2phen]$ or as the hexacarbonyldinickelate salt, $[Ni(phen)_3][Ni_2(CO)_6]$.[74] These formulations were confirmed by elemental analyses, magnetic moments, infrared spectroscopy and conductivity studies. Hieber *et al.*[74] also claim the $[Ni_2(CO)_6]^{2-}$ dianion as an intermediate in the reduction of $Ni(CO)_4$ to the supposed $[Ni_4(CO)_9]^{2-}$ (*vide infra*) by sodium in THF. This result could not be reproduced by Longoni *et al.*[50] and instead they obtained mixtures of the $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ dianions. However, a tentative assignment of an infrared stretching frequency was attributed to a $[Ni_2(CO)_x]^{2-}$ species **E** (where x is unknown) given in Table 2. Its method of preparation is described in a later section.

2.7.2. **B**: $[Ni_3(CO)_8]^{2-}$. A red trinuclear $[Ni_3(CO)_8]^{2-}$ dianion has also been reported to be present in dark red solutions obtained when $Ni(CO)_4$ is reduced by lithium amalgam[76] or by alkali hydroxides in methanol,[77] and when $Ni(CO)_4$ is reacted with pyridine as described above.[75] In the first method the reduction of $Ni(CO)_4$ with Li(Hg) in THF is reported to produce $Li_2[Ni_3(CO)_8]$ which was crystallised from THF or acetone as a dark red, air sensitive, pyrophoric solvate (7 mol THF or 5 mol acetone).[76] Both solvated products were soluble in acetone, methanol and water and moderately soluble in THF. Acidification of an aqueous solution of $Li_2[Ni_3(CO)_8]$ produced an unstable red substance (presumed to be $H_2[Ni_3(CO)_8]$) which was obtained by extraction into ether. Similar reductions of $Ni(CO)_4$ with Na, K, or Mg amalgams yielded the Na^+, K^+, and Mg^{2+} salts of the supposed $[Ni_4(CO)_9]^{2-}$ dianion (*vide infra*). Attempts by Longoni *et al.*[50] to reproduce these methods of preparation using the Na or Li amalgam did not result in the detection of a nickel trimer. Instead, the most reduced species obtained under these experimental conditions is the pentanuclear dianion $[Ni_5(CO)_{12}]^{2-}$.

The second method of preparation by Sternberg *et al.*[77] involved the reaction of $Ni(CO)_4$ in a saturated solution of NaOH which was shaken under a helium atmosphere for 80 h. The dark red product solution was shaken with oxygen-free water for 1 h and left to stand overnight. A solid material settled out and the clear red supernatant was analysed for nickel and treated chemically to determine the amount of carbon monoxide present. The results of these analyses showed that the aqueous solution contained nickel and carbon monoxide in a ratio of 3 : 8. An aliquot of the red solution was treated with an aqueous solution of $[Ni(phen)_3]Cl_2$ and neutralised with acetic acid. A dark brown precipitate, presumed to be $[Ni(phen)_3][Ni_3(CO)_8]$, was filtered, washed and decomposed to determine the amount of carbon monoxide evolved. The ratio of Ni/CO was also found to be 3 : 8, the same as previously determined for the red solution. This method of preparation was repeated by Cassar and Foà[78] and they report the isolation of a $[Ni_3(CO)_8]^{2-}$ species as its tetrabutylammonium salt (ν_{CO} in DMSO at 1970 vs, 1915 s, 1780 s cm^{-1}). The complex was not obtained in pure form, however, as there is evidence that other nickelates formed during its crystallisation. Interestingly the infrared stretching frequencies are very similar to those obtained for the $[Ni_5(CO)_{12}]^{2-}$ dianion (Table 1). The unexpected observation is that this species dissolved in DMSO to form a red solution under an atmosphere of carbon monoxide. This can be explained by the possible presence of water in the solvent which is known to convert the pentanuclear species into the red $[Ni_6(CO)_{12}]^{2-}$ species as shown in eq. (3) but only under an atmosphere of nitrogen. Under

Table 2. Infrared carbonyl absorption frequencies of uncharacterised carbonylnickelates detected in solution but which have not yet been isolated

Possible anion[a]	Colour	Solvent	ν_{CO} (cm^{-1})
E: $[Ni_2(CO)_x]^{2-}$	orange		1870 s[b]
F: $[Ni_3(CO)_y]^{2-}$	red–violet	THF	1945 ms, 1920 s
G: $[Ni_4(CO)_z]^{2-}$	red–orange	THF	1945 s, 1920 sh, 1870 mw, 1790 w, 1765 m

[a] The formulation of these dianions by Longoni *et al.*[50] has been made on the basis of either analytical data or infrared data. The exact numbers of carbonyl ligands, namely x, y and z, thought to be associated with these species was not stated.

[b] Only the most intense carbonyl absorption in the infrared spectrum has been reported and there is no mention of the solvent used in this analysis.

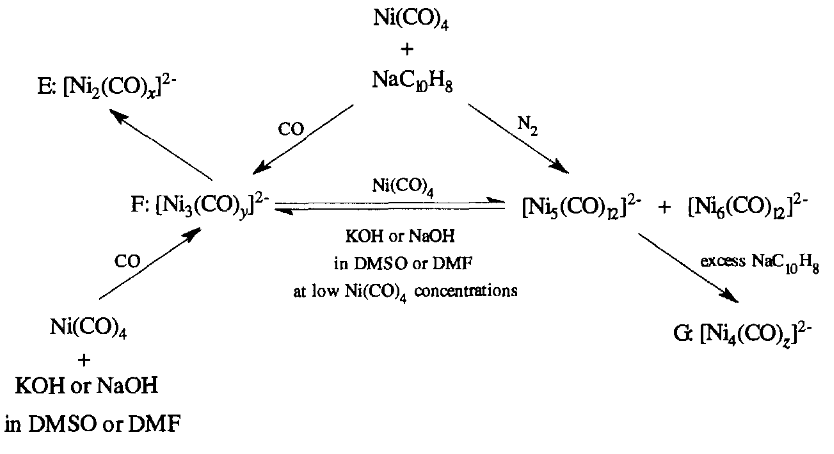
the experimental conditions of Cassar and Foà, however, the $[Ni_5(CO)_{12}]^{2-}$ dianion is known to convert to the colourless $[HNi_2(CO)_6]^-$ species (*vide infra*). This is consistent with the observation of Cassar and Foà that the red DMSO solution does turn colourless after 1 h at 105°C. Hence the existence of the postulated trimeric species is still unconfirmed.

2.7.3. **C**: $[Ni_4(CO)_9]^{2-}$. Earlier reports claim the formation of the red tetranuclear $[Ni_4(CO)_9]^{2-}$ dianion from the reduction of $Ni(CO)_4$ in THF using alkali amalgams (Na, K or Mg),[76] or from disproportionation reactions of $Ni(CO)_4$ induced by a mixture of nitrogen Lewis bases, pyridine and ethylenediamine.[74] In this latter method, the dianion was obtained as its $[Ni(en)_3]^{2+}$ (where en = ethylenediamine) red paramagnetic salt (2.92 μ_B, where μ_B = Bohr magnetons). The infrared carbonyl stretching frequencies for the supposed tetranuclear $Na_2[Ni_4(CO)_9]\cdot 2(CH_3)_2CO$ salt in THF were reported as 1980 vs, 1818 ms and 1799 ms cm^{-1}.[76] The product obtained by Longoni *et al.*,[50] in their attempts to reproduce either of these reactions, is a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ in both instances. The infrared carbonyl stretching frequencies of the $Na_2[Ni_6(CO)_{12}]$ salt in THF have been reported as 1980 s, 1815 m and 1795 m cm^{-1}.[50] Therefore on the basis not only of the similarity of infrared data but also on the evidence that $[Ni_4(CO)_9]^{2-}$ is always reported as the most frequently isolated compound on reduction of $Ni(CO)_4$ under a variety of conditions,[74–76,79] there is little doubt that the tetramer can be reformulated as the structurally characterised $[Ni_6(CO)_{12}]^{2-}$ cluster.[50]

2.7.4. **D**: $[Ni_5(CO)_9]^{2-}$. The $[Ni_5(CO)_9]^{2-}$ dianion has been claimed to be the final product obtained as its $[NiL_6]^{2+}$ salt (where L = pyridine, morpholine, picoline) or $[NiL'_4]^{2+}$ (where L′ = piperidine) from the reaction of $Ni(CO)_4$ with the appropriate nitrogen heterocycle[75] as mentioned above. The $[Ni(phen)_3][Ni_5(CO)_9]$ solid was barely soluble in acetone and was recrystallised from DMF/water. Characterisation of this and other salts of $[Ni_5(CO)_9]^{2-}$ involved molecular weight determinations and conductivity studies. Due to the lack of spectroscopic and other analytical data, the existence of the postulated species is still unconfirmed.

2.7.5. *Species* **E**, **F** *and* **G**. There is spectroscopic evidence for the existence of other reduced anionic species **E**, **F**, and **G**, which have yet to be isolated and characterised.[50] The reactions leading to these uncharacterised species have been summarised in Scheme 4. The colours and infrared frequencies of selected absorption maxima for these proposed carbonylnickelate species are collected in Table 2. As discussed previously, $Ni(CO)_4$ is reduced by half an equivalent of sodium naphthalide (or sodium anthracide) in THF to $[Ni_5(CO)_{12}]^{2-}$ under an atmosphere of nitrogen [eq. (4)]. However, when excess reducing agent is used, this procedure results in further reduction to a red–orange anionic species **G** which is postulated by Longoni *et al.* to be a $[Ni_4(CO)_z]^{2-}$ carbonyl dianion (where z is unknown). Furthermore, when the reduction is performed under carbon monoxide or the reaction procedure is reversed and $Ni(CO)_4$ is added dropwise to a suspension of sodium sand in a solution of naphthalene or anthracene in THF, the red–violet anionic species **F**, $[Ni_3(CO)_y]^{2-}$, is produced (where y is unknown).

The uncharacterised species have also been detected under different reduction conditions. For



Scheme 4.

example, the first product formed by the reduction of $Ni(CO)_4$ under carbon monoxide with alkali hydroxides in solvents such as DMF or DMSO is the red–violet species **F**. This readily reacts with the unreacted $Ni(CO)_4$ to give the $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ dianions. However, when most of the $Ni(CO)_4$ has been consumed, the $[Ni_5(CO)_{12}]^{2-}$ dianion is reduced by the hydroxide ions back to the red–violet anion **F** and to the orange anion **E**, $[Ni_2(CO)_x]^{2-}$ (where x is unknown).

It is not possible to say if these uncharacterised species are formed when the reduction reaction is carried out in saturated methanolic solutions of alkali hydroxides since these solutions are difficult to monitor by infrared spectroscopy due to their high background absorptions.

Finally, it has been reported that other reduced anionic species are formed by the reduction of $Ni(CO)_4$ with alkali metals in hexamethylphosphoramide (HMPA) as solvent but no formulations or evidence, spectroscopically or otherwise, of these species has been given.[50]

2.8. *Bonding properties of nickel cluster ions: experimental and theoretical studies*

Size-selected Ni_n^+ cluster ions ($n = 1$–20) have been generated in molecular beams using quadrupole mass spectrometric experiments performed by Fayet and co-workers.[80,81] The techniques used in such experiments are very useful for investigating the physical and chemical properties of metal clusters of a specific size. These studies have shown that the nickel ions react with carbon monoxide in the gas phase to yield nickel carbonyl cluster complexes of the type $[Ni_x(CO)_y]^+$ and $[Ni_x(CO)_zC]^+$ ($x = 1$–13) and the number of carbonyl ligands thought to be associated with these cluster species, namely y and z, correlate very well to the electron-counting rules proposed by Lauher.[82] The most favourable molecular geometry for any given transition metal cluster can be calculated on the basis of the theoretical work of Lauher which furthermore enables the bonding capabilities of such clusters to be predicted. The results of molecular beams experiments by Fayet *et al.*[80] have since been reinterpreted by Mingos and Wales[83] in terms of the *polyhedral skeletal electron pair theory*[84] which provides a more complete account of the stoichiometries of these clusters and also provides strong circumstantial evidence for a face-capping growth sequence of nickel cluster complexes.

Using a similar approach to Lauher whereby the isolated metal cluster is considered and the cluster valence orbitals which are energetically accessible for metal–metal and metal–ligand bonding are identified, Evans has performed extended Hückel molecular orbital calculations on $[Ni_3(CO)_6]^{2-}$ and other trinuclear metal carbonyl species.[85] The bonding properties of trinuclear species can be identified by an alternative approach also adopted by Evans which involves the study of orbital properties of the metal carbonyl fragments which form the cluster vertices. The electronic structure calculations for $[Ni_3(CO)_6]_n^{2-}$ clusters ($n = 1, 2, 3$) and also for a similar series of platinum clusters have been performed by Bullett.[86]

There have been several theoretical investigations of the electronic structure of nickel carbonyl cluster compounds[87–89] and analyses of the chemical bonding.[90] Similarly to the previous studies, Ackermann and co-workers[46,91,92] have performed a linear combination of Gaussian-type orbitals and local density functional calculations of a series of low- and high-nuclearity nickel carbonyl clusters and their ligand-free core metal framework for analyses of their electronic and magnetic properties. The largest cluster considered is the hypothetical $[Ni_{44}(CO)_{48}]^{n-}$ where the net charge n varies (i.e. $n = 0, 2, 4, 6$). While the bare Ni_{44} cluster (i.e. the ligands are ignored) is calculated to have a magnetisation of 32.7 unpaired electrons,[92] the addition of 48 carbonyl ligands strongly reduces the total magnetic moment to 3.37 unpaired electrons[91] for $n = 0$. An increase in the negative charge on the $[Ni_{44}(CO)_{48}]^{n-}$ cluster results in small increases in the total number of unpaired electrons up to 3.57 per cluster[91] for $n = 6$. Hence the calculations predict that bare nickel clusters are somewhat similar to the bulk metal. In contrast, the low-nuclearity carbonyl ligated clusters containing 20 metal atoms or less do not show any metallic behaviour. The ligands in smaller clusters induce strong modifications in the electronic structure of the metal atoms and therefore the clusters differ significantly from the solid metal. Recent calculations[93] have demonstrated that the addition of carbonyl (and other) ligands to a bare nickel cluster increases the length of the metal–metal bonds.

Bare nickel clusters, Ni_n, from $n = 51$–180 are generated in the gas phase by a pulsed laser cluster vaporisation source when a focused Nd : YAG (532 nm) beam strikes a rotating, translating nickel sample.[94] Examinations of their magnetic properties have shown that these clusters appear to be superparamagnetic possessing a magnetic moment per atom of 0.88 μ_B which is greater than the bulk metal value of 0.61 μ_B. This study reveals a trend whereby the magnetic moments increase as both the cluster size and the magnetic field are increased and both occur in an approximate linear relationship. In another study, clusters of the transition metals Ni, Fe, Co and Cu ranging in size from 13 to 180 atoms are generated in molecular beams by laser vaporisation of isotopically pure metal targets in a flow tube.[95] The purpose of this work was to determine the geometrical structures of neutral metal clusters using a chemical probe method. The clusters are reacted with molecules such as $H_2(D_2)$, H_2O, NH_3 and N_2 in a flow-tube reactor using helium as the carrier gas and after undergoing further treatment they are photoionised and mass analysed in a time-of-flight mass spectrometer.

3. SYNTHESIS AND CHARACTERISATION OF NICKEL CARBONYL HYDRIDE CLUSTERS

3.1. *Introduction*

Lower nuclearity metal clusters often contain one or two cavities that could quite comfortably accommodate interstitial atoms such as hydrogen. However, there is a distinct tendency for polynuclear carbonyls to contain interstitial hydrogen atoms only when the cluster possesses an excess of unoccupied cavities and therefore an increase in the number of metal atoms increases the number of cavities accessible to hydrogen.[70] This trend is demonstrated in two derivatives belonging to the series $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2, 3, 4$) discussed in this section. The $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ anions are the smallest carbonylnickelates known to contain hydrogen interstitially. There are bimetallic carbonyl hydride clusters of nickel that are known to contain Pt,[96,97] or Rh,[60] for example, but these are outside the scope of this review. Two of the highest nuclearity nickel carbonyl species discovered have been shown to contain both interstitial carbon and hydrogen atoms and these are discussed in Section 4.

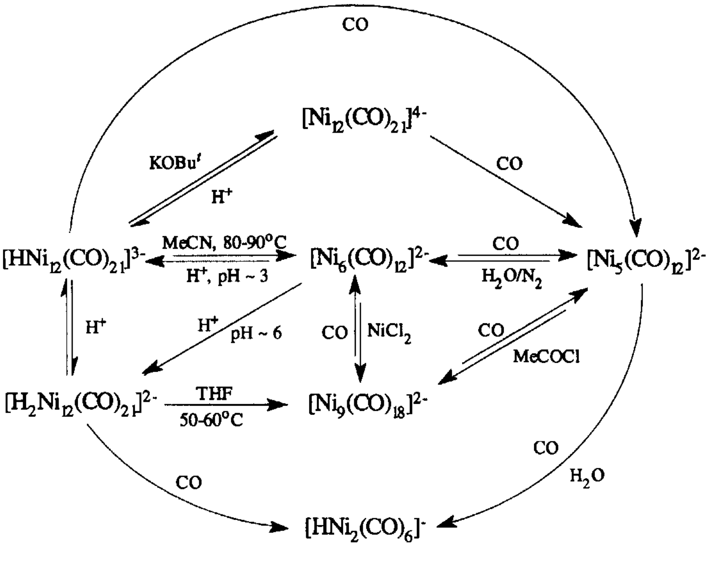
The determination of exact locations of hydrido ligands is not a trivial task and usually requires neutron diffraction data to gain accurate structural information. This process is expensive and not readily accessible, and requires large single crystals which are not always available. Although the use of X-ray data for the direct location of the hydrogen atoms is problematical because of the presence of heavy atoms in the structure, there is no alternative if neutron diffraction data cannot be obtained. The location of the hydride can be cautiously proposed and possibly confirmed by potential energy calculations.

The nickel carbonyl hydrides which possess a hydride ligand on the external and therefore exposed part of the molecule are somewhat different from the carbonylnickelates containing interstitial hydrogen. Both classes included in this section. There is only one known well characterised member of the former group, the nickel carbonyl hydride dimer, $[HNi_2(CO)_6]^-$, which has been isolated and structurally characterised.[98] The difference between carbonyl hydride clusters and interstitial hydrides is discussed in detail by Chini *et al.*[99] The use of computer graphics to assign hydride locations is most readily applicable to clusters with non-interstitial hydrides.[100]

The main route to the cluster hydride anions is by reaction of $[Ni_3(CO)_6]_n^{2-}$ ($n = 2, 3$) with acids. The syntheses and characterisations of those species are described below and the infrared carbonyl stretching absorptions for all the characterised carbonylnickelate hydrides with various cations and solvents are collected in Table 1. There are no infrared data available on the vibrations due to Ni—H(interstitial) bonds but they are expected to occur at low frequencies. For example, the ruthenium cluster, $[HRu_6(CO)_{18}]^-$, which contains an interstitial hydride in an octahedral cavity, has a ν_{RuH} stretching absorption at 825 cm^{-1}. The assignment of the metal–hydrogen stretching mode can be confirmed by deuterium substitution experiments which shift the band to lower frequencies. Hence, the ν_{RuD} absorption of $[DRu_6(CO)_{18}]^-$ occurs at 600 cm^{-1}. The interconversions between the nickel hydride dimer and the carbonylnickelate clusters with and without interstitial hydrogen are summarised in Scheme 5.

3.2. $[HNi_{12}(CO)_{21}]^{3-}$

Synthesis. The monohydride carbonylnickelate, $[HNi_{12}(CO)_{21}]^{3-}$, can be prepared from $[Ni_6(CO)_{12}]^{2-}$ in several ways. The highest yielding synthesis (up to 70%) is achieved by the reaction



Scheme 5.

of $[NMe_4]_3[Ni_6(CO)_{12}]$ with $FeCl_3$ in wet methanol whilst the reaction is monitored by infrared spectroscopy.[51] Water was added and the methanol removed in order to precipitate a mixture of cluster products. Any unconverted $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_9(CO)_{18}]^{2-}$ were removed by washing with ether and THF. The red $[NMe_4]^+$ salt of the monohydride was extracted into acetone and obtained as a powder or microcrystalline material after removal of the solvent. This synthesis is carried out under very similar conditions to those used in the preparation of $[Ni_9(CO)_{18}]^{2-}$. The reason for this can be understood from results reported by Ceriotti *et al.* where the reactions of $[Ni_6(CO)_{12}]^{2-}$ with acids in organic solvents were monitored by infrared and ^1H NMR spectroscopy.[66] In non-aqueous solutions it was shown that the hydrolysis involves intermediate formation of the $[Ni_9(CO)_{18}]^{2-}$ dianion, not previously detected in aqueous solutions. Hence, the overall conversion of $[Ni_6(CO)_{12}]^{2-}$ into $[HNi_{12}(CO)_{21}]^{3-}$ is more complicated than represented in eq. (31) and is likely to occur through a sequence of reactions which includes those represented by eqs (8) and (32). The $[Ni_6(CO)_{12}]^{2-}$ dianion is initially oxidised to $[Ni_9(CO)_{18}]^{2-}$ which undergoes a redox disproportionation in acid to $[HNi_{12}(CO)_{21}]^{3-}$ and $Ni(CO)_4$.

$$2[\mathrm{Ni_6(CO)_{12}}]^{2-} + \mathrm{H}^+ \xrightarrow{\mathrm{pH\,6}} [\mathrm{HNi_{12}(CO)_{21}}]^{3-} + 3\mathrm{CO} \tag{31}$$

$$3[\mathrm{Ni_6(CO)_{12}}]^{2-} + 2\mathrm{H}^+ \longrightarrow 2[\mathrm{Ni_9(CO)_{18}}]^{2-} + \mathrm{H_2} \tag{8}$$

$$2[\mathrm{Ni_9(CO)_{18}}]^{2-} + \mathrm{H}^+ \longrightarrow [\mathrm{HNi_{12}(CO)_{21}}]^{3-} + 3\mathrm{Ni(CO)_4} + 3\mathrm{Ni} + 3\mathrm{CO} \tag{32}$$

In the presence of strong acids it is difficult to isolate the monohydride as it is consumed to form the dihydride derivative via the reaction given in eq. (33) which is discussed later. Nevertheless, the hydrolysis of $[Ni_6(CO)_{12}]^{2-}$ to $[HNi_{12}(CO)_{21}]^{3-}$ can be effected in methanol with careful addition of acetic acid in order to limit the process mainly to eq. (32). This is not a preferred method since a slight excess of acid can result in complete decomposition to $Ni(CO)_4$ and Ni^{2+} salts.

$$2[\mathrm{Ni_6(CO)_{12}}]^{2-} + 2\mathrm{H}^+ \xrightarrow{\mathrm{pH\,3\text{–}4}} [\mathrm{H_2Ni_{12}(CO)_{21}}]^{2-} + 3\mathrm{CO} \tag{33}$$

An alternative method involves the reaction of $[Ni_6(CO)_{12}]^{2-}$ in aqueous solutions buffered at pH 6–7 either with NH_4Cl, or with a mixture of Na_2HPO_4 and NaH_2PO_4.[66,70] Under neutral conditions (pH 7) maximum conversion to the monohydride species is very slow, requiring up to two weeks. This occurs via eq. (34). Thus, addition of $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ to deoxygenated water raises the pH of the solution to the range 9–10 after several days.

$$2[\mathrm{Ni_6(CO)_{12}}]^{2-} + \mathrm{H_2O} \xrightarrow{\text{very slow}} [\mathrm{HNi_{12}(CO)_{21}}]^{3-} + 3\mathrm{CO} + \mathrm{OH}^- \tag{34}$$

There still remain substantial amounts of the red hexanuclear nickel dianion in the alkaline solution. The rate of conversion to the monohydride can be increased under slightly acidic conditions, i.e. by adjusting the solution to pH 6, the reaction given in eq. (31) goes to completion in a few days. The monohydride carbonylnickelate is precipitated by addition of tetramethylammonium chloride. Yields of 50–60% are obtained owing to the formation of $Ni(CO)_4$ and nickel metal as by-products. The presence of $Ni(CO)_4$ is to be expected since both $[HNi_{12}(CO)_{21}]^{3-}$ and $[Ni_6(CO)_{12}]^{2-}$ are readily degraded by carbon monoxide at atmospheric pressure. The presence of nickel metal, however, implies that eq. (31) is an over-simplification of the hydrolysis process.

Similarly to the behaviour of the $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion [eq. (15)], the $[HNi_{12}(CO)_{21}]^{3-}$ derivative is rapidly degraded by carbon monoxide (1 atm, 25°C) and disproportionates to several lower nuclearity nickel complexes according to eq. (35).[66]

$$[HNi_{12}(CO)_{21}]^{3-} + 17CO \longrightarrow [Ni_5(CO)_{12}]^{2-} + [HNi_2(CO)_6]^{-} + 5Ni(CO)_4 \qquad (35)$$

The characterisation of the $[HNi_{12}(CO)_{21}]^{3-}$ trianion is described along with that of $[H_2Ni_{12}(CO)_{21}]^{2-}$ in the following section.

3.3. $[H_2Ni_{12}(CO)_{21}]^{2-}$

Synthesis. The red–violet $[H_2Ni_{12}(CO)_{21}]^{2-}$ dianion has been obtained by the oxidative coupling of $[Ni_6(CO)_{12}]^{2-}$ species in deoxygenated water, THF or methanol under acidic conditions (pH 3–4) by controlled addition of dilute phosphoric or sulfuric acid[66] according to eq. (33). As discussed previously, when these experiments are performed in non-aqueous solutions, monitoring by infrared and ^1H NMR spectroscopy has shown that the formation of the dihydride in eq. (35) actually proceeds via a sequence of three reactions [eqs (8), (33) and (36)].

$$[HNi_{12}(CO)_{21}]^{3-} + H^+ \rightleftharpoons [H_2Ni_{12}(CO)_{21}]^{2-} \qquad (36)$$

The syntheses of both $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ have been carried out in one pot directly from $Ni(CO)_4$[66] as indicated in Scheme 3. Reduction of nickel tetracarbonyl with KOH in DMF or DMSO results in a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$. Quenching with water converts the former into the latter via eq. (3) (*vide supra*). Acidification of the solution to the appropriate pH produces the desired hydride according to eqs (21) and (22). Since the potassium and hydronium salts of $[H_2Ni_{12}(CO)_{21}]^{2-}$ are poorly soluble in water at low pH, the dihydride is more readily and selectively available. Therefore, an alternative preparation of the monohydride is to deprotonate the dihydride with alkali hydroxides in methanol or with potassium t-butoxide in acetone.

The tetrasubstituted ammonium, phosphonium and arsonium salts of $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ have been precipitated from such aqueous or methanolic solutions upon addition of excess halide salts of the cations.[66] All of the salts of these two hydrides are generally very soluble in polar organic solvents. The dihydride salts have been recrystallised from acetone/isopropyl alcohol or THF/toluene and the monohydride salts from either acetone/isopropyl alcohol or acetonitrile/diisopropyl ether.

Characterisation of $[HNi_{12}(CO)_{21}]^{3-}$ *and* $[H_2Ni_{12}(CO)_{21}]^{2-}$. Single crystal X-ray diffraction studies have been reported for $[AsPh_4]_3[HNi_{12}(CO)_{21}]$ (see PR-51 Fig. 7 for an illustration of the trianion) and for the $[AsPh_4]^+$, $[PPN]^+$, and $[PPh_4]^+$ salts of the $[H_2Ni_{12}(CO)_{21}]^{2-}$ dianion.[70,101] These studies reveal a common geometry of the non-hydride atoms of these anions. The structure of both anions is similar to that of $[Ni_{12}(CO)_{21}]^{4-}$ discussed previously (see PR-51 Fig. 6) and consists of a planar $Ni_6(CO)_3(\mu_2\text{-}CO)_6$ fragment of D_{3h}–$\bar{6}2m$ symmetry capped symmetrically on both sides by two equivalent almost eclipsed $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties connected to the central Ni_6 plane by Ni—Ni interactions. The 12-atom nickel fragment forms a hexagonal close packed (*a* : *b* : *a* stacking pattern) metal lattice (containing two octahedral and six tetrahedral holes) surrounded by nine terminal and 12 doubly bridging carbonyl ligands. It has been noted that the insertion of a hydrogen atom into the clusters has caused a small swelling of the octahedron as demonstrated by the lengthening of the Ni—Ni distances when compared with the octahedral cavities without interstitial hydrogen atoms and this effect has also been observed in the X-ray crystal structure of $[HCo_6(CO)_{15}]^{-}$.[102,103]

Single crystal neutron diffraction studies of $[AsPh_4]_3[HNi_{12}(CO)_{21}]$ and $[PPh_4]_2[H_2Ni_{12}(CO)_{21}]$, reveal the locations of the interstitial hydrogen atoms, providing the first detailed crystallographic description of the interaction of interstitial hydrogens with a close-packed fragment of metal atoms.[104] The results show hydrogen occupation of one octahedral hole in the trianion and both octahedral holes in the dianion. The hydrogen atoms were not located exactly at the centres of the octahedral holes as found in $[HCo_6(CO)_{15}]^-$,[102,103] for example, but are assigned to positions distinctly closer to the central hexanickel plane than to the two outer trinickel planes. In the case of the monohydrido trianion, the hydride is sufficiently close to the central Ni_6 plane as to suggest that the hydrogen is triply bridged to only the central three nickel atoms surrounding the octahedral hole.

The metal skeletons of both anions $[H_2Ni_{12}(CO)_{21}]^{2-}$ and $[Ni_{12}(CO)_{21}]^{4-}$ have ideal D_{3h} symmetries but the $[HNi_{12}(CO)_{21}]^{3-}$ monohydride possesses a reduced symmetry, C_{3v}, which can be explained by the occupation of only one octahedral site.[70] The general trend exhibited in the $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2, 3, 4$) series is a contraction of the metal distances as the number of hydrides is diminished. The fact that the tetrahedral hole remains vacant, since no dodecanickel species with more than two hydrides has been found, may indicate that only the octahedral cavities are accessible to the hydrogen atoms.

Both hydrido anions have been analysed by infrared spectroscopy and the results are included in Table 1. The carbonyl absorptions are relatively insensitive to variations in the counterion or the solvent. The frequencies increase as expected, as the number of hydrides increases and the negative charge of the anion decreases. Low temperature vibrational studies at *ca* 110 K have also been carried out on the Ni_{12} hydrides[105] in order to identify the M—H modes which are normally difficult to detect. These occur at *ca* 667 cm^{-1} as a weak and broad absorption for the $[H_2Ni_{12}(CO)_{21}]^{2-}$ dianion and *ca* 684 cm^{-1} as a sharper absorption for the $[HNi_{12}(CO)_{21}]^{3-}$ trianion. Both signals gain intensity as the temperature is lowered. Deuterium labelling was used to confirm the assignment of these signals with the result that they disappeared due to the presence of stronger Ni—CO stretching and bending modes in the 470–500 cm^{-1} region where the Ni—D stretching modes were expected to occur. Such vibrational studies could be useful in evaluating the importance of M—H interactions as well as providing an additional analytical tool for the detection of hydrogen in clusters of increasing size.

The ^1H NMR spectra of the monohydride and dihydride derivatives in acetone-d_6 show sharp high-field resonances at $\delta -24.2$ and -18.3 ppm, respectively, which are unchanged on varying the temperature between 40 and -80°C.[66] Relative integration of the NMR bands confirmed the number of hydrogen atoms to be one for the trianion and two for the dianion. The positions of these resonances are explained by the highly shielded nature of the interstitial hydrides and the fact that they are located in distorted octahedral cavities and therefore experience anisotropic paramagnetic chemical shift effects. In contrast, if the hydrogen atoms are located at the centre of the cluster in a high-symmetry octahedral environment, e.g. in $[HCo_6(CO)_{15}]^-$,[103] or $[HRu_6(CO)_{18}]^-$,[106] they generally show resonances (recorded < -70°C) at low fields namely δ 23.5 and 16.4 ppm respectively.

Variable temperature ^{13}C NMR experiments were performed at 25 MHz on ^{13}C-enriched (*ca* 30–40%) samples and the results collected in a table by Longoni *et al.*[47] Some of the results are presented here. At -80°C the $[H_2Ni_{12}(CO)_{21}]^{2-}$ spectrum has two equally intense resonances at δ 239.9 and 219.3 ppm with relative intensities of six each for the two types of bridging carbonyl ligands (on the inner, B_i, and outer fragments, B_o, respectively) and two resonances at δ 189.3 and 196.0 ppm in the intensity ratio 3 : 6 for the two types of terminal carbonyl ligands (T_i and T_o). The low temperature spectrum is thus consistent with the solid-state structure. Increasing the temperature to -62°C causes the resonances at δ 219.3 and 196.0 ppm to almost disappear. At 25°C a resonance at δ 208.3 ppm appears due to exchange between the bridging and terminal carbonyl ligands of the outer Ni_3 triangles and the resonances at δ 239.9 and 189.3 ppm start to collapse. The resonances due to the terminal and bridging carbonyl ligands on the outer fragments are significantly broader than those due to the respective carbonyl ligands on the inner fragments.

The ^{13}C NMR (25 MHz) spectrum of $[HNi_{12}(CO)_{21}]^{3-}$ at -80°C is very similar to that of the dihydride with two equally intense resonances at δ 248.1 and 228.1 ppm and two resonances at δ 190.5 and 196.8 ppm (3 : 6) and the assignments for these are the same as described for the dihydride. This result was interpreted by Longoni *et al.*[47] in terms of equivalence of the outer carbonyl groups, suggesting that the hydride atom is probably fluxional and rapidly migrates at least between the two octahedral cavities on either side of the central layer. On increasing the temperature carbonyl migration similar to that in the dihydride was observed.

Variable temperature magnetic susceptibility measurements, performed at room temperature and below, on a solid sample of the $[PPh_3CH_2Ph]_2[H_2Ni_{12}(CO)_{21}]$ dihydride salt have been reported.[96] The data reveal a temperature independent diamagnetic contribution being the dominant effect except in the low-temperature range (<70 K) where some paramagnetism is evident. Only small susceptibilities are obtained ($\mu_{eff} = 1.2\ \mu_B$ per cluster, $\chi_{dia} = -6.6 \times 10^{-4}$ cm^3 mol^{-1}).

3.4. $[HNi_2(CO)_6]^-$

Synthesis. As indicated in Scheme 5, the monohydride $[HNi_2(CO)_6]^-$ is relatively easy to prepare by two different routes involving the reaction of carbonylnickelate clusters with carbon monoxide.[98] This extremely labile dimeric species was previously obtained in solution by hydrolysis of the $[Ni_5(CO)_{12}]^{2-}$ cluster dianion under carbon monoxide according to eq. (37).[50]

$$[Ni_5(CO)_{12}]^{2-} + H_2O + 6CO \xrightarrow{THF} [HNi_2(CO)_6]^- + 3Ni(CO)_4 + OH^- \qquad (37)$$

However, since this monoanion was not isolated at that time it was formulated then[15,50] and more recently as $[HNi(CO)_3]^-$,[107] on the basis of the close similarity of its NMR and infrared spectra[108] to those of the $[Ni(CO)_3X]^-$ anions (X = Cl, Br, I,[71] Me,[109] CN[110]). On the basis of the differences in the symmetries of the dimer and the hydrido mononuclear species it seems unlikely that the ν_{CO} stretching frequencies would be coincident. Therefore, definitive evidence for the existence of $[HNi(CO)_3]^-$ is yet to be provided. The earlier attempts to isolate the dimer with tetrasubstituted ammonium cations resulted in recondensation to a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ whereas the use of tetrasubstituted phosphonium or arsonium cations resulted in the formation of $Ni(CO)_3L$ (L = phosphine or arsine). Moreover, decomposition of $[HNi_2(CO)_6]^-$ to $Ni(CO)_4$ has been observed when the reaction of eq. (37) is carried out in the presence of excess water.

The preferred route is to react a solution of the interstitial dihydride $[PPN]_2[H_2Ni_{12}(CO)_{21}]$ in THF with carbon monoxide (2 h) according to eq. (38).[66,98]

$$[H_2Ni_{12}(CO)_{21}]^{2-} + 23CO \xrightarrow{THF} 2[HNi_2(CO)_6]^- + 8Ni(CO)_4 \qquad (38)$$

Isolation of the monohydride is made possible by the use of anhydrous conditions and the particular stability of salts of the $[PPN]^+$ cation. After the solvent is removed under vacuum, the residue is recrystallised either by dissolving in anhydrous THF under carbon monoxide followed by addition of n-heptane or by extraction in toluene and slow diffusion of n-heptane (presumably under carbon monoxide) to obtain colourless crystals of $[PPN][HNi_2(CO)_6]$ in yields of up to 35%.[66]

A third route to the dinickel monohydride was reported by Kleimann *et al.*[108] and involves the low temperature reaction of the $[Na(THF)_4][NHi(CO)_3]$ monohydride (*vide infra*) with tetramethylethylenediamine (TMEDA) in ether (-50°C) as shown in eq. (39).

$$2[Na(THF)_4][HNi(CO)_3] + 2TMEDA \xrightarrow[-50^\circ C]{ether} [Na(TMEDA)_2][HNi_2(CO)_6] + NaH + 8THF \qquad (39)$$

After 10 min the yellow crystalline product was obtained by filtration, washed with ether and dried at -30°C to give nearly quantitative yields (98%) of $[Na(TMEDA)][HNi_2(CO)_6]$.

Characterisation. The $[HNi_2(CO)_6]^-$ monoanion has been characterised by infrared spectroscopy (Table 1), ^1H NMR (singlet at δ -8.6 ppm) and an X-ray crystallographic analysis of $[PPN][HNi_2(CO)_6]$.[98] The reported structure of $[HNi_2(CO)_6]^-$ consists of two pyramidal $Ni(CO)_3$ moieties joined by a Ni—Ni bond of 2.864 Å, and with the carbonyl ligands in an eclipsed conformation. The crystal structure supports the possibility of the hydrogen atom bridging the two nickel atoms close to the mirror plane which bisects the Ni—Ni bond. This view is confirmed by potential energy map calculations which reveal two possible symmetry-related bridging sites on this mirror plane and suggest the possibility of the hydrogen atom being randomly distributed between the two bridging sites.[111] The presence of a terminally-bonded hydrogen atom is excluded on the grounds of non-bonding contacts.

The crystal structure of the $[PPN][HNi_2(CO)_6]$ salt also reveals an unusual linear form of the $[PPN]^+$ cation.

In contrast to the interpretation of the X-ray analysis results, recent molecular orbital calculations carried out on the $[HNi_2(CO)_6]^-$ monoanion suggest that the two nickel atoms are joined exclusively by single bonds to the bridging hydride and that there is no direct Ni—Ni bond.[112] Unfortunately, the original structural parameters are no longer available.[113] There is a need for an accurate redetermination of the structure, preferably also involving a neutron diffraction study,[114] to resolve this question.

3.5. *Preparation of other uncharacterised nickel carbonyl hydride clusters*

There are four nickel hydride complexes that have been reported but which have not yet been structurally characterised.

3.5.1. **H**: $[HNi(CO)_3]^-$. Kleimann *et al.*[108] were the first to report the low temperature synthesis of the $[HNi(CO)_3]^-$ monohydride complex from the temperature sensitive aluminium and gallium nickel hydride ethylene complexes but, as also reported by other workers,[50,54] their attempts to prepare the monohydride directly from $Ni(CO)_4$ have been unsuccessful. The $[HNi(CO)_3]^-$ complex is nonetheless prepared by reaction of $[Na(THF)_6][(i\text{-}Bu)_3Al—H—Ni(C_2H_4)_2]$ with carbon monoxide in THF at −78°C according to eq. (40).

$$[Na(THF)_6][(i\text{-}Bu)_3Al—H—Ni(C_2H_4)_2] + 3CO \xrightarrow[-78^\circ C]{THF} [Na(THF)_4][HNi(CO)_3] + 2C_2H_4 + THF \cdot Al(i\text{-}Bu)_3 \quad (40)$$

During the 20 min reaction time, the original yellow solution turns red–brown as ethene in the 16-electron complex is replaced by carbon monoxide to form an 18-electron complex with the liberation of triisobutylaluminium. Twelve hours after the addition of cold ether, the product is precipitated as fine yellow crystals which are separated, washed with cold pentane and dried under high vacuum at −50°C to give $[Na(THF)_4][HNi(CO)_3]$ in 47% yield. The complex is soluble in THF, sparingly soluble in ether and insoluble in pentane; it is unstable both in solution and in the solid state at temperatures above −20°C and therefore decomposes upon warming to produce $[Na(THF)_4]_2[Ni_6(CO)_{12}]$.

The $[Na(THF)_4][HNi(CO)_3]$ salt was characterised by low temperature ^1H and ^{13}C NMR in THF-d_8. The spectra are temperature dependent between −30 and −80°C. A hydride signal is observed at δ −8.3 ppm and a resonance for the carbonyl carbon atoms at δ 202.1 ppm. The infrared spectrum (THF, −40°C) shows carbonyl stretching absorptions at 2009 and 1954 cm^{-1} which compare well with the carbonyl absorptions for $LNi(CO)_3$ complexes with C_{3v} symmetry. As mentioned in an earlier section, ν_{CO} infrared stretching frequencies at 2005 ms and 1950 s cm^{-1} have been reported and tentatively assigned to a species formulated as $[HNi(CO)_3]^-$.[50] However, the species was later isolated and found to be $[HNi_2(CO)_6]^-$.[98] The high conductivity measured in THF indicated that the complex dissociates almost entirely into solvated Na^+ and $[HNi(CO)_3]^-$ ions. As discussed previously, the possibility of the species being the $[HNi_2(CO)_6]^-$ dimer cannot be excluded since the NMR and infrared data are indistinguishable, although the thermal stability of the $[Na(THF)_4]^+$ salt of "$[HNi(CO)_3]^-$" differs significantly from that of $[PPN][HNi_2(CO)_6]$.

Recently two new alternative routes directly from $Ni(CO)_4$ to the purported $[HNi(CO)_3]^-$ anion have been devised.[107] The first involves the low temperature (−78°C) reaction of $Ni(CO)_4$ with $Li[BEt_3H]$ (superhydride) in THF according to the equilibrium of eq. (41).

$$Ni(CO)_4 + H^- \rightleftharpoons [HNi(CO)_3]^- + CO \quad (41)$$

This equilibrium is shifted to the right by removal of carbon monoxide under a slight vacuum. The product (presumably as its lithium salt) was characterised purely by its ^1H NMR spectrum which was in agreement with the data obtained by Kleimann *et al.*[108] The instability of the solid prevented the use of elemental analysis to confirm the above formulation.

The second method involves the reaction of $Ni(CO)_4$ with MeONa presumably in THF at 20°C under an atmosphere of hydrogen. Addition of ether 15-crown-5 was used to enhance the nucleophilicity of MeO^-. Monitoring the reaction under pressure of hydrogen (20 atm) by Cylindrical Internal Reflectance (CIR) infrared spectroscopy provided evidence for the formation of a novel intermediate species $[Ni(CO)_3(COOMe)]^-$ (ν_{CO} 2036 w, 1939 s, 1599 m cm^{-1}). The latter is consumed by reaction with hydrogen and the overall reaction can be thought of as occurring in two sequential steps described by eq. (42).

$$Ni(CO)_4 + MeO^- \rightleftharpoons [Ni(CO)_3(COOMe)]^- \rightleftharpoons [HNi(CO)_3]^- + HCOOMe \qquad (42)$$

When this reaction is performed at −78°C under a nitrogen atmosphere the presence of a red-fuchsia species of unknown formulation was detected by infrared analysis (ν_{CO} 2008 m, 1937 sh, 1917 vs cm^{-1}). However, isolation of the species was not possible since it was transformed into a series of reduced nickel species upon warming. The final product of this conversion process was identified as the stable $[Ni_6(CO)_{12}]^{2-}$ dianion.

3.5.2. **I**: $[HNi(CO)_3]_2$. Behrens and Lohöfer report the reduction of $Ni(CO)_4$ to the neutral $[HNi(CO)_3]_2$ dimer by alkali metals (Li, Na, K or Ca) in liquid ammonia at −33°C according to eq. (43).[73,115]

$$2Ni(CO)_4 + 2Na + 2NH_3 \xrightarrow{-33^\circ C} [HNi(CO)_3]_2 + 2CO + 2NaNH_2 \qquad (43)$$

Sodium is given as the example in eq. (43) as it is reported to be the most suitable metal for these reactions in ammonia. The blue alkali/alkaline earth metal solution is added in small portions to a suspension of solid $Ni(CO)_4$ (m.p. −25°C) in liquid ammonia and, as the reaction proceeds, the solution changes to a deep red colour relatively rapidly in the presence of Na and Li. The $NaNH_2$ and Na_2CO_3 by-products are insoluble in NH_3. They are removed by filtration and any excess $Ni(CO)_4$ is removed by evaporation. Therefore a pure solution of $[HNi(CO)_3]_2$ is obtained. It is thought that the sodium hexacarbonyldinickelate $Na_2[Ni_2(CO)_6]$ species is initially formed in the reaction and is a labile intermediate which undergoes total ammonolysis to the bright red $[HNi(CO)_3]_2 \cdot 4NH_3$ dimer [see eq. (44)]. The tetraammoniate was noted by Calderazzo *et al.*[16] to react with water to give the purported enneacarbonyltetranickelate $[Ni_4(CO)_9]^{2-}$ dianion (namely $[Ni_6(CO)_{12}]^{2-}$ as explained earlier) and at temperatures above −30°C the dimer rapidly decomposes to $Ni(CO)_4$ and NH_3.

$$Na_2[Ni_2(CO)_6] + 6NH_3 \longrightarrow [HNi(CO)_3]_2 \cdot 4NH_3 + 2NaNH_2 \qquad (44)$$

The presence of free H_2 can be detected if a solution of the dihydridohexacarbonyldinickelate in liquid ammonia is left at room temperature in a pressure chamber for a long period of time. Isolation of the cinnabar red tetraammoniate $[HNi(CO)_3]_2 \cdot 4NH_3$ from the reaction mixture was achieved by evaporation of the liquid ammonia at −33°C. The tetraammoniate can be warmed to room temperature under high vacuum. The $[HNi(CO)_3]_2$ dimer is formed as the NH_3 is slowly removed, and this is accompanied by some decomposition to $Ni(CO)_4$ and carbon monoxide. If the red filtrate is warmed up in a pressure chamber, the tetraammoniate begins to decompose at 50–60°C and at 70°C decomposition is very rapid. At low temperatures the dimer is soluble in absolute alcohol, pyridine and acetone but it is insoluble in ether, benzene and petroleum ether. Bubbling carbon monoxide through a solution of $[HNi(CO)_3]_2 \cdot 4NH_3$ in liquid ammonia at −35°C results in the formation of $Ni(CO)_4$ as shown in eq. (45).

$$[HNi(CO)_3]_2 + 2CO \longrightarrow 2Ni(CO)_4 + H_2 \qquad (45)$$

The neutral hydride dimer $[HNi(CO)_3]_2$ has not yet been isolated but analysis has been carried out on the red solution in order to identify its composition by "indirect methods". Quantitative analyses of the molar ratios of Na consumed and of carbon monoxide liberated per mole of $Ni(CO)_4$ have indicated that the expected formation of the sodium tricarbonylnickelate(II) monomer, $Na_2[Ni(CO)_3]$, does not occur in this case. The dimeric nature of the "$HNi(CO)_3$" fragment was confirmed with the aid of a tensimetric molecular weight determination (method of Stock and Pohland[116]) in liquid ammonia at −33°C. The molecular weight was found to be 288 amu as is expected for the dimer. The amount of nickel was elucidated by decomposition of the red complex in HCl at −30°C to $Ni(CO)_4$ and $Ni(OH)_2$ and determination of nickel as nickel dimethylglyoxime using a Kjeldahl method. The oxidation state of the nickel in this reaction was determined to be −1 by reacting the ammonia complex with dilute nitric acid under high vacuum and then examining the molar ratio of the reaction products as shown below in eq. (46). The hydrogen atoms in the dimer were found to be non-acidic and could not be replaced by a metal.[73] Treatment of the ammonia complex with dilute nitric acid, water, aqueous alkali cyanide solutions and I_2 in liquid ammonia have shown that no trinuclear nickel complexes, such as $Na_2[Ni_3(CO)_8]$, are formed.[115]

$$2[HNi(CO)_3]_2 + 2H^+ \longrightarrow 3Ni(CO)_4 + Ni^{2+} + 3H_2 \qquad (46)$$

3.5.3. **J**: $[HNi_4(CO)_9]^-$. Hieber *et al.*[74] report the preparation of the tetranuclear $[HNi_4(CO)_9]^-$ hydride by acidification of a yellow solution of $[Ni(CO)_2phen]$ which has been buffered with NaOAc. As mentioned above $[Ni(CO)_2phen]$ can also be formulated as $[Ni(phen)_3][Ni_2(CO)_6]$. The following salts were obtained after the addition of the various metal cationic salts; black–brown $[Ni(phen)_3][HNi_4(CO)_9]$, black–brown $[Fe(phen)_3][HNi_4(CO)_9]$ and red–brown $[NEt_4][HNi_4(CO)_9]$. Another method involves the reaction of "$[Ni_4(CO)_9]^{2-}$" (namely $Na_2[Ni_6(CO)_{12}]$ as shown earlier[50]), formed from a mixture of ethylenediamine, pyridine and $Ni(CO)_4$ (described above), and various salts with acetic acid to form violet–red $[NMe_4][HNi_4(CO)_9]$ and dark-violet $[Cr(C_6H_6)_2][HNi_4(CO)_9]$.

The nickel dimer $[HNi(CO)_3]_2$ under basic conditions is reported to form the $[HNi_4(CO)_9]^-$ hydride along with other decomposition products according to eq. (47).[76]

$$16[HNi(CO)_3]_2 + 4OH^- \longrightarrow 15Ni(CO)_4 + Ni + 4[HNi_4(CO)_9]^- + 12H_2 + 4H_2O \qquad (47)$$

The $[HNi_4(CO)_9]^-$ monoanion was also reported by Hieber *et al.*[75] to have been prepared as its $[Ni(en)_3]^{2+}$ salt. Brick red crystals of $[Ni(en)_3][Ni_4(CO)_9]$ were isolated from a mixture of $Ni(CO)_4$, pyridine and ethylenediamine. Dissolution of this salt in acetone followed by separation of decomposition products, acidification with an aqueous acetic acid/acetate buffer solution and addition of $[Ni(en)_3]Cl_2$ precipitates red–violet microcrystals of $[Ni(en)_3][HNi_4(CO)_9]_2$. The product identity was determined by elemental analysis. It has been speculated that the fully characterised $[HNi_{12}(CO)_{21}]^{3-}$ trianion corresponds to the $[HNi_4(CO)_9]^-$ monoanion[66] since the analytical results reported for the two compounds are very similar, and their syntheses and chemical behaviour are similar. However, it is difficult to substantiate this suggestion without any spectroscopic data for the putative $[HNi_4(CO)_9]^-$ anion.

Hieber and Ellermann[76] report the preparation of $[HNi_4(CO)_9]^-$ from the reaction of $Na_2[Ni_4(CO)_9]$ in THF with an ethanolic solution of $[Ni(phen)_3]Cl_2$. Elemental analyses of the recrystallised products were interpreted in terms of the formation of a mixture of the $[Ni(phen)_3]^{2+}$ salts of the $[Ni_4(CO)_9]^{2-}$ and $[HNi_4(CO)_9]^-$ anions. It is assumed that this product arises from the reported hydrolysis of $[Ni_4(CO)_9]^{2-}$ [equilibrium (48)].[76]

$$[Ni_4(CO)_9]^{2-} + H_2O \rightleftharpoons [HNi_4(CO)_9]^- + OH^- \qquad (48)$$

On the contrary, Longoni *et al.*[50] report that the $[Ni_6(CO)_{12}]^{2-}$ dianion (i.e. "$[Ni_4(CO)_9]^{2-}$") is stable in neutral aqueous solution under nitrogen and can be recovered unchanged after several days. However, after longer periods (about two weeks) the red Ni_6 solution was observed to have changed to a green–brown colour with infrared and ^1H NMR spectra which correspond to the fully characterised $[HNi_{12}(CO)_{21}]^{3-}$ species. As mentioned earlier, this monohydride has been more conveniently prepared by hydrolysis of $[Ni_6(CO)_{12}]^{2-}$ in slightly acidic conditions ($pH \sim 6$). There has been no indication of the formation of the hypothetical $[HNi_6(CO)_{12}]^-$ species which would be the equivalent of the purported $[HNi_4(CO)_9]^-$ species.

3.5.4. **K**: $[HNi_5(CO)_9]^-$. The preparation of the pentanuclear $[HNi_5(CO)_9]^-$ monohydride as its tetramethylammonium salt has been reported by Hieber *et al.*[75] In the absence of air, reduction of $Ni(CO)_4$ with pyridine in a refluxing methanolic solution of KOH (15 h) was observed by a colour change in the reacting solution from an initial yellow to a deep red–brown colour once the reaction was complete. The $Ni(OH)_2$ was removed by filtration followed by the addition of benzene and enough water to produce two layers. The yellow benzene phase containing $[Nipy(CO)_3]$, $Ni(CO)_4$ and pyridine was discarded and the aqueous methanolic phase was washed again with benzene and the insoluble decomposition products were removed by filtration. The red aqueous solution which remained was diluted with an aqueous sodium acetate/acetic acid buffer solution and mixed with a 10% solution of tetramethylammonium hydroxide. Precipitation of $[NMe_4][HNi_5(CO)_9]$ as a microcrystalline brown product was achieved after leaving this mixture of 0°C for one day. The solid was separated by filtration and recrystallised from acetone/petroleum ether. Other products obtained by fractional precipitation of the red solution by the addition of ammonia were $[NMe_4][HNi_4(CO)_9]$ and $[NMe_4]_2[Ni_4(CO)_9]$. The elemental analyses were reported.

The $[HNi_5(CO)_9]^-$ monoanion has been isolated from a preparation of $[Ni_5(CO)_9]^{2-}$.[75] As mentioned above, the $[Ni_5(CO)_9]^{2-}$ dianion is formed from the reaction of $Ni(CO)_4$ with pyridine followed by concentration of the solution *in vacuo* to produce a red–brown solution of $[Ni(py)_6][Ni_5(CO)_9]$. The $[Ni(phen)_3]^{2+}$ salt of $[Ni_5(CO)_9]^{2-}$ can be precipitated by shaking this red–brown solution with Na_2S and NaOH in $MeOH–H_2O$ (20 : 1) followed by filtration to remove NiS. Addition of $[Ni(phen)_3]Cl_2$ to the filtrate precipitates $[Ni(phen)_3][Ni_5(CO)_9]$. Extraction of the precipitate with acetone removes soluble $[Ni(phen)_3][HNi_5(CO)_9]_2$ which can be recovered as red–brown pyrophoric needle-like crystals by diluting the extracts with aqueous hydrochloric acid and cooling to $-15°C$ for several days. Precipitation is completed by addition of an aqueous solution of sodium sulfate. The product was obtained by filtration and washed to remove excess sulfate and then dried over P_2O_5 under high vacuum. It is soluble in acetone but only slightly soluble in alcohol. Elemental analysis was used to determine the formula of the product. No spectroscopic data have been reported for the $[HNi_5(CO)_9]^-$ anion.

3.6. *The chemistry of the carbonylnickelates*

The chemical behaviour of the carbonylnickelates is indeed complicated and by no means completely elucidated. This section briefly outlines some aspects of the chemistry of the nickel carbonyl clusters. The syntheses have been already discussed in detail and summarised in Scheme 5; therefore some information may be repeated from a different perspective.

The salts of all the known carbonylnickelates are air sensitive both in solution and in the solid state, and air oxidation results in the formation of some $Ni(CO)_4$ and other decomposition products such as Ni^0 and Ni^{2+} salts. The salts of the $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2, 3, 4$) anions decompose in air to nickel carbonate and some $Ni(CO)_4$.

Both $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ have similar nett chemical behaviour in solution due to their easy interconversion [eq. (1)]. For example, they both react with water under carbon monoxide to give a colourless solution of the $[HNi_2(CO)_6]^-$ dimer. Elemental sulfur is an alternative agent to carbon monoxide for decreasing the nuclearity of a nickel cluster as evidenced in its ability to convert the $[Ni_6(CO)_{12}]^{2-}$ dianion to the $[Ni_5(CO)_{12}]^{2-}$ cluster as given in eq. (49).[117]

$$[Ni_6(CO)_{12}]^{2-} + S \longrightarrow [Ni_5(CO)_{12}]^{2-} + NiS \qquad (49)$$

The $[Ni_5(CO)_{12}]^{2-}$ dianion readily converts to the $[Ni_6(CO)_{12}]^{2-}$ dianion by reaction with water under nitrogen [eq. (3)]. In contrast $[Ni_6(CO)_{12}]^{2-}$ has limited stability to hydrolysis under nitrogen; i.e. after several days some conversion to $[HNi_{12}(CO)_{21}]^{3-}$ occurs [eq. (34)]. This conversion occurs much faster under acidic conditions (pH 6) [eq. (31)] with the intermediate formation of $[Ni_9(CO)_{18}]^{2-}$ [eq. (8)] detected by infrared and ^1H NMR spectroscopy. Further protonation to the red–violet $[H_2Ni_{12}(CO)_{21}]^{2-}$ dihydride is achieved by increasing the acidity of the aqueous $[Ni_6(CO)_{12}]^{2-}$ solution to pH ~ 3 according to eqs (34), (36) and the overall eq. (33). It is worth noting that the ease of hydrolysis decreases in the series $Ni_5 > Ni_6 > Ni_9 > Ni_{12}H > Ni_{12}H_2$ as expected from the higher delocalisation of charge and consequent lowering of the nucleophilicity of the cluster.[50]

As summarised in Scheme 1, the carbonylnickelate species are all closely related to each other by a number of equilibria. For example, the condensation of $[Ni_6(CO)_{12}]^{2-}$ with $Ni(CO)_4$ occurs slowly under static vacuum at 40°C to give the dark-red $[Ni_9(CO)_{18}]^{2-}$ cluster [eq. (6)] with intermediate formation of $[Ni_7(CO)_{15}]^{2-}$ as shown by infrared monitoring.[88] The $[Ni_7(CO)_{15}]^{2-}$ dianion has also been observed as an intermediate in the rapid degradation of $[Ni_9(CO)_{18}]^{2-}$ by carbon monoxide to give a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $Ni(CO)_4$ [eq. (11)] by careful monitoring of the volume of carbon monoxide added. The $[Ni_9(CO)_{18}]^{2-}$ dianion may be prepared more easily by oxidation of the hexanuclear complex with a stoichiometric amount of $Ni(EtOH)_xCl_2$ [eq. (7)]. The relatively low stability of the $[Ni_9(CO)_{18}]^{2-}$ dianion is evidenced by its reaction with iodide ions to give $[Ni_6(CO)_{12}]^{2-}$ and decomposition products as shown in eq. (50).[64] The reaction of the enneanuclear dianion with triphenylphosphine gives similar degradation products as shown in eq. (51).[117]

$$[Ni_9(CO)_{18}]^{2-} + 2I^- \longrightarrow [Ni_6(CO)_{12}]^{2-} + 2[Ni(CO)_3I]^- + Ni \qquad (50)$$

$$[Ni_9(CO)_{18}]^{2-} + 6PPh_3 \longrightarrow [Ni_6(CO)_{12}]^{2-} + 3Ni(CO)_2(PPh_3)_2 \qquad (51)$$

High-pressure infrared studies of solutions containing the $[Ni_6(CO)_{12}]^{2-}$ dianion as its $[PPN]^+$ and Na^+ salts under applied pressure of carbon monoxide or syngas ($CO/H_2 = 1:2$) have been reported.[55] The spectra of solutions in an unstirred stainless steel CIRCLE Accessory infrared cell were obtained using CIR along a ZnSe crystal. Conversion of $[Ni_6(CO)_{12}]^{2-}$ into $Ni(CO)_4$ and

$[Ni_3(CO)_x]^{2-}$ (where x is unknown) via intermediate formation of $[Ni_5(CO)_{12}]^{2-}$ is implicated from infrared spectra, when an acetonitrile solution of the $[PPN]^+$ salt is pressurised with carbon monoxide or syngas (20 atm). Additional infrared stretching absorptions at 1995 sh and 1946 sh cm^{-1} which have been tentatively assigned to $[Ni_7(CO)_{15}]^{2-}$ have been observed in a THF solution of $Na_2[Ni_6(CO)_{12}]$ containing $[PPN]BPh_4$ under syngas (1 atm). However, these ν_{CO} stretching absorptions disappear under pressure of syngas (20 atm) concomitant with the formation of another unisolated species characterised by an absorption at 1959 sh cm^{-1}. When all of the above systems involving $[Ni_6(CO)_{12}]^{2-}$ under pressure of carbon monoxide or syngas are heated to 100°C the reduced anionic nickel species are all completely converted into $Ni(CO)_4$ which is the only infrared observable carbonyl species present. This result is to be expected, but what is unusual is the absence of any nickel hydride species when hydrogen is present in the reactant gas, namely when syngas is used.

Solid $[NMe_4]_2[Ni_5(CO)_{12}]$ decomposes on heating at ~75°C to nickel metal whereas the more stable $[NMe_4]_2[Ni_6(CO)_{12}]$ salt decomposes in the solid over the temperature range 190–230°C. In both cases thermogravimetric analysis produces no evidence for the formation of intermediate products in the solids.[50]

The two hydride derivatives $[HNi_{12}(CO)_{21}]^{3-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$ also display a limited thermal stability both in solution and in the solid state, the monohydride being the more stable. When a solution of $[H_2Ni_{12}(CO)_{21}]^{2-}$ in acetone[47] or THF[66] is heated to 60°C the dihydride is transformed cleanly into $[Ni_9(CO)_{18}]^{2-}$ according to eq. (8). This ready transformation could be initiated by elimination of H_2 since the $[HNi_{12}(CO)_{21}]^{3-}$ does not react under the same conditions using acetone[47] or acetonitrile[66] as solvent. Analogously, the $[HNi_{12}(CO)_{21}]^{3-}$ monohydride is stable in acetonitrile at room temperature but on warming at 80°C is rapidly converted into $[Ni_6(CO)_{12}]^{2-}$ according to the apparent stoichiometry (52).

$$4[HNi_{12}(CO)_{21}]^{3-} \xrightarrow[80\text{–}90^\circ C]{MeCN} 6[Ni_6(CO)_{12}]^{2-} + 3Ni(CO)_4 + 9Ni + 2H_2 \qquad (52)$$

The $[Ni_6(CO)_{12}]^{2-}$ dianion is also seen as an intermediate product in the thermal decomposition in solution of $[Ni_{12}(CO)_{21}]^{4-}$, which results ultimately in nickel metal and $Ni(CO)_4$ at temperatures above 120°C.

The stability of the $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2, 3$) derivatives in solution is considerably dependent upon the particular anion and solvent. Thus, $[H_2Ni_{12}(CO)_{21}]^{2-}$ is stable in alcohols, acetone and THF but unstable in other solvents such as acetonitrile, DMF and DMSO due to concomitant autodeprotonation and autodecomposition reactions which afford a mixture of $Ni(CO)_4$, $[HNi_{12}(CO)_{21}]^{3-}$ and as yet uncharacterised species. All of these reactions are generally not affected by the counterion. However, the stability of the $[HNi_{12}(CO)_{21}]^{3-}$ monohydride may depend on the counterion. When THF is used as solvent at 25°C the monohydride converts to $[Ni_9(CO)_{18}]^{2-}$ according to eq. (10).

As previously discussed, the $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2, 3, 4$) anions exhibit instability towards carbon monoxide (1 atm, 25°C) resulting in rapid degradation to $Ni(CO)_4$ and lower nuclearity species such as $[Ni_5(CO)_{12}]^{2-}$ and $[HNi_2(CO)_6]^-$ [see eqs (15), (35) and (38)]. In contrast, both dodecanickel hydrides are stable under an atmosphere of hydrogen. The interstitial hydrogen is reversibly exchanged with deuterium over a period of 24 h as shown in eq. (53) where $n = 2, 3$. Monitoring by NMR spectroscopy shows the disappearance of the hydride signals under deuterium and their reappearance when exposed again to hydrogen.[66]

$$[H_{4-n}Ni_{12}(CO)_{21}]^{n-} \underset{H_2}{\overset{D_2}{\rightleftharpoons}} [D_{4-n}Ni_{12}(CO)_{21}]^{n-} \qquad (53)$$

In contrast, the use of these hydride species in hydrogenation or hydroformylation of 1-pentene under pressure of hydrogen (1–50 atm) has been unsuccessful.

The $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$ ($n = 2, 3$) derivatives have been shown by infrared analysis to be unstable towards oxidation by oxygen, iodine or Ni^{2+} salts resulting in complete decomposition with no detectable intermediates.

3.7. *Application of carbonylnickelates in catalysis*

Interest in the chemistry of the metal cluster complexes has been aroused by their ability to produce facile multicentre transformation of small molecules and hence their potential in the production of new homogeneous and heterogeneous catalysts.[118,119] In theory, polymetallic compounds are expected to have several advantages over monometallic systems in terms of their catalytic activity by consideration of their electrochemistry.[19] These include (i) the ability to undergo multielectron transfer processes and thus to act as an "electron reservoir"; (ii) the ability to activate small molecules such as CO, N_2, CO_2, H_2 and olefins via metal–ligand bonds; (iii) the potential to break metal–metal bonds electrochemically thus yielding reactive sites which facilitate the coordination of incoming molecules on certain metal atoms; (iv) the potential to decompose after adsorption on a catalytic support yielding small metal crystallites. (Metal crystallites are typically electronically unsaturated and stabilised either by strong interactions with a support (e.g. a metal oxide) or by being trapped in the cavity of a zeolite or inert matrix; in contrast, molecular metal carbonyl clusters can be described as small (< 15 Å) metal aggregates electronically saturated and stabilised by ligands and free charges.[120])

In practice, there are numerous examples of transition metal carbonyl clusters which function as homogeneous catalysts or catalyst precursors for reactions such as the water–gas shift reaction and the hydrogenation of carbon dioxide in alcohols or the carbonylation of alcohols to produce alkyl formates (Ru), olefin hydrogenation and isomerisation (Ru), hydrogenation of carbon monoxide at elevated temperatures and pressures (Ru or Rh), oxidation by molecular oxygen of aliphatic ketones to carboxylic acids (Rh) and hydroformylation of alkenes to aldehydes (Co).[121] Interestingly, it has been shown by *in situ* infrared studies that often these cluster species, under the appropriate reaction conditions, fragment to monomeric species which are more likely to be responsible for catalytic activity. There are also many examples where carbonyl cluster complexes are supported on oxide carriers in heterogeneous processes such as the hydrogenation of carbon dioxide to methane using ruthenium carbonyls.[119]

Stüss-Fink[122] describes metal clusters as occupying a "no-man's-land between mononuclear metal complexes on the one side and polynuclear metal surfaces on the other, and thus between typical homogeneous and typical heterogeneous catalysts". There is evidence for the low-nuclearity nickel carbonyl cluster anions (i.e. $\leqslant 12$ nickel atoms) functioning as unconventional homogeneous catalysts, and the large metal carbonyl clusters as molecular models for poorly understood heterogeneous catalysts.[120] For example nickel carbonyl cluster anions have been shown to be good homogeneous catalysts or catalyst precursors for industrial processes and for carbonylation reactions in organic synthesis (*vide infra*). They can be described according to the separate catalytic processes in which they participate. Indeed, aside from cobalt which is used mainly in hydroformylation reactions, nickel has been cited as the most frequently used metal in homogeneous transition metal catalysis.[123]

3.7.1. *Acetylene polymerisation catalyst.* The salts of $[NMe_4]_2[Ni_5(CO)_{12}]$, $[NMe_4]_2[Ni_6(CO)_{12}]$, $[NMe_4]_2[H_2Ni_{12}(CO)_{21}]$ and $[NEt_4]_3[HNi_{12}(CO)_{21}]$ in acetone are efficient catalysts for the polymerisation of acetylene.[124] Improved yields of polymer (20–30 g) are produced per gram of catalyst as compared to the original heterogeneous catalyst ($AlEt_3/Ti(OPr)_4/-20$ to 80°C, C_2H_2) which produced significantly lower yields (~ 2 g).[125] Although the reaction is normally performed under mild conditions at room temperature (20°C, 1 atm C_2H_2), the $[NMe_4]_2[H_2Ni_{12}(CO)_{21}]$ species is active at temperatures as low as -40°C.

3.7.2. *Carbon monoxide methanation catalyst.* The hexanuclear $Na_2[Ni_6(CO)_{12}]$ species on an oxide support has been found to be an efficient, highly dispersed catalyst precursor for carbon monoxide methanation.[126] The properties of this cluster give rise to desirable improved low temperature activity and higher nickel dispersion making it a more effective precursor than the conventional nickel catalyst derived from $Ni(NO_3)_2$.

3.7.3. *Low temperature homogeneous methanol synthesis catalyst.* An extremely active catalyst system for the conversion of synthesis gas (CO/H_2, 1 : 2) to methanol comprises $Ni(CO)_4$ and alkaline alcoholates in THF or methanol.[127] This catalyst operates at significantly lower temperatures (80–120°C) and pressures (20–30 atm) than the current industrial heterogeneous process (230–300°C and 50–100 atm).[128] An *in situ* investigation of the $Ni(CO)_4$/MeONa catalytic system using CIR infrared spectroscopy has revealed the involvement of the $[HNi(CO)_3]^-$ monomeric species (or the $[HNi_2(CO)_6]^-$ dimer) in the catalysis.[107] A catalytic cycle was devised from these results in which a combination of MeONa and $[HNi(CO)_3]^-$ is suggested to convert methanol to formaldehyde. The nickel hydride, $[HNi(CO)_3]^-$, is suggested to convert formaldehyde to methanol.

3.7.4. *Intramolecular cyclocarbonylation of* 1*-bromo-*1,4*-dienes.* There are many applications of $Ni(CO)_4$ in organic synthesis. One example in which $Ni(CO)_4$ is used as a catalyst precursor is a process which cyclises halodienes into five-membered rings. Such methods are in demand by synthetic chemists since this class of compounds is found in natural products and has outstanding biological activity. The active catalyst is produced by the reaction of $Ni(CO)_4$ in a basic solution of triethylamine in a mixture of methanol and acetonitrile, under a slow stream of argon. The homogeneous solution was observed to change to a red–purple colour. Addition of the substrate, bromodiene, caused an immediate reaction to form cyclopentane which was complete in only a few minutes and in almost quantitative yields.[129] The reaction conditions for the catalyst preparation are reminiscent of the preparations of carbonylnickelates as previously discussed[54,64,77] and therefore these species have been implicated (but not isolated) in such reactions. Furthermore, in the presence of air, no colour developed in the reaction solution and no reaction was observed over several hours. This is consistent with the air sensitive nature of the carbonylnickelate species. Under similar conditions to the above example, $Ni(CO)_4$ can be used to convert vinyl halides into five- and six-membered lactones.[130]

3.7.5. *Carbonylation of allyl and aryl halides.* Allyl chlorides have been reported to react with $Ni(CO)_4$ under phase transfer conditions to form butenoic acids. An aqueous solution of NaOH in the presence of an ammonium salt (e.g. triethylbenzylammonium chloride) mixed with $Ni(CO)_4$ in a solvent such as acetonitrile forms an active system for the conversion of propenyl chloride to vinylacetic and crotonic acids.[131] Infrared techniques have been used to identify the presence of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ carbonylnickelates under these reaction conditions; when these species were used in place of the $Ni(CO)_4$ the same reaction products were formed. The use of these anionic nickel cluster complexes allows the reaction to be performed in the presence of acetylene without undesirable acetylene insertion products being formed.

The carbonylation of aromatic halides into their corresponding acids is catalysed by $Ni(CO)_4$ in polar aprotic solvents such as DMF, DMSO, HMPA, *N*-methylpyrrolidone and *N*-methylformamide in the presence of a base such as $Ca(OH)_2$ under an atmosphere of carbon monoxide at 100°C.[78] The possible formation of anionic nickel complexes under the experimental conditions was realised; to test whether any of these species was catalytically active the purported $[Ni_3(CO)_8]^{2-}$ carbonylnickelate was prepared according to the method of Sternberg *et al.*[77] The $[NBu_4]_2[Ni_3(CO)_8]$ salt was found to carbonylate bromobenzene into benzoic acid by stirring in DMSO under a carbon monoxide atmosphere at 105°C for 1 h.

3.7.6. *Carboxylation of organic halides.* The treatment of a wide variety of organic halides, RX (where X = halide), with several equivalents of $Ni(CO)_4$ in alcoholic medium (R′OH) containing 2–3 equivalents of the corresponding sodium or potassium alkoxide results in formation of the esters RCOOR′.[132] The $Ni(CO)_4$ system is also active in the aminocarbonylation of amines in methanol solvent. It was noted that a solution of $Ni(CO)_4$ in potassium t-butoxide in t-butyl alcohol produced a more powerful carboxylating system than the corresponding methanol–methoxide system. In one embodiment of this reaction $Ni(CO)_4$ was added under an atmosphere of argon to a dried methanolic solution of MeONa followed by the addition of the 1-bromo-4-t-butylcyclohexene reagent. The reaction mixture was stirred at 60°C for 6 h during which time a deep red colour developed. Under these conditions it is expected that the red colour was due to the presence of $[Ni_6(CO)_{12}]^{2-}$; however, this cannot be confirmed since the active system was not investigated further. After the reaction was completed, the mixture was cooled and the nickel species decomposed during the work-up. The methyl 4-t-butyl-1-cyclohexencarboxylate product was isolated as a colourless liquid in 71% yield.

Another example involves complexes derived from $Ni(CO)_4$ which are generated by reaction with organolithium reagents at -50°C; these species react with α,β-unsaturated carbonyl compounds to form 1,4-dicarbonyl derivatives.[133] This is a useful method for the direct formation of 1,4-dicarbonyl structures by intermolecular coupling which is not possible using classical synthetic reactions.

4. SYNTHESIS AND CHARACTERISATION OF NICKEL CARBONYL CARBIDE AND CARBIDE HYDRIDE CLUSTERS

4.1. *Introduction*

Interest in both the experimental and theoretical studies of carbido-transition-metal carbonyl clusters has been generated in part by their use as models for intermediates in heterogeneous Fischer–Tropsch processes in which surface-bound carbides are postulated to play an important role in the catalytic hydrogenation of carbon monoxide.[120,134] Although the existence of an Ni_3C binary phase had been known since 1957 from the work of Nagakura,[135] it was not until 1982 that the first nickel carbide clusters were reported to have been synthesised and characterised by Ceriotti *et al.*[136] In less than a decade, the range of monocarbide and polycarbide carbonyl clusters of nickel that had been structurally characterised grew to include those containing from seven to 38 nickel atoms and from one to six interstitial carbide atoms, some of which have been described in general reviews on transition metal clusters.[10,137,138] Generally the carbide atoms are located in cavities surrounded by either seven or eight metal atoms rather than six as commonly found in molecular carbonyl carbide clusters of other metals and also in the Ni_3C bulk phase.[135] Molecular orbital calculations performed by Halet and Mingos[139] on dicarbido-transition metal clusters, including several carbonyl clusters of nickel, have been useful in explaining the types of bonds and bond orders encountered in such compounds.

Although there are several examples of nickel carbonyl carbide clusters known today that are bimetallic, e.g. Ni—M where M = Co,[24,65,140–142] Fe,[143,144] or Re,[145] here we present only the syntheses and characterisation of 13 homonuclear carbonyl carbide clusters of nickel, two of which may each contain a single interstitial hydride. Since most of the syntheses were reported in short communications, much of the experimental detail is not available. The carbide clusters of nickel have been presented here in order of increasing numbers of atoms and ligands with the following priority: nuclearity of nickel, number of carbonyl ligands, carbide and then hydride number. Most of these clusters have been characterised by X-ray diffraction analysis. Those clusters which are not yet structurally characterised have been subjected to other types of analysis. For example, infrared spectroscopy has proven to be a convenient and useful technique for the characterisation of all of these clusters and the respective carbonyl stretching absorptions are collected in Table 3. This method of analysis has not been utilised to its maximum capacity since there are very few data

Table 3. Infrared carbonyl absorption frequencies of various nickel carbonyl carbide cluster anions and the colours of their solid salts

Anion	Colour	Cation	Solvent	ν_{CO} (cm^{-1})	Ref.
$[Ni_7(CO)_{12}C]^{2-}$	brown[a]	$[NBu_4]^{+b}$	THF	1975 s, 1824 mw, 1810 mw	117
$[Ni_8(CO)_{16}C]^{2-}$	dark red	$[NBu_4]^+$	THF	1995 s, 1850 s	146
$[Ni_9(CO)_{17}C]^{2-}$	dark red	$[NBu_4]^+$	THF	2000 s, 1855 ms, 1800 m, br	146
$[Ni_{10}(CO)_{16}C_2]^{2-}$	red	$[AsPh_4]^+$, $[PPN]^+$	THF	2000 s, 1975 ms, 1875 m, 1820 m	148
$[Ni_{10}(CO)_{18}C]^{2-a}$	dark red	$[NMe_4]^+$	THF	2005 s, 1800 ms	146
$[Ni_{11}(CO)_{15}C_2]^{4-}$	–	$[NEt_3CH_2Ph]^{+b}$	MeCN	2000 w, sh, 1970 sh, 1945 s, 1760 ms, 1740 sh	117
$[Ni_{12}(CO)_{16}C_2]^{4-}$	–	$[NBu_4]^{+b}$	MeCN	2005 sh, 1980 ms, 1940 s, 1830 s	117
$[Ni_{16}(CO)_{23}C_4]^{4-}$	brown	$[NMe_4]^+$, $[PPh_4]^+$, $[PPN]^+$	MeCN	1988 vs, 1949 mw, 1800 sh	149
$[Ni_{34}(CO)_{38}C_4]^{6-c}$	–	$[NEt_4]^+$	MeCN	1992 s, 1853 s	150
$[HNi_{34}(CO)_{38}C_4]^{5-}$	–	$[NMe_3CH_2Ph]^+$	Me_2CO	2008 s, 1862 s	150
$[Ni_{35}(CO)_{39}C_4]^{6-}$	–	$[NEt_4]^+$	MeCN	1998 s, 1864 s, 1850 sh	150
$[Ni_{38}(CO)_{42}C_6]^{6-c}$	–	–	MeCN	1992 ms, 1890 sh, 1873 s, 1861 s	151
$[HNi_{38}(CO)_{42}C_6]^{5-}$	dark brown[a]	$[NBu_4]^+$	Me_2CO	2002 ms, 1907 sh, 1891 s, 1874 s	151

[a] These dianions were presumably isolated as brown solids since they were obtained from brown solutions.

[b] The counterions of the dianions used for the infrared measurements and the colours of the corresponding salts were not reported. However, the dianions were isolated with these particular cations and so it is assumed that those salts were used in the infrared analysis.

[c] The X-ray crystal structures of the salts of these clusters have not yet been determined and their colours have not been reported.

available on the vibrations due to Ni—C(carbide) bonds; these vibrations have been reported in the range 500–900 cm^{-1} for other transition metal carbide clusters containing Fe, Co and Rh.[143] The ^{13}C and ^{1}H NMR data are given when available.

The known methods for introducing a carbide atom in a metal cluster involve either the thermally induced disproportionation of a coordinated carbon monoxide ligand or the reaction of reagents such as CCl_4, CH_2Cl_2, or S with a neutral or anionic cluster.[146] The temperatures required for the first method cannot be reached before the nickel carbonyl clusters thermally decompose to $Ni(CO)_4$ and nickel metal. Hence, the second method is the most widely used, with $[Ni_6(CO)_{12}]^{2-}$ being the best precursor to the carbide clusters of nickel. Finally, the carbide nickel clusters themselves, including $[Ni_9(CO)_{17}C]^{2-}$ and $[Ni_{10}(CO)_{18}C]^{2-}$, were later used as convenient precursors to several other carbide clusters simply by degradation reactions with various reagents such as triphenylphosphine. All of these methods are summarised in Scheme 6 together with the synthetic routes to the carbide hydride carbonylnickelates.

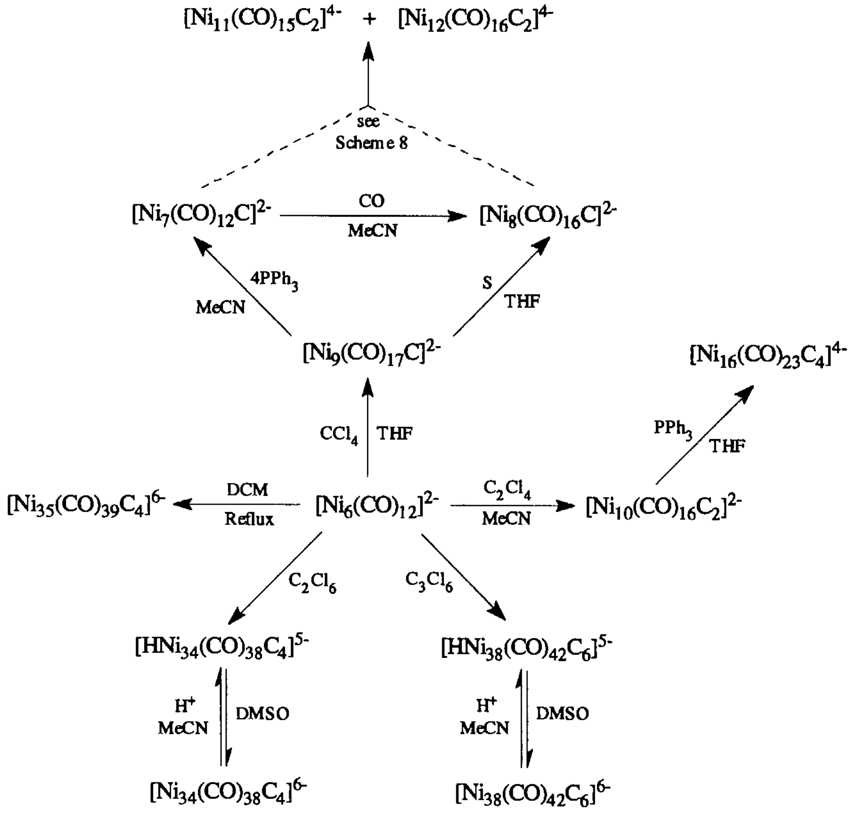
4.2. $[Ni_7(CO)_{12}C]^{2-}$

Synthesis. The lowest nuclearity nickel monocarbide dianion yet reported was prepared by reaction of triphenylphosphine (4 equivalents) with $[Ni_9(CO)_{17}C]^{2-}$ in acetonitrile[117] according to eq. (54). The precipitate of $Ni(CO)_2(PPh_3)_2$ was removed by filtration.

$$[Ni_9(CO)_{17}C]^{2-}+4PPh_3\xrightarrow{MeCN}[Ni_7(CO)_{12}C]^{2-}+2Ni(CO)_2(PPh_3)_2+CO \qquad (54)$$

Addition of a tetrabutylammonium salt to the filtrate precipitated $[NBu_4]_2[Ni_7(CO)_{12}C]$. The heptanuclear salt was recrystallised from THF toluene. The yield of product was not reported.

Characterisation. X-ray diffraction studies of $[NBu_4]_2[Ni_7(CO)_{12}C]$ reveal a metal frame which is approximately based on a trigonal prism formed from six nickel atoms encapsulating the carbide atom and capped on a square face by the seventh nickel atom[117] (see PR-51 Fig. 8). The interstitial



Scheme 6.

carbide atom is coordinated to seven metal atoms. The frequencies of the carbonyl stretching absorptions are given in Table 3.

4.3. $[Ni_8(CO)_{16}C]^{2-}$

Synthesis. The octanuclear $[Ni_8(CO)_{16}C]^{2-}$ dianion is synthesised by reaction of carbon monoxide with either preformed $[Ni_9(CO)_{17}C]^{2-}$ or $[Ni_{10}(CO)_{18}C]^{2-}$.[146] The decanuclear monocarbide is readily degraded to the enneanuclear monocarbide by carbon monoxide according to eq. (55); the enneanuclear carbide is in equilibrium with the octanuclear dianion as shown in eq. (56).

$$[Ni_{10}(CO)_{18}C]^{2-} + 3CO \longrightarrow [Ni_9(CO)_{17}C]^{2-} + Ni(CO)_4 \tag{55}$$

$$[Ni_9(CO)_{17}C]^{2-} + 3CO \rightleftharpoons [Ni_8(CO)_{16}C]^{2-} + Ni(CO)_4 \tag{56}$$

This degradation–condensation equilibrium is completely shifted to the right under carbon monoxide (25°C, 1 atm) and the species on the left are favoured under an atmosphere of nitrogen. Hence the $[Ni_8(CO)_{16}C]^{2-}$ dianion can be prepared by reaction of a stirred solution of $[NBu_4]_2[Ni_9(CO)_{17}C]$ with carbon monoxide in THF for 1 h. After evaporation of the reaction solution and crystallisation of the residue in THF/cyclohexane by the slow diffusion technique, dark red crystals of $[NBu_4]_2[Ni_8(CO)_{16}C]$ are isolated in 69% yield.

An alternative synthesis of the $[Ni_8(CO)_{16}C]^{2-}$ dianion involves the reaction of elemental sulfur with a solution of $[Ni_9(CO)_{17}C]^{2-}$ in THF.[117] The reaction given in eq. (57) is driven by the precipitation of NiS as a by-product. However, if excess sulfur is added to the $[Ni_8(CO)_{16}C]^{2-}$ dianion this results in its complete degradation to $Ni(CO)_4$ and NiS.

$$[Ni_9(CO)_{17}C]^{2-} + S \xrightarrow{THF} [Ni_8(CO)_{16}C]^{2-} + NiS + CO \tag{57}$$

The $[Ni_8(CO)_{16}C]^{2-}$ dianion was originally prepared and isolated in low yields by another method which involved reaction of $[Ni_6(CO)_{12}]^{2-}$ with $SiCl_4$ in anhydrous THF.[65,136] As shown in Scheme 7, the rather complicated mixture of products obtained underwent subsequent degradation with carbon monoxide in wet THF to give mostly $Ni(CO)_4$ and some $[Ni_8(CO)_{16}C]^{2-}$.

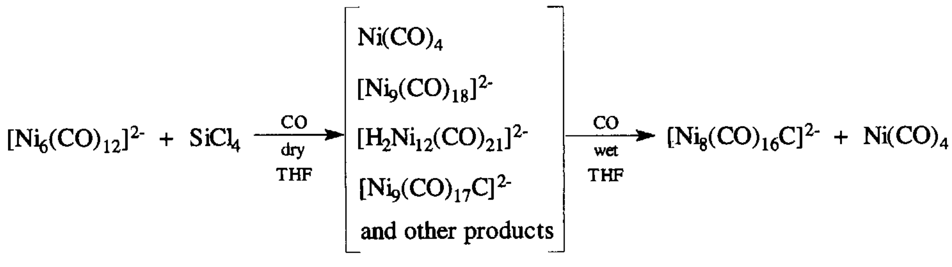
The characterisation of $[Ni_8(CO)_{16}C]^{2-}$ is described with that of the $[Ni_9(CO)_{17}C]^{2-}$ dianion in the following section.

4.4. $[Ni_9(CO)_{17}C]^{2-}$

Synthesis. The enneanuclear $[Ni_9(CO)_{17}C]^{2-}$ dianion is obtained in high yield (80%) by reaction of $[NBu_4]_2[Ni_6(CO)_{12}]$ with CCl_4 (0.4–0.5 equivalents) in THF for 3 h as represented in eq. (58).[146]

$$2[Ni_6(CO)_{12}]^{2-} + CCl_4\,(+CO) \xrightarrow[THF]{N_2} [Ni_9(CO)_{17}C]^{2-} + 2Ni(CO)_4 + Ni^{2+} + 4Cl^- \tag{58}$$

It is important that the CCl_4 is added dropwise to the solution of the hexanuclear cluster since an excess of this reagent readily results in progressive oxidation to $Ni(CO)_4$ and Ni^{2+} salts. The resulting product solution was evaporated and the residue was suspended in methanol. Precipitation of $[NBu_4]_2[Ni_9(CO)_{17}C]$ was completed by addition of an aqueous solution of $[NBu_4]Br$. The salt is soluble in THF, acetone, and acetonitrile and sparingly soluble in alcohols, water and non-polar solvents.



$$[Ni_6(CO)_{12}]^{2-} + SiCl_4 \xrightarrow[\text{dry THF}]{CO} \left[\begin{array}{l} Ni(CO)_4 \\ [Ni_9(CO)_{18}]^{2-} \\ [H_2Ni_{12}(CO)_{21}]^{2-} \\ [Ni_9(CO)_{17}C]^{2-} \\ \text{and other products} \end{array}\right] \xrightarrow[\text{wet THF}]{CO} [Ni_8(CO)_{16}C]^{2-} + Ni(CO)_4$$

Scheme 7.[65]

Of relevance to the Fischer–Tropsch synthesis, it has been shown that some nickel carbide clusters react with strong protonic acids to produce C_1—C_4 hydrocarbons which have been detected in the gas phase. The results of isotopic tracer studies with $[Ni_8(^{13}CO)_{16}C]^{2-}$ (30–90% ^{13}C enriched) and $[Ni_9(CO)_{17}{}^{13}C]^{2-}$ (95% ^{13}C enriched) indicate that the carbide atom is the main source of the observed C_2—C_4 hydrocarbons.[120]

Characterisation of $[Ni_8(CO)_{16}C]^{2-}$ *and* $[Ni_9(CO)_{17}C]^{2-}$. The $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$ dianions have been characterised by the usual methods of infrared spectroscopy (Table 3), elemental analysis and X-ray diffraction analysis of their tetrabutylammonium salts[146] (see PR-51 Figs 10 and 11 for illustrations of the respective dianions). The frequencies of the ν_{NiC} modes have been assigned by Stanghellini *et al.*;[145] these are included in Table 4. Both structures are based on two square $Ni_4(CO)_4(\mu_2\text{-}CO)_4$ moieties condensed along the C_4 axis in a staggered conformation giving rise to an elongated square-antiprismatic metal framework. Their structural formulae can best be described as $[Ni_8(CO)_8(\mu_2\text{-}CO)_8C]^{2-}$ of crystallographic D_4 and idealised D_{4d} symmetries and $[Ni_9(CO)_9(\mu_2\text{-}CO)_4(\mu_3\text{-}CO)_4C]^{2-}$ of crystallographic C_4 and idealised C_{4v} symmetries. Thus, it can be envisaged that the $[Ni_9(CO)_{17}C]^{2-}$ dianion arises from the $[Ni_8(CO)_{16}C]^{2-}$ dianion by capping a square metal face with a Ni(CO) fragment and in the process converting four carbonyl ligands from edge-bridging to triply-bridging modes. As a comparison, therefore, with Ni_3C in the bulk phase, where the carbide atom is located in an octahedral cavity, the carbide atoms in these two examples are encapsulated in a square antiprismatic cage.[65] The Ni—Ni average bond distance in these two compounds (2.55 Å) is intermediate between the Ni—Ni bond distance in bulk nickel metal (2.50 Å) and in Ni_3C (2.63 Å).[147] It should be noted that theoretical studies of several carbonylnickelates, including $[Ni_8(CO)_{16}C]^{2-}$, conclude that although the metal atom framework of a cluster often assumes a closed-packed geometry typical of bulk metals, this does not imply that the clusters are emulating metals.[89] Hence, the analogy between molecular clusters and surfaces is more apparent than substantial for these cluster compounds.

Variable temperature magnetic susceptibility measurements, performed at room temperature and below, on a solid sample of the $[NBu_4]_2[Ni_9(CO)_{17}C]$ monocarbide salt have been reported.[96] The data follow a trend similar to that obtained for the $[H_2Ni_{12}(CO)_{21}]^{2-}$ cluster where the temperature independent diamagnetic contribution is the dominant effect except in the low temperature range (<70 K) where some paramagnetism is evident. Only small susceptibilities are obtained ($\mu_{eff} = 2.1$ μ_B per cluster, $\chi_{dia} = 4.1 \times 10^{-4}$ cm^3 mol^{-1}).

4.5. $[Ni_{10}(CO)_{16}C_2]^{2-}$

Synthesis. The first homometallic nickel dicarbide cluster, $[Ni_{10}(CO)_{16}C_2]^{2-}$, was originally obtained unselectively and in low yields by thermal condensation of $[Ni_9(CO)_{17}C]^{2-}$ in diglyme at 120°C.[148] The improved synthesis of the decanuclear dicarbide cluster was achieved in yields of up to 60% by reaction in acetonitrile of $[Ni_6(CO)_{12}]^{2-}$, as its $[AsPh_4]^+$ or $[PPN]^+$ salt, with C_2Cl_4 as shown in eq. (59).[148] This method is similar to the preparation of $[Ni_9(CO)_{17}C]^{2-}$ from the reaction of $[Ni_6(CO)_{12}]^{2-}$ with CCl_4 in THF [*cf* eq. (53)].

Table 4. Infrared absorptions ν_{NiC} (cm^{-1}) of some nickel carbonyl carbide cluster anions[145]

	ν_{NiC}(cm^{-1})		
Anion	Mode	^{12}C	^{13}C
$[Ni_8(CO)_{16}C]^{2-}$	B_2	524	–
	E	580	557
$[Ni_9(CO)_{17}C]^{2-}$	A_1	522	506
	E	582	560
$[Ni_{10}(CO)_{18}C]^{2-}$	$E_1{}^a$	584	–

[a] For a presumed D_{4d} symmetry.

$$2[Ni_6(CO)_{12}]^{2-}+C_2Cl_4 \longrightarrow [Ni_{10}(CO)_{16}C_2]^{2-}+Ni(CO)_4+Ni^{2+}+4Cl^-+4CO \qquad (59)$$

Isolation of $[Ni_{10}(CO)_{16}C_2]^{2-}$ was achieved by evaporation of the product solution *in vacuo* and then by washing of the residue with a 5% methanolic solution of either cation as its chloride salt. The crude product was recrystallised from either THF/cyclohexane or acetone/isopropyl alcohol.

It is interesting to note that $[Ni_{10}(CO)_{16}C_2]^{2-}$ reacts with carbon monoxide and hydrogen to give almost pure ethylene[120] as shown in eq. (60).

$$[Ni_{10}(CO)_{16}C_2]^{2-}+16CO+2H_2 \longrightarrow [Ni_5(CO)_{12}]^{2-}+5Ni(CO)_4+C_2H_4 \qquad (60)$$

Characterisation. The structure and stoichiometry of $[AsPh_4]_2[Ni_{10}(CO)_{16}C_2]$ were determined by single crystal X-ray analysis;[148] overall the crystal displays a C_{2h}–$2/m$ idealised symmetry. Other data such as elemental analysis and infrared spectra (Table 3) are in agreement with the crystal structure. The ^1H NMR spectrum confirmed the absence of any hydridic protons resonating in the region δ 20 to -40 ppm. The structure of the $[Ni_{10}(CO)_6(\mu_2\text{-}CO)_{10}C_2]^{2-}$ dianion may be envisaged as being derived from the condensation of two μ_4-Ni capped trigonal-prisms sharing a common square face (see PR-51 Fig. 12). The interstitial carbide atoms are bonded to each other (1.40 Å) and this C_2 fragment is lodged in the bi-prismatic central moiety of the metal cage. Each carbide atom is coordinated to seven nickel atoms. An alternative, useful description of the metal framework is as two staggered isosceles nickel triangle layers either side of a planar nickel quadrilaterial.[44]

4.6. $[Ni_{10}(CO)_{18}C]^{2-}$

Synthesis. Although remarkably similar in its structural formula to $[Ni_{10}(CO)_{16}C_2]^{2-}$, there is chemical evidence of the existence of another carbide $[Ni_{10}(CO)_{18}C]^{2-}$ dianion which has been isolated as its red crystalline tetramethylammonium salt.[146] This formulation has not yet been confirmed by X-ray diffraction. The reported preparation of the $[NMe_4]_2[Ni_{10}(CO)_{18}C]$ is presented here.

The reaction of CCl_4 with $[Ni_6(CO)_{12}]^{2-}$ in THF to form the $[Ni_9(CO)_{17}C]^{2-}$ dianion [eq. (58)] was discussed above. The isolation of $[Ni_9(CO)_{17}C]^{2-}$ is thought to result from a series of reactions which include those given in eqs (61) and (62) via an intermediate species which has been formulated as the $[Ni_{10}(CO)_{18}C]^{2-}$ dianion. The degradation of $[Ni_{10}(CO)_{18}C]^{2-}$ by the evolving carbon monoxide, shown in eq. (55), may also be involved in the formation of $[Ni_9(CO)_{17}C]^{2-}$. The appearance of a carbonyl absorption band at *ca* 1950 cm^{-1} in the infrared spectrum has been attributed to the presence of $[Ni(CO)_3Cl]^-$ in the product solution.

$$2[Ni_6(CO)_{12}]^{2-}+CCl_4 \xrightarrow[THF]{N_2} [Ni_{10}(CO)_{18}C]^{2-}+Ni(CO)_4+Ni^{2+}+4Cl^-+2CO \qquad (61)$$

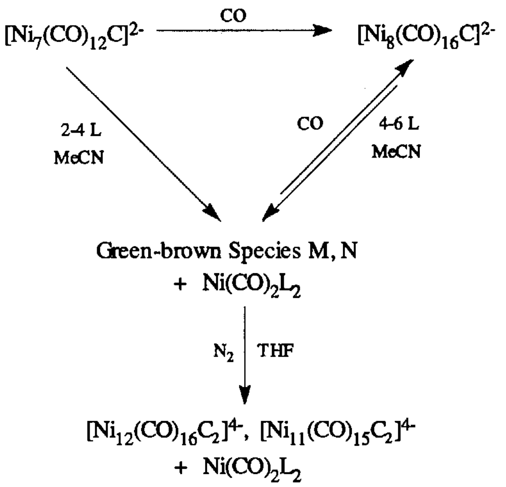
$$[Ni_{10}(CO)_{18}C]^{2-}+2CO+Cl^- \longrightarrow [Ni_9(CO)_{17}C]^{2-}+[Ni(CO)_3Cl]^- \qquad (62)$$

It has been possible to isolate the $[NMe_4]_2[Ni_{10}(CO)_{18}C]$ salt[146] when the reaction is performed in the following way. Carbon tetrachloride is added dropwise to a solution of $[Ni_6(CO)_{12}]^{2-}$ in acetonitrile as its tetramethylammonium instead of its tetrabutylammonium salt and carbon monoxide is constantly removed by a slow stream of nitrogen. The addition of CCl_4 is stopped when unreacted $[Ni_6(CO)_{12}]^{2-}$ is still present after a period of 2 h instead of 3 h to minimise any further conversion of $[Ni_{10}(CO)_{18}C]^{2-}$ into $[Ni_9(CO)_{17}C]^{2-}$. The resulting solution is evaporated to dryness and the residue extracted with THF and filtered leaving behind the more insoluble $[NMe_4]_2[Ni_9(CO)_{17}C]$. The $[NMe_4]_2[Ni_{10}(CO)_{18}C]$ product was precipitated from the filtrate by the addition of cyclohexane to give a 34% yield (based on Ni). This salt is soluble in THF, acetone and acetonitrile but is sparingly soluble in alcohols, water and non-polar solvents.

Characterisation. This dianion has been characterised by infrared spectroscopy (the frequencies of the ν_{CO} modes[146] are collected in Table 3 and the ν_{NiC} modes[145] have been assigned and are given in Table 4), elemental analysis and by ^{13}C NMR. A ^{13}C NMR resonance at δ 278 ppm is thought to arise from the carbide carbon atom.[14] The long relaxation times, e.g. 325 s at 4.7 T and the low chemical shift anisotropy suggests by comparison with organic species that the carbide atom is approximately *sp*^{3} hybridised as predicted by Hückel molecular orbital calculations. Both the tetramethylammonium and tetrabutylammonium salts have been isolated in crystalline form but owing to the poor quality of these crystals the dianion has not yet been structurally characterised. Ceriotti *et al.*[146] suggest a structure deduced from the infrared spectrum which contains only terminal and triply-bridging carbonyl stretching absorptions. The carbide atom is suggested to be located inside a μ_4-Ni bicapped square-antiprismatic structure of nickel atoms somewhat similar to the capped end of the $[Ni_9(CO)_{17}C]^{2-}$ dianion.

4.7. $[Ni_{11}(CO)_{15}C_2]^{4-}$, $[Ni_{12}(CO)_{16}C_2]^{4-}$ *and other uncharacterised species*

The reported synthetic route to $[Ni_{11}(CO)_{15}C_2]^{4-}$ and $[Ni_{12}(CO)_{16}C_2]^{4-}$ is by degradation of $[Ni_7(CO)_{12}C]^{2-}$ and $[Ni_8(CO)_{16}C]^{2-}$ dianions when reacted with phosphorous ligands, L, such as PPh_3, $P(OPh)_3$ or bis(diphenylphosphine)ethane in acetonitrile[117] as shown in Scheme 8. The details of this preparation are not included in the short communication and no subsequent report with detailed experimental material has appeared. However, this reaction is thought to occur sequentially via two intermediate species M and N which have yet to be structurally characterised. Ceriotti *et al.*[117] speculate that these species could be hexa- and penta-nuclear carbide clusters possibly stabilised by coordinated phosphine and/or solvent. They have been tentatively formulated here as $[Ni_6(CO)_xC]^{2-}$ and $[Ni_5(CO)_yC]^{2-}$, respectively (where x and y are unknown). The only reported method of characterisation is by infrared spectroscopy and the carbonyl absorption frequencies are collected in Table 5. In fact, under the right conditions, these species have been shown to be precursors of $[Ni_{11}(CO)_{15}C_2]^{4-}$ and $[Ni_{12}(CO)_{16}C_2]^{4-}$. Recrystallisation in a THF/toluene solution of the cluster species M and N under an atmosphere of nitrogen causes a transformation resulting



L = PPh_3, similar results have been obtained for $P(OPh)_3$ and $Et(PPh_2)_2$
M = $[Ni_6(CO)_xC]^{2-}$
N = $[Ni_5(CO)_yC]^{2-}$ where x, y are unknown

Scheme 8.

Table 5. Infrared carbonyl absorption frequencies of uncharacterised nickel carbonyl carbide cluster anions detected in solution but which have not yet been isolated

Possible anion[a]	Colour	Solvent	ν_{CO} (cm^{-1})
M : $[Ni_6(CO)_xC]^{2-}$	green–brown	MeCN	1970 s, 1950 sh, 1830 mw, 1780 mw
N : $[Ni_5(CO)_yC]^{2-}$	green–brown	MeCN	1950 s, 1935 sh, 1810 mw, 1775 mw

[a] The formulation of these anions by Ceriotti *et al.*[117] as the penta- and hexa-nuclear carbide clusters was based on infrared data. The number of both carbonyl ligands namely x and y and interstitial carbides in the anions was not stated. On the basis of the size of the interstitial sites in the nickel framework, it is expected that no more than one interstitial carbide is likely to be found.

in a mixture of crystalline salts of the two dicarbide tetraanions. It is not clear how the tetraanions are formed but it is likely that species M gives rise to $[Ni_{12}(CO)_{16}C_2]^{4-}$ and N or (N and M) gives rise to $[Ni_{11}(CO)_{15}C_2]^{4-}$.

The reversibility of the reaction of $[Ni_8(CO)_{16}C]^{2-}$ to form the two green–brown species M and N is dependent on the presence or absence of carbon monoxide in the system as illustrated in Scheme 8. Thus, if the green–brown species or the $[Ni_7(CO)_{12}C]^{2-}$ dianion is stirred under an atmosphere of carbon monoxide, the only products that crystallise are $[Ni_8(CO)_{16}C]^{2-}$ and $Ni(CO)_2L_2$. This scheme is derived from a larger scheme created by Ceriotti *et al.*[117] and is altered slightly with respect to the direction of the equilibrium arrows. The arrows are the reverse of those which appear to be incorrectly reported in the original scheme since they contradict the text.

Characterisation of $[Ni_{11}(CO)_{15}C_2]^{4-}$ *and* $[Ni_{12}(CO)_{16}C_2]^{4-}$. X-ray crystal structure analysis was used to ascertain the stoichiometry and structure of the $[NEt_3CH_2Ph]_4[Ni_{11}(CO)_{15}C_2]$ and $[NBu_4]_4[Ni_{12}(CO)_{16}C_2]$ salts (see PR-51 Figs 14 and 15 for illustrations of the respective anions). The ORTEP drawings of these tetraanions are incorrectly labelled in the original communication[117] where the figure legend for Fig. 2 appears under Fig. 3 and *vice versa*. The metal framework structures, however, are remarkably similar to the $[Ni_{10}(CO)_{16}C_2]^{2-}$ dianion where the carbide atoms are coordinated to seven nickel atoms and they also exhibit very short interatomic C—C distances. Hence, the progressive capping of such a structure would effectively describe the structures of, first, $[Ni_{11}(CO)_{15}C_2]^{4-}$ and then $[Ni_{12}(CO)_{16}C_2]^{4-}$. These cluster anions belong to the symmetry groups $P\bar{1}$ and $P2_1/c$ respectively.

4.8. $[Ni_{16}(CO)_{23}C_4]^{4-}$

Synthesis. Quantitative yields of the $[Ni_{16}(CO)_{23}C_4]^{4-}$ tetraanion were produced somewhat unexpectedly from the disproportionation-induced condensation reaction of $[Ni_{10}(CO)_{16}C_2]^{2-}$ with four equivalents of triphenylphosphine in THF,[149] as represented in eq. (63). This reaction holds a unique place in the syntheses of transition metal carbides in that it was the first known example of a molecular carbonyl cluster which contained more than two interstitial carbide atoms within the metal framework.

$$2[Ni_{10}(CO)_{16}C_2]^{2-}+8PPh_3 \xrightarrow{THF} [Ni_{16}(CO)_{23}C_4]^{4-}+4Ni(CO)_2(PPh_3)_2+CO \qquad (63)$$

Salts of $[Ni_{16}(CO)_{23}C_4]^{4-}$ with counterions such as $[NMe_4]^+$, $[PPh_4]^+$ and $[PPN]^+$ were obtained using the above procedure. Recrystallisation was achieved by the slow diffusion of diisopropyl ether into acetonitrile solutions of these salts. These salts are also sparingly soluble in THF and acetone.

An alternative, but less selective, route to the tetracarbide uses the procedure illustrated in eq. (54) in which $[Ni_{10}(CO)_{16}C_2]^{2-}$ is obtained by the reaction of $[Ni_6(CO)_{12}]^{2-}$ with C_2Cl_4 in acetonitrile. The only difference in this case is the choice of counterions. Thus when $[Ni_6(CO)_{12}]^{2-}$ is used as a reactant as its tetramethylammonium salt (rather than as a salt of the bulkier cations $[PPh_4]^+$ or $[PPN]^+$), the major product is $[Ni_{16}(CO)_{23}C_4]^{4-}$ in yields of *ca* 20% (based on nickel).

Characterisation. The $[NMe_4]_4[Ni_{16}(CO)_{23}C_4]$ salt was structurally characterised by X-ray diffraction studies.[149] There are 12 terminal and ten edge-bridging carbonyl ligands and one additional unique face-bridging carbonyl ligand and hence the structure of the tetraanion can be described as $[Ni_{16}(CO)_{12}(\mu_2\text{-}CO)_{10}(\mu_3\text{-}CO)(C_2)_2]^{4-}$ (see PR-51 Fig. 16). The metal framework consists of a hexadecanuclear tetracapped cubooctahedron of idealised C_{2h} symmetry containing two independent interstitial C_2 moieties with an unusually short average interatomic C—C distance of 1.38 Å. The range of Ni—Ni bond distances observed is 2.355–3.028 Å with the average distance being 2.604 Å.

The infrared spectra of various salts of the brown $[Ni_{16}(CO)_{23}C_4]^{4-}$ cluster in acetonitrile are in agreement with the above-mentioned structure. The carbonyl stretching absorptions are collected in Table 3. The nickel–carbide vibrations have not as yet been assigned. The results of ^1H NMR studies reveal the absence of any resonances in the region δ 20 to -40 ppm that could be attributed to hydrides.

4.9. $[Ni_{34}(CO)_{38}C_4]^{6-}$ *and* $[HNi_{34}(CO)_{38}C_4]^{5-}$

Synthesis. The $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ ($n = 6, 5$) derivatives are prepared by the reaction of two equivalents of $[Ni_6(CO)_{12}]^{2-}$ (as the $[NEt_4]^+$, $[NMe_3CH_2Ph]^+$, $[NBu_4]^+$ salts) with C_2Cl_6 in acetonitrile or acetone.[150] The reaction has the disadvantage of being non-selective and affords variable mixtures of $[Ni_{10}(CO)_{16}C_2]^{2-}$ and $[Ni_{16}(CO)_{23}C_4]^{4-}$ along with the $[Ni_{34}(CO)_{38}C_4]^{6-}$ and $[HNi_{34}(CO)_{38}C_4]^{5-}$ tetracarbides. The latter two Ni_{34} clusters are separated by utilising their poor solubility in THF and acetone. The reaction mixture is evaporated to dryness, followed by extraction of the residue with THF and acetone to remove the more soluble clusters leaving behind the $[Ni_{34}(CO)_{38}C_4]^{6-}$ salts.

Protonation of an acetonitrile solution of the $[Ni_{34}(CO)_{38}C_4]^{6-}$ hexaanion is achieved by the addition of dilute phosphoric acid. The observation of this protonation reaction by the changes in the infrared spectra is the only evidence for the presence of the hydride atom. The two clusters are related by the reversible equilibrium that is shown in eq. (64). Recrystallisation of $[NMe_3CH_2Ph]_5[HNi_{34}(CO)_{38}C_4]$ was achieved in acetonitrile and diisopropyl ether.

$$[Ni_{34}(CO)_{38}C_4]^{6-} + H^+ \underset{DMSO}{\overset{MeCN}{\rightleftharpoons}} [HNi_{34}(CO)_{38}C_4]^{5-} \qquad (64)$$

Characterisation. Both derivatives belonging to the $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ ($n = 6, 5$) group have been characterised by infrared spectroscopy and elemental analysis with the respective counterions $[NEt_4]^+$ and $[NMe_3CH_2Ph]^+$. The infrared carbonyl stretching frequencies are collected in Table 3. The structure of the monohydride $[NMe_3CH_2Ph]_5[HNi_{34}(CO)_{38}C_4]$ salt has been determined by single crystal X-ray diffraction studies.[150] Although the $[NEt_4]_6[Ni_{34}(CO)_{38}C_4]$ salt has yet to be structurally characterised, the structure of the hexanion is likely to be almost identical to that of the protonated analogue $[HNi_{34}(CO)_{10}(\mu_2\text{-}CO)_{26}(\mu_3\text{-}CO)_2C_4]^{5-}$ except for the absence of the hydride. There are ten terminal, 26 edge-bridging and two face-bridging carbonyl ligands. The four carbide atoms are embedded in the complex metal framework and they are independent of each other unlike the polycarbide ligands described above which are linked together by C—C bonds. The metal framework is so complex that a formal stepwise building procedure described and illustrated by Ceriotti *et al.*[150] or in the Polyhedron Report[44] (PR-51 Figs 18–20) are the best ways to describe its geometry and thus is not mentioned in any detail here.

Variable temperature magnetic susceptibility measurements and high-field magnetisation measurements performed at room temperature and below on a solid sample of $[NEt_4]_5[HNi_{34}(CO)_{38}C_4]$ have been reported.[96] Only small susceptibilities are obtained ($\mu_{eff} = 8.5\ \mu_B$ per cluster, $\chi_{dia} = -13.4 \times 10^{-4}\ cm^3\ mol^{-1}$) but these are ten times as large as the corresponding susceptibilities obtained for the lower-nuclearity nickel clusters such as $[Ni_9(CO)_{17}C]^{2-}$ and $[H_2Ni_{12}(CO)_{21}]^{2-}$. The data follow a similar trend to that reported for these latter species when there is a very weak positive temperature independent term plus the paramagnetic term only in the low temperature range (< 70 K). The paramagnetism is much stronger in the $[HNi_{34}(CO)_{38}C_4]^{5-}$ cluster, however, a result which may be expected due to its resemblance to bulk nickel metal which is ferromagnetic. Nonetheless, as the cluster possesses an even electron system, a possible explanation for the small paramagnetic moments has not yet been found and therefore it is simply accepted as an intrinsic property of these metal carbonyl cluster species.

4.10. $[Ni_{35}(CO)_{39}C_4]^{6-}$

Synthesis. The $[Ni_{35}(CO)_{39}C_4]^{6-}$ hexaanion is obtained thermally in unspecified yield by refluxing $[NEt_4]_2[Ni_6(CO)_{12}]$ in DCM.[150] The $[NEt_4]_6[Ni_{35}(CO)_{39}C_4]$ salt is isolated from the decomposition products and recrystallised from acetonitrile and diisopropyl ether. No further details of this preparation have been reported.

Characterisation. The $[NEt_4]_6[Ni_{35}(CO)_{39}C_4]$ cluster has been characterised by X-ray diffraction, infrared spectroscopy and by elemental analysis. The carbonyl stretching absorptions are collected in Table 3. Single crystal X-ray diffraction analysis of this salt has been used to determine its structure.[150] The hexaanion can best be described as $[Ni_{35}(CO)_{10}(\mu_2\text{-}CO)_{27}(\mu_3\text{-}CO)_2C_4]^{6-}$, since there are ten terminal, 27 edge-bridging and two face-bridging carbonyl ligands surrounding a complicated metal framework (see PR-51 Fig. 23). The unusual structure of the nickel atoms can be explained by the swelling effect brought about by the four encapsulated isolated carbide atoms. Similar to the structure of the $[HNi_{34}(CO)_{38}C_4]^{5-}$ cluster, two carbide atoms are caged in trigonal-prismatic cavities whereas the other two are encapsulated in two distorted capped trigonal prisms. The structure of the anion can be thought of as being derived from $[HNi_{34}(CO)_{38}C_4]^{5-}$ by condensation of an extra Ni(CO) moiety over one of the faces.

4.11. $[Ni_{38}(CO)_{42}C_6]^{6-}$ *and* $[HNi_{38}(CO)_{42}C_6]^{5-}$

Synthesis. The $[HNi_{38}(CO)_{42}C_6]^{5-}$ species has been prepared in an atmosphere of nitrogen by the reaction of $[Ni_6(CO)_{12}]^{2-}$ as its tetrabutylammonium salt with hexachloropropene (0.6 equivalents) in THF.[151] The product mixture is evaporated to dryness. Subsequent removal of the more soluble by-products is achieved by extraction with water, methanol and then THF. The brown hexacarbide cluster is then extracted from the residue by washing with acetone and precipitation of the $[NBu_4]_5[HNi_{38}(CO)_{42}C_6]$ salt occurs by the addition of isopropyl alcohol. The presence of a reversible equilibrium as shown in eq. (65), between two individual species upon acidification, suggests the presence of a hydride atom. Similar behaviour was also exhibited by the $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ ($n = 6, 5$) derivatives under the same conditions.

$$[Ni_{38}(CO)_{42}C_6]^{6-} + H^+ \underset{DMSO}{\overset{MeCN}{\rightleftharpoons}} [HNi_{38}(CO)_{42}C_6]^{5-} \tag{65}$$

Characterisation. Both $[H_{6-n}Ni_{38}(CO)_{42}C_6]^{n-}$ ($n = 6, 5$) derivatives have been analysed by infrared spectroscopy and the carbonyl stretching absorptions are collected in Table 3. A single crystal of the $[NBu_4]_5[HNi_{38}(CO)_{42}C_6]$ species has been examined by X-ray diffraction.[151] The overall structure of the pentaanion shows idealised D_{3d} and crystallographic $\bar{1}$ symmetry (see PR-51 Fig. 24). The carbide atoms form the corners of a non-bonded C_6 octahedron and they are each caged into one of six Ni_8 square-antiprismatic moieties. There do not appear to be any face-bridging carbonyl ligands outside the metal cage and the anion has the formulation $[HNi_{38}(CO)_6(\mu_2\text{-}CO)_{36}C_6]^{5-}$. The hydride atom was not located crystallographically, nor detected by ^1H NMR spectroscopy.

5. SUMMARY

The syntheses of the structurally characterised carbonylnickelates have a common fundamental origin. Thus, all of the clusters that have been discussed can be derived either directly or indirectly by reduction of $Ni(CO)_4$, an important but toxic source of nickel in its zero oxidation state. Indeed, the concentrations of both $Ni(CO)_4$ and carbon monoxide in basic solutions determine the selectivity to particular clusters due to the involvement of these clusters in a number of equilibria. The most commonly isolated species produced by reduction of $Ni(CO)_4$ is $[Ni_6(CO)_{12}]^{2-}$, precipitated with various counterions. This hexanuclear species is the starting material for the production of many other carbonylnickelates, with and without hydride and carbide atoms, as it is safer, more stable and hence more convenient to handle than $Ni(CO)_4$ itself. The nickel carbonyl cluster anions and neutral dimers reported earliest, namely complexes **A–K** in the table of contents, have been included in this review. However, with the exception of species $[Ni_4(CO)_9]^{2-}$, (**C**), which has been reformulated as $[Ni_6(CO)_{12}]^{2-}$, no conclusive formulations can be assigned to these species due to the absence of sufficient structural and spectroscopic data.

The two characterised carbonyl clusters containing interstitial hydrides are prepared by progressive acidification of solutions of $[Ni_{12}(CO)_{21}]^{4-}$ or $[Ni_6(CO)_{12}]^{2-}$. The trend appears that interstitial hydride atoms occur only when there is an excess of unoccupied cavities inside the metal structure. The presence of hydride atoms in the largest carbide cluster anions such as $[HNi_{38}(CO)_{42}C_6]^{5-}$ and $[HNi_{34}(CO)_{38}C_4]^{5-}$ is only inferred from chemical data. There is an X-ray crystallographic report, however, of one carbonyl nickel dimer, namely $[HNi_2(CO)_6]^-$, that contains a hydride ligand. This ligand is thought to bridge the two nickel atoms, but the crystallographic data are no longer available. The hydride was located on the basis of potential energy maps calculations and the correlations between these calculations and distortions in the $[Ni_2(CO)_6]^{2-}$ framework.

While there are only four carbonylnickelates, and two further carbonylnickelates which contain interstitial (presumably) hydrides, there also exist at least ten cluster anions which contain interstitial carbide atoms. The numbers of carbide atoms observed are 1, 2, 4 and 6, with both isolated atoms and pairs of carbide atoms close enough to form C—C bonds. Interstitial carbide atoms are found in the smaller carbonylnickelates starting from $[Ni_7(CO)_{12}C]^{2-}$ but are not restricted to them, the largest carbide containing cluster being $[Ni_{38}(CO)_{42}C_6]^{6-}$. The carbide clusters are typically obtained from the reaction of $[Ni_6(CO)_{12}]^{2-}$ with reagents such as CCl_4, C_2Cl_4, C_2Cl_6, C_3Cl_6 and CH_2Cl_2, or by reactions of larger carbide clusters with triphenylphosphine.

Generally all the above carbonylnickelates are strongly coloured, air sensitive and easily decompose to $Ni(CO)_4$ and other products such as Ni^0 and Ni^{2+} salts if not stored under an inert atmosphere. They tend to be more stable as solid salts than in solution. The larger clusters also disproportionate to $Ni(CO)_4$ and smaller cluster species under mild conditions. The major difference between the chemical behaviour of the nickel carbonyl clusters, both with and without hydrides, and the carbide clusters is the difference in their lability and tendency to interconvert. While the former are very labile and easily interconvert, the carbide carbonyl clusters are relatively non-labile by comparison and do not readily interconvert.

The field of known nickel carbonyl clusters, whilst substantial, is not as extensive as those of clusters of other metals. It is not unreasonable to suppose that the number of known nickel carbonyl clusters with or without hydride and/or carbide ligands might be increased. The complementary Polyhedron Report on the structural systematics of these clusters suggests several possibilities.[44] In addition, there are several contradictory or unconfirmed claims that need clarification or substantiation.

The formation or otherwise of the species $[Ni_2(CO)_6]^{2-}$, $[Ni_3(CO)_8]^{2-}$, $[Ni_5(CO)_9]^{2-}$ and $[HNi_5(CO)_9]^-$ **(K)**, need to be confirmed and their formulations definitively established. The same is true of the species $[Ni_2(CO)_x]^{2-}$ **(E)**, $[Ni_3(CO)_y]^{2-}$ **(F)**, and $[Ni_4(CO)_z]^{2-}$ **(G)**, the key monomer, $[HNi(CO)_3]^-$ **(H)**, and the neutral dimer, $[HNi(CO)_3]_2$ **(I)**, the only neutral example of the nickel carbonyl clusters. If this neutral dimer can be authenticated, the possibility of an extended family of neutral nickel carbonyl clusters (and possibly their hydride and carbide analogues and derivatives) needs to be considered. Similarly, the possibility that $[HNi_4(CO)_9]^-$ **(J)** is in fact $[HNi_{12}(CO)_{21}]^{3-}$ needs to be examined.

A re-examination of the structure of $[HNi_2(CO)_6]^-$, particularly by neutron diffraction, would be valuable as would structural characterisation of $[Ni_{10}(CO)_{18}C]^{2-}$ and the determination of the exact location of the hydrides in $[HNi_{34}(CO)_{38}C_4]^{5-}$ and $[HNi_{38}(CO)_{42}C_6]^{5-}$ by neutron diffraction analysis and/or ^1H NMR spectroscopy.

The clusters are derived ultimately by reduction of $Ni(CO)_4$, under a variety of conditions (solvent, nature of reductant, nature of counter ion, composition of atmosphere, etc.). Accordingly, a systematic electrochemical (cyclic voltammetry, coulometry)/infrared examination of the redox properties of $Ni(CO)_4$ in a variety of solvents, at varying temperatures and in the presence of a range of co-reactants could be expected to be extremely profitable as a means of identifying the optimum synthetic conditions for the preparations of known clusters, the identification of new clusters, the interconversions between cluster species and the reactions of clusters with a variety of substrates. The electrochemistry of $Ni(CO)_4$ has received limited attention.[152,153] Irreversible oxidations are observed in trifluoroacetic acid (+0.80 V *vs* sce) and acetonitrile (+1.26 V *vs* sce) and an irreversible reduction is reported (−2.70 V *vs* sce) in acetonitrile. The irreversibility of the reduction is not unexpected if the electrochemical reduction of $Ni(CO)_4$ generates cluster species. The toxicity of $Ni(CO)_4$ need not inhibit such a study, since the volumes used would be small, the measurements can be made remotely and $Ni(CO)_4$ entrained in the flushing gases can be readily destroyed with an appropriate chemical trap.

REFERENCES

1. L. Mond, C. Langer and F. Quincke, *J. Chem. Soc.* 1890, **57**, 749.
2. E. Abel, *Chem. Br.* 1989, **25**, 1014.
3. W. Hieber, *Adv. Organomet. Chem.* 1970, **8**, 1.
4. P. Chini, *Inorg. Chim. Acta* 1968, **2**, 31.
5. P. Chini, *Pure Appl. Chem.* 1970, **23**, 489.
6. P. Chini, *J. Organomet. Chem.* 1980, **200**, 37.
7. G. González-Moraga, *Cluster Chemistry.* Springer, Berlin (1993).
8. M. I. Bruce, in *The Chemistry of Metal Cluster Complexes* (Edited by D. F. Shriver, H. D. Kaesz and R. D. Adams), Ch. 8. VCH Publishers, New York (1990).
9. D. M. P. Mingos and D. J. Wales, in *Introduction to Cluster Chemistry* (Edited by R. N. Grimes), Ch. 1. Prentice-Hall, Englewood Cliffs, New Jersey (1990).
10. M. D. Vargas and J. N. Nicholls, *Adv. Inorg. Chem. Radiochem.* 1986, **30**, 123.
11. H. Vahrenkamp, *Adv. Organomet. Chem.* 1983, **22**, 169.
12. D. M. P. Mingos and D. J. Wales, in *Introduction to Cluster Chemistry* (Edited by R. N. Grimes), p. 35. Prentice-Hall, Englewood Cliffs, New Jersey (1990).

13. S. Aime, *Inorg. Chim. Acta* 1982, **62**, 51.
14. B. T. Heaton, *Pure Appl. Chem.* 1988, **60**, 1757.
15. P. Chini, G. Longoni and V. G. Albano, *Adv. Organomet. Chem.* 1976, **14**, 285.
16. F. Calderazzo, R. Ercoli and G. Natta, in *Organic Synthesis via Metal Carbonyls* (Edited by I. Wender and P. Pino), p. 67. Interscience, New York (1968).
17. R. B. King, *Rev. Roum. Chim.* 1991, **36**, 353.
18. P. Lemoine, *Coord. Chem. Rev.* 1988, **83**, 169.
19. P. Lemoine, *Coord. Chem. Rev.* 1982, **47**, 55.
20. M. D. Curtis, P. D. Williams and W. M. Butler, *Inorg. Chem.* 1988, **27**, 2853.
21. M. Bochmann, I. Hawkins, L. J. Yellowlees, M. B. Hursthouse and R. L. Short, *Polyhedron* 1989, **8**, 1351.
22. V. G. Albano, F. Demartin, M. C. Iapalucci, F. Laschi, G. Longoni, A. Sironi and P. Zanello, *J. Chem. Soc., Dalton Trans.* 1991, 739.
23. A. J. Whoolery and L. F. Dahl, *J. Am. Chem. Soc.* 1991, **113**, 6683.
24. A. Ceriotti, R. Della Pergola, L. Garlaschelli, G. Longoni, M. Manassero, N. Masciocchi, M. Sansoni and P. Zanello, *Gazz. Chim. Ital.* 1992, **122**, 365.
25. V. G. Albano, F. Demartin, M. C. Iapalucci, G. Longoni, M. Monari and P. Zanello, *J. Chem. Soc., Dalton Trans.* 1992, 497.
26. T. E. North, J. B. Thoden, B. Spencer, A. Bjarnason and L. F. Dahl, *Organometallics* 1992, **11**, 4326.
27. D. F. Rieck, J. A. Gavney Jr, R. L. Norman, R. K. Hayashi and L. F. Dahl, *J. Am. Chem. Soc.* 1992, **114**, 10369.
28. J. P. Zebrowski, R. K. Hayashi, A. Bjarnason and L. F. Dahl, *J. Am. Chem. Soc.* 1992, **114**, 3121.
29. D. F. Rieck, A. D. Rae and L. F. Dahl, *J. Chem. Soc., Chem. Commun.* 1993, 585.
30. A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, G. Piva, G. Piro, M. Sansoni and B. T. Heaton, *J. Organomet. Chem.* 1986, **301**, C5.
31. P. Chini, A. Cavalieri and S. Martinengo, *Coord. Chem. Rev.* 1972, **8**, 3.
32. V. G. Albano, G. Ciani and P. Chini, *J. Chem. Soc., Dalton Trans.* 1974, 432.
33. A. Fumagalli, G. Longoni, P. Chini, A. Albinati and S. Brückner, *J. Organomet. Chem.* 1980, **202**, 329.
34. A. Ceriotti, R. Della Pergola, L. Garlaschelli, M. Manassero, N. Masciocchi and M. Sansoni, *J. Chem. Soc., Dalton Trans.* 1991, 2357.
35. R. Della Pergola, L. Garlaschelli, F. Demartin, M. Manassero, N. Masciocchi and G. Longoni, *J. Chem. Soc., Dalton Trans.* 1988, 201.
36. A. Ceriotti, P. Chini, A. Fumagalli, T. F. Koetzle, G. Longoni and F. Takusagawa, *Inorg. Chem.* 1984, **23**, 1363.
37. J. K. Ruff, R. P. White Jr and L. F. Dahl, *J. Am. Chem. Soc.* 1971, **93**, 2159.
38. T. L. Hall and J. K. Ruff, *Inorg. Chem.* 1981, **20**, 4444.
39. G. Longoni, *Pure Appl. Chem.* 1990, **62**, 1183.
40. A. Ceriotti, F. Demartin, B. T. Heaton, P. Ingallina, G. Longoni, M. Manassero, M. Marchionna and N. Masciocchi, *J. Chem. Soc., Chem. Commun.* 1989, 786.
41. D. F. Rieck, R. A. Montag, T. S. McKechnie and L. F. Dahl, *J. Am. Chem. Soc.* 1986, **108**, 1330.
42. V. G. Albano, F. Demartin, M. C. Iapalucci, G. Longoni, A. Sironi and V. Zanotti, *J. Chem. Soc., Chem. Commun.* 1990, 547.
43. M. Melník, T. Šramko, M. Dunaj-Jurco and V. Mišút, *Rev. Inorg. Chem.* 1992, **12**, 1.
44. A. F. Masters and J. T. Meyer, *Polyhedron* 1995, **14**, 339.
45. F. A. Cotton, *Q. Rev., Chem. Soc.* 1966, **20**, 389.
46. L. Ackermann, N. Rösch, B. I. Dunlap and G. Pacchioni, *Int. J. Quantum Chem., Quantum Chem. Symp.* 1992, **26**, 605.
47. G. Longoni, B. T. Heaton and P. Chini, *J. Chem. Soc., Dalton Trans.* 1980, 1537.
48. *Hazards in the Chemical Laboratory* (Edited by S. G. Luxon), 5th edn. p. 595. Royal Society of Chemistry, Cambridge (1992).
49. *CRC Handbook of Chemistry and Physics* (Edited by R. C. Weast), 69th edn. CRC Press, Boca Raton, Florida (1988).
50. G. Longoni, P. Chini and A. Cavalieri, *Inorg. Chem.* 1976, **15**, 3025.
51. D. A. Nagaki, PhD Thesis, University of Wisconsin-Madison (1986).
52. R. E. Bachman and K. H. Whitmire, *Acta Crystallogr., Sect. C* 1993, **49**, 1121.
53. A. Ceriotti, G. Longoni and G. Piva, *Inorg. Synth.* 1989, **26**, 312.
54. J. C. Calabrese, L. F. Dahl, A. Cavalieri, P. Chini, G. Longoni and S. Martinengo, *J. Am. Chem. Soc.* 1974, **96**, 2616.
55. J. K. Beattie, T. W. Hambley, A. F. Masters and J. T. Meyer, *Inorg. Chim. Acta* 1993, **213**, 49.
56. N. J. Nelson, N. E. Kime and D. F. Shriver, *J. Am. Chem. Soc.* 1969, **91**, 5173.
57. W. F. Edgell and J. Lyford IV, *J. Am. Chem. Soc.* 1971, **93**, 6407.

58. J. S. Kristoff and D. F. Shriver, *Inorg. Chem.* 1974, **13**, 499.
59. C. D. Pribula and T. L. Brown, *J. Organomet. Chem.* 1974, **71**, 415.
60. D. A. Nagaki, J. V. Badding, A. M. Stacy and L. F. Dahl, *J. Am. Chem. Soc.* 1986, **108**, 3825.
61. L. D. Lower, PhD Thesis, University of Wisconsin-Madison (1976).
62. G. Longoni, P. Chini, L. D. Lower and L. F. Dahl, *J. Am. Chem. Soc.* 1975, **97**, 5034.
63. D. A. Nagaki, L. D. Lower, G. Longoni, P. Chini and L. F. Dahl, *Organometallics* 1986, **5**, 1764.
64. G. Longoni and P. Chini, *Inorg. Chem.* 1976, **15**, 3029.
65. G. Longoni, A. Ceriotti, R. Della Pergola, M. Manassero, M. Perego, G. Piro and M. Sansoni, *Philos. Trans. R. Soc. London, Ser. A* 1982, **308**, 47.
66. A. Ceriotti, P. Chini, R. Della Pergola and G. Longoni, *Inorg. Chem.* 1983, **22**, 1595.
67. L. Lower, L. F. Dahl, G. Longoni and P. Chini, *Abstracts of Papers*, 170*th Natl. Am. Chem. Soc.*, Chicago, Illinois, INORG 68. American Chemical Society, Washington DC (1975).
68. P. Chini, G. Longoni, M. Manassero and M. Sansoni, *Abstr. Eighth Ital. Assoc. Crystallogr.*, Ferrara, Italy, Communication 34 (1977).
69. M. Manassero, personal communication of unpublished X-ray crystal structure data (1994).
70. P. Chini, G. Longoni and S. Martinengo, *Chim. Ind.* 1978, **60**, 989.
71. L. Cassar and M. Foà, *Inorg. Nucl. Chem. Lett.* 1970, **6**, 291.
72. C. Brown, B. T. Heaton, L. Longhetti, D. O. Smith, P. Chini and S. Martinengo, *J. Organomet. Chem.* 1979, **169**, 309.
73. H. Behrens and F. Lohöfer, *Z. Naturforsch., B* 1953, **8**, 691.
74. W. Hieber, W. Kroder and E. Zahn, *Z. Naturforsch., B* 1960, **15**, 325.
75. W. Hieber, J. Ellermann and E. Zahn, *Z. Naturforsch., B* 1963, **18**, 589.
76. W. Hieber and J. Ellermann, *Z. Naturforsch., B* 1963, **18**, 595.
77. H. W. Sternberg, R. Markby and I. Wender, *J. Am. Chem. Soc.* 1960, **82**, 3638.
78. L. Cassar and M. Foà, *J. Organomet. Chem.* 1973, **51**, 381.
79. H. Behrens, H. Zizlsperger and R. Rauch, *Chem. Ber.* 1961, **94**, 1497.
80. P. Fayet, M. J. McGlinchey and L. H. Wöste, *J. Am. Chem. Soc.* 1987, **109**, 1733.
81. P. Fayet, *Chimia* 1988, **42**, 400.
82. J. W. Lauher, *J. Am. Chem. Soc.* 1978, **100**, 5305.
83. D. M. P. Mingos and D. J. Wales, *J. Am. Chem. Soc.* 1990, **112**, 930.
84. D. M. P. Mingos, *Acc. Chem. Res.* 1984, **17**, 311.
85. J. Evans, *J. Chem. Soc., Dalton Trans.* 1980, 1005.
86. D. W. Bullett, *Chem. Phys. Lett.* 1985, **115**, 450.
87. G. Pacchioni, P. Fantucci and V. Valenti, *J. Organomet. Chem.* 1982, **224**, 89.
88. P. Fantucci, G. Pacchioni and V. Valenti, *Inorg. Chem.* 1984, **23**, 247.
89. G. Pacchioni and N. Rösch, *Inorg. Chem.* 1990, **29**, 2901.
90. G. Pacchioni, L. Ackermann and N. Rösch, *Gazz. Chim. Ital.* 1992, **122**, 205.
91. N. Rösch, L. Ackermann and G. Pacchioni, *J. Am. Chem. Soc.* 1992, **114**, 3549.
92. N. Rösch, L. Ackermann, G. Pacchioni and B. I. Dunlap, *J. Chem. Phys.* 1991, **95**, 7004.
93. N. Rösch, L. Ackermann and G. Pacchioni, *Inorg. Chem.* 1993, **32**, 2963.
94. J. G. Louderback, A. J. Cox, L. J. Lising, D. C. Douglass and L. A. Bloomfield, *Z. Phys. D* 1993, **26**, 301.
95. E. K. Parks, L. Zhu, J. Ho and S. J. Riley, *Z. Phys. D* 1993, **26**, 41.
96. B. J. Pronk, H. B. Brom, L. J. De Jongh, G. Longoni and A. Ceriotti, *Solid State Commun.* 1986, **59**, 349.
97. A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, M. Marchionna, G. Piva and M. Sansoni, *Angew. Chem., Int. Ed. Engl.* 1985, **24**, 697.
98. G. Longoni, M. Manassero and M. Sansoni, *J. Organomet. Chem.* 1979, **174**, C41.
99. P. Chini, G. Longoni, S. Martinengo and A. Ceriotti, *ACS Adv. Chem. Ser.* 1978, **167**, 1.
100. K. Henrick, M. McPartlin and J. Morris, *Angew. Chem., Int. Ed. Engl.* 1986, **25**, 853.
101. R. W. Broach, PhD Thesis, University of Wisconsin-Madison (1977).
102. D. W. Hart, R. G. Teller, C. Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini and T. F. Koetzle, *Angew. Chem., Int. Ed. Engl.* 1979, **18**, 80.
103. D. W. Hart, R. G. Teller, C. Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini and T. F. Koetzle, *J. Am. Chem. Soc.* 1981, **103**, 1458.
104. R. W. Broach, L. F. Dahl, G. Longoni, P. Chini, A. J. Schultz and J. M. Williams, *ACS Adv. Chem. Ser.* 1978, **167**, 93.
105. P. L. Stanghellini and G. Longoni, *J. Chem. Soc., Dalton Trans.* 1987, 685.
106. C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, P. Machin and M. McPartlin, *J. Chem. Soc., Chem. Commun.* 1976, 945.
107. M. Marchionna, L. Basini, A. Aragno, M. Lami and F. Ancillotti, *J. Mol. Catal.* 1992, **75**, 147.

108. W. Kleimann, K.-R. Pörschke and G. Wilke, *Chem. Ber.* 1985, **118**, 323.
109. K.-R. Pörschke, K. Jonas, G. Wilke, R. Benn, R. Mynott, R. Goddard and C. Krüger, *Chem. Ber.* 1985, **118**, 275.
110. F. Joó and H. Alper, *Organometallics* 1985, **4**, 1775.
111. G. Ciani, D. Giusto, M. Manassero and A. Albinati, *J. Chem. Soc., Dalton Trans.* 1976, 1943.
112. B. Jeżowska-Trzebiatowska and B. Nissen-Sobocińska, *J. Organomet. Chem.* 1987, **322**, 331.
113. M. Manassero, personal communication.
114. R. Bau and T. F. Koetzle, *Pure Appl. Chem.* 1978, **50**, 55.
115. H. Behrens and F. Lohöfer, *Chem. Ber.* 1961, **94**, 1391.
116. A. Stock and E. Pohland, *Ber. Dtsch. Chem. Ges.* 1925, **58**, 657.
117. A. Ceriotti, G. Piro, G. Longoni, M. Manassero, N. Masciocchi and M. Sansoni, *New J. Chem.* 1988, **12**, 501.
118. R. D. Adams, in *Metal–Metal Bonds and Clusters in Chemistry and Catalysis* (Edited by J. P. Frackler Jr), p. 75. Plenum Press, New York (1990).
119. D. J. Darensbourg, in *Metal–Metal Bonds and Clusters in Chemistry and Catalysis* (Edited by J. P. Frackler Jr), p. 41. Plenum Press, New York (1990).
120. G. Longoni, A. Ceriotti, M. Marchionna and G. Piro, *NATO ASI Ser., Ser. C (Surf. Organomet. Chem.: Mol. Approaches Surf. Catal.)* 1988, **231**, 157.
121. W. L. Gladfelter and K. J. Roesselet, in *The Chemistry of Metal Cluster Complexes* (Edited by D. F. Shriver, H. D. Kaesz and R. D. Adams), Ch. 7. VCH Publishers, Weinheim (1990).
122. G. Süss-Fink, *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 72.
123. W. Keim, *Angew. Chem., Int. Ed. Engl.* 1990, **29**, 235.
124. S. Ceriotti, G. Longoni and P. Chini, *J. Organomet. Chem.* 1979, **174**, C27.
125. G. Natta, G. Mazzanti and P. Corradini, *Atti Accad. Naz. Lincei, Rend. Cl. Sci. Fis. Mat. Nat.* 1958, **25**, 3; *Chem. Abstr.* 1959, **53**, 13985i.
126. J. F.-Y. Temure and Y.-Q. Yin, *Cuihua Xuebao* 1991, **12**, 120.
127. D. Mahajan, R. S. Sapienza, W. A. Slegeir and T. E. O'Hare, U.S. Patent 4,935,395 (1990).
128. S. Lee, *Methanol Synthesis Technology*, p. 4. CRC Press, Boca Raton, Florida (1990).
129. A. Llebaria, F. Camps and J. M. Moretó, *Tetrahedron* 1993, **49**, 1283.
130. M. F. Semmelhack and S. J. Brickner, *J. Org. Chem.* 1981, **46**, 1723.
131. M. Foà and L. Cassar, *Gazz. Chim. Ital.* 1979, **109**, 619.
132. E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.* 1969, **91**, 1233.
133. E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.* 1969, **91**, 4926.
134. E. L. Muetterties and J. Stein, *Chem. Rev.* 1979, **79**, 479.
135. S. Nagakura, *J. Phys. Soc. Jpn* 1957, **12**, 482.
136. A. Ceriotti, G. Longoni, M. Manassero, M. Perego and M. Sansoni, *15th Congr. Naz. Chim. Inorg.*, p. 97. Italy, 1982.
137. M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.* 1981, **28**, 203.
138. J. S. Bradley, *Adv. Organomet. Chem.* 1983, **22**, 1.
139. J.-F. Halet and D. M. P. Mingos, *Organometallics* 1988, **7**, 51.
140. A. Arrigoni, A. Ceriotti, R. Della Pergola, G. Longoni, M. Manassero, N. Masciocchi and M. Sansoni, *Angew. Chem., Int. Ed. Engl.* 1984, **23**, 322.
141. A. Ceriotti, R. Della Pergola, G. Longoni, M. Manassero, N. Masciocchi and M. Sansoni, *J. Organomet. Chem.* 1987, **330**, 237.
142. A. Ceriotti, R. Della Pergola, G. Longoni, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.* 1984, 1181.
143. V. E. Lopatin, M. Ts. Tsybenov, L. A. Sheludyakova and L. I. Bagryantseva, *Zh. Obschch. Khim.* (English) 1986, **56**, 148.
144. M. Tachikawa, R. L. Geerts and E. L. Muetterties, *J. Organomet. Chem.* 1981, **213**, 11.
145. P. L. Stanghellini, R. Rossetti, G. D'Alfonso and G. Longoni, *Inorg. Chem.* 1987, **26**, 2769.
146. A. Ceriotti, G. Longoni, M. Manassero, M. Perego and M. Sansoni, *Inorg. Chem.* 1985, **24**, 117.
147. A. F. Wells, *Structural Inorganic Chemistry*, 5th edn. Oxford University Press, London (1984).
148. A. Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, L. Resconi and M. Sansoni, *J. Chem. Soc., Chem. Commun.* 1985, 181.
149. A. Ceriotti, G. Longoni, M. Manassero, N. Masciocchi, G. Piro, L. Resconi and M. Sansoni, *J. Chem. Soc., Chem. Commun.* 1985, 1402.
150. A. Ceriotti, A. Fait, G. Longoni, G. Piro, L. Resconi, F. Demartin, M. Manassero, N. Masciocchi and M. Sansoni, *J. Am. Chem. Soc.* 1986, **108**, 5370.
151. A. Ceriotti, A. Fait, G. Longoni, G. Piro, F. Demartin, M. Manassero, N. Masciocchi and M. Sansoni, *J. Am. Chem. Soc.* 1986, **108**, 8091.
152. C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.* 1975, 879.
153. C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.* 1976, 636.