Carbon-13 Nuclear Magnetic Resonance Studies on Nickel Carbonyl Clusters

By **Giuliano Longoni**, Centro del CNR per lo Studio della Sintesi e Della Struttura dei Composti dei Metalli di Transizione, Via G. Venezian 21, 20133 Milano, Italy
Brian T. Heaton,* Chemical Laboratory, University of Kent, Canterbury CT2 7NH
(the late) **Paolo Chini**, Instituto di Chimica dell'Università, Via G. Venezian 21, 20133 Milano, Italy

Carbon-13 n.m.r. spectra, over a range of temperature, are reported for $[Ni_5(CO)_{12}]^{2-}$, $[Ni_6(CO)_{12}]^{2-}$, $[Ni_9(CO)_{18}]^{2-}$, and $[Ni_{12}(CO)_{21}H_{4-x}]^{x-}$ (x = 2 or 3). At −80 °C the spectra of $[Ni_6(CO)_{12}]^{2-}$, $[Ni_9(CO)_{18}]^{2-}$, and $[Ni_{12}(CO)_{21}H_2]^{2-}$ are consistent with their solid-state structures; terminal–bridge carbonyl exchange is observed at higher temperatures with the lowest-energy process involving exchange on the *outer* metal triangles. Similar behaviour is found for $[Ni_{12}(CO)_{21}H]^{3-}$ and in addition H migration may occur. Spectroscopic and chemical evidence is presented for the formation of a new cluster, $[Ni_7(CO)_{15}]^{2-}$, and its fluxional behaviour is reported. At 60 °C $[Ni_{12}(CO)_{21}H_2]^{2-}$ is transformed cleanly into $[Ni_9(CO)_{18}]^{2-}$ whereas $[Ni_{12}(CO)_{21}H]^{3-}$ does not react under the same conditions.

OVER the last few years high nuclearity carbonyl clusters (h.n.c.c.s) have been shown to undergo a variety of intramolecular rearrangements involving ligand- and/or metal-atom migrations, although the factors controlling these migrations are still not well understood.[1] Carbonyl migration can occur by: (1) complete randomisation of carbonyls over the metal skeleton, *e.g.* $[Rh_6(CO)_{15}]^{2-}$; [2] (2) partial migration of the carbonyls (a) on a localised face of the metal polyhedron, *e.g.* $[Rh_7(CO)_{16}]^{3-}$,[3] (b) around a specific pathway over the metal polyhedron, *e.g.* $[Rh_{13}(CO)_{24}H_{5-x}]^{x-}$ (x = 2 or 3),[4] (c) on a specific metal atom, *e.g.* $[Os_6(CO)_{18}]$.[5] Hydride migration can occur around the periphery of the metal skeleton, *e.g.* $[Ru_4(CO)_{12-x}H_4\{P(OMe)_3\}_x]$ (x = 1—4),[6] or within the metal polyhedron.[4] Two different examples of h.n.c.c.s undergoing internal metal-polyhedron rearrangements have recently been reported, $[Pt_n(CO)_{2n}]^{2-}$ (n = 9, 12, or 15) [7] and $[Rh_9(CO)_{21}P]^{2-}$; [8] the Rh_9 cluster undergoes both carbonyl and metal-polyhedral rearrangements which are probably interdependent, whereas the platinum clusters exhibit rotation of the intact $Pt_3(CO)_6$ unit.

In view of this last result, it was of interest to obtain structural information on the nickel clusters $[Ni_n(CO)_{2n}]^{2-}$ (n = 6 or 9) [9,10] in solution, especially since the geometries of the nickel polyhedra [11,12] are different from their isoelectronic platinum analogues [13] in the solid state. We now report a variable-temperature ^{13}C n.m.r. study of these two nickel clusters together with the fluxional behaviour of the other presently known nickel h.n.c.c.s, *viz.* $[Ni_5(CO)_{12}]^{2-}$ [9,14] and $[Ni_{12}(CO)_{21}H_{4-x}]^{x-}$ (x = 2 or 3).[15] Spectroscopic and chemical evidence is also presented for the formation of a new cluster, $[Ni_7(CO)_{15}]^{2-}$.

RESULTS

$[Ni_5(CO)_{12}]^{2-}$. The solid-state structure of this cluster [14] is shown schematically in Figure 1 and, consistent with this structure, the ^{13}C n.m.r. spectra both at −80 and 25 °C show three sharp resonances at 257.2, 203.5, and 197.6 p.p.m. in the intensity ratio 1 : 2 : 1 due to the three types of carbonyls, B_i, T_o, and T_i respectively (Figure 1, Table).

$[Ni_6(CO)_{12}]^{2-}$. A limiting slow-exchange spectrum consisting of two equally intense resonances at 237.0 and 196.3 p.p.m. was observed at −80 °C. This is entirely consistent with the solid-state structure, which consists of two $Ni_3(CO)_3(\mu\text{-}CO)_3$ units stacked so that the nickel atoms adopt an antiprismatic arrangement.[11] 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.

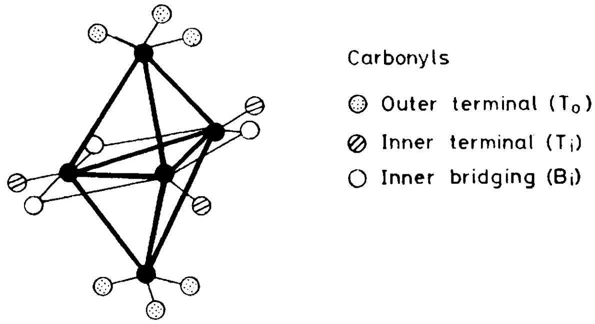

FIGURE 1 Schematic structure of $[Ni_5(CO)_{12}]^{2-}$

$[Ni_9(CO)_{18}]^{2-}$. At −80 °C there are two resonances in the intensity ratio 1 : 2 at 236.3 and 230.4 p.p.m. due to the bridging carbonyls on the inner and outer triangles respectively; the resonances due to the terminal carbonyls on the inner and outer triangles are accidentally coincident at 195.2 p.p.m. with relative intensity 3. This spectrum is consistent with a symmetrical stacking of three $Ni_3(CO)_3(\mu\text{-}CO)_3$ units either in a staggered or eclipsed conformation

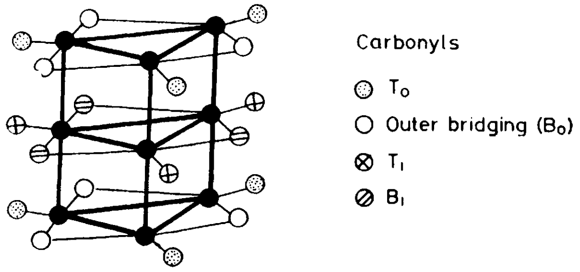

FIGURE 2 Schematic structure of $[Ni_9(CO)_{18}]^{2-}$

in solution (Figure 2), although the solid-state structure has one outer triangle essentially eclipsed by the inner triangle and the other is essentially staggered.[12] At 25 °C terminal–bridge carbonyl exchange occurs on the outer triangle as evidenced by the loss of the resonance at 230.4 p.p.m. and a corresponding decrease in relative intensity of the terminal resonance at 195.2 p.p.m. (Table).

$[Ni_{12}(CO)_{21}H_2]^{2-}$. A schematic representation of the solid-state structure of this cluster is shown in Figure 3; the hydrides are found by neutron diffraction to be in octahedral holes symmetrically situated on either side of the central layer.[15] As a result, there are only two types of bridging carbonyls (B_i and B_o) in the ratio 6 : 6 and two types of terminal carbonyls (T_i and T_o) in the ratio 3 : 6, and the ^{13}C n.m.r. spectrum at −80 °C is entirely consistent with this geometry (Figure 4 and Table). There is no evidence for any $^1H-^{13}C$ coupling. The resonances due to B_o,T_o are significantly broader than those due to B_i,T_i and this is accentuated on increasing the temperature, until at −62 °C the resonances at 219.3 and 196.0 p.p.m. have almost disappeared. Increasing the temperature further causes the remaining two resonances to start to collapse and at 25 °C a resonance at 208.3 p.p.m. appears due to the approach to the fast-exchange limiting spectrum due to B_o,T_o exchange. At higher temperatures (60 °C), $[Ni_{12}(CO)_{21}H_2]^{2-}$ undergoes (30 min) a clean conversion into $[Ni_9(CO)_{18}]^{2-}$ according to equation (1). This ready

$$4[Ni_{12}(CO)_{21}H_2]^{2-} \longrightarrow 4[Ni_9(CO)_{18}]^{2-} + 3[Ni(CO)_4] + 4H_2 + 9Ni \qquad (1)$$

transformation could be initiated by elimination of hydrogen since $[Ni_{12}(CO)_{21}H]^{3-}$ does not react under the same conditions.

Carbon-13 n.m.r. spectra of nickel carbonyl anions

θ_c/°C	Compound	Solvent	δ(CO)/p.p.m.[a,b]			
			T_o	B_o	T_i	B_i
−80	$[Ni_5(CO)_{12}]^{2-}$	*c*	203.5 (6)		197.6 (3)	257.2 (3)
−30		*c*	204.5 (6)		198.4 (3)	257.8 (3)
−22		*d*	205.9 (6)		199.9 (3)	260.4 (3)
25		*c*	*e*		200.2 (3)	259.1 (3)
25		*d*	205.9 (6)		200.1 (3)	259.7 (3)
−80	$[Ni_6(CO)_{12}]^{2-}$	*c*	196.3 (6)	237.0 (6)		
−30		*c*	197.6 (6)	237.7 (6)		
−22		*d*	198.8 (6)	239.1 (6)		
25		*c*	*f*	*f*		
		d	*f*	*f*		
−80	$[Ni_7(CO)_{15}]^{2-}$	*c*	198.8 (3) [g] 195.3 (3) [h]	234.9 (3)	193.7 (3)	245.4 (3)
−30		*c*	198.8 (3) [g] *f,h*	*f*	193.7 (3)	245.4 (3)
25		*c*	200.55 (3) [g] *f,h*	*f*	196.4 (3)	246.4 (3)
25		*d*	200.45 (3) [g] *f,h*	*f*	196.1 (3)	247.9 (3)
−80	$[Ni_9(CO)_{18}]^{2-}$	*c*	195.2 (6)	230.4 (6)	195.2 (3)	236.3 (3)
−30		*c*	195.8 (6)	230.4 (6)	195.8 (3)	236.9 (3)
25		*c*	*f*	*f*	196.7 (3)	237.9 (3)
−81	$[Ni_{12}(CO)_{21}H_2]^{2-}$	*c*	196.0 (6)	219.3 (6)	189.3 (3)	239.9 (6)
−30		*c*	*f*	*f*	189.6 (3)	240.2 (6)
25		*c*	208.3		*f*	*f*
−80	$[Ni_{12}(CO)_{21}H]^{3-}$	*c*	196.8 (6)	228.1 (6)	190.5 (3)	248.1 (6)
−30		*c*	*f*	*f*	191.8 (3)	248.2 (6)
25		*c*	*f*	*f*	*f*	*f*

[a] T_o = Outer terminal carbonyls, T_i = inner terminal carbonyls, B_o = outer bridging carbonyls, B_i = inner bridging carbonyls. [b] In p.p.m. from $SiMe_4$. The carbonyl chemical shifts have been calculated by referencing to solvent resonances using δ(CO) of acetone = 206.0 p.p.m. and δ(CN) of acetonitrile = 117.9 p.p.m. Relative intensities are given in parentheses. [c] $(CD_3)_2CO$. [d] CD_3CN. [e] Under solvent resonance. [f] Collapsed. [g] Apical CO groups on unique Ni (see Figure 5). [h] Basal CO groups on Ni_3 triangle remote from capping atom (see Figure 5).

$[Ni_{12}(CO)_{21}H]^{3-}$. The ^{13}C spectrum of the monohydride at −80 °C is very similar to that of the dihydride. If the solid-state structure [15] is maintained in solution, then the occupancy of only one of the pair of octahedral holes by the hydrogen atom should make the outer layers inequivalent. As a result, the observed ^{13}C n.m.r. spectrum can be explained by either assuming the H to be static and invoking accidental coincidences for the inequivalent bridging and inequivalent terminal carbonyls on the outer layers, or by assuming H migration between octahedral holes on either side of the central layer, which would make the outer layers equivalent. Because of the behaviour of $[Rh_{13}(CO)_{24}H_{5-x}]^{x-}$ we prefer the second explanation. No evidence was found for $^1H-^{13}C$ coupling or for inter-hydrogen exchange between the mono- and di-hydrides at −80 °C even though both species undergo rapid H exchange with H_2 and acid. Carbonyl migration, similar to that observed in the di-

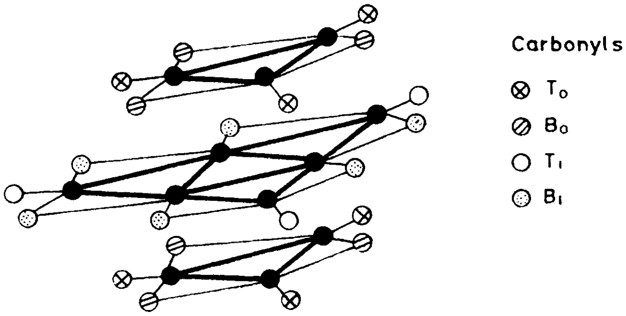

FIGURE 3 Schematic structure of $[Ni_{12}(CO)_{21}H_{4-x}]^{x-}$ (x = 2 or 3): hydrogens have been omitted for clarity

hydride, is found on increasing the temperature. Thus at −40 °C the resonances due to B_o,T_o are considerably broadened and at room temperature all the resonances are completely collapsed. Unlike $[Ni_{12}(CO)_{21}H_2]^{2-}$, no reaction occurs on heating to 60 °C but the fast-exchange limiting spectrum is not reached at this temperature.

It should be noted that, in accord with what is usually found on increasing the charge on a cluster, the chemical shifts of the bridging carbonyls in $[Ni_{12}(CO)_{21}H]^{3-}$ occur at significantly lower field than in $[Ni_{12}(CO)_{21}H_2]^{2-}$, although the chemical shifts of the terminal carbonyls are not much different.

FIGURE 4 Variable-temperature $^{13}C-\{^1H\}$ n.m.r. spectra of $[Ni_{12}(CO)_{21}H_2]^{2-}$ in $(CH_3)_2CO-(CD_3)_2CO$. S = Solvent

$[Ni_7(CO)_{15}]^{2-}$. This new species was first detected as an impurity, present in trace amounts, in the ^{13}C n.m.r. spectrum of $[Ni_9(CO)_{18}]^{2-}$ prepared as described in the Experimental section. At −80 °C there are five equally intense resonances at 245.4, 234.9, 198.8, 197.7, and 195.3 p.p.m. which are attributed to $[Ni_7(CO)_{15}]^{2-}$. The most probable structure of this new cluster is shown in Figure 5; it results from capping one of the equilateral triangles in the trigonal-antiprismatic $[Ni_6(CO)_{12}]^{2-}$ with one $Ni(CO)_3$ group. However, at this stage, we cannot rule out other structures such as a capped trigonal-prismatic arrangement of nickel atoms and, in both the antiprismatic and prismatic metal-polyhedral structures, different arrangements of the 'bridging' carbonyls are possible. Between −30 and 25 °C two of the five resonances disappear and we assign these to the terminal,bridging carbonyls on the Ni_3 triangle remote from the unique nickel, by analogy with the fluxional behaviour found for $[Rh_7(CO)_{16}]^{3-}$ (Table). Because of these n.m.r. observations we have reinvestigated the chemistry of nickel carbonyl anions and, as a result, find convincing evidence for this new species.

The complex $[Ni_7(CO)_{15}]^{2-}$ can be obtained by the reaction of $[Ni_6(CO)_{12}]^{2-}$ with $[Ni(CO)_3I]^-$ under a nitrogen atmosphere at room temperature. Thus on addition of a solution of $[N(PPh_3)_2][Ni(CO)_3I]$ in acetonitrile to a solution of $[Ni_6(CO)_{12}]^{2-}$ in the same solvent bands at 1 990s, 1 940w, 1 820(sh), and 1 800ms in the i.r. spectrum increase in intensity with a corresponding decrease in intensity of the bands due to $[Ni_6(CO)_{12}]^{2-}$. The reaction appears to be an equilibrium [equation (2)] which is not completely shifted to

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

the right even on addition of twice the required amount of $[Ni(CO)_3I]^-$.

Although previously not recognised, $[Ni_7(CO)_{15}]^{2-}$ has now also been shown to be an important intermediate in the condensation of $[Ni(CO)_4]$ with $[Ni_6(CO)_{12}]^{2-}$ to give $[Ni_9(CO)_{18}]^{2-}$ as well as in degradation of $[Ni_9(CO)_{18}]^{2-}$ by CO to give a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni(CO)_4]$. Thus it has previously been reported[9] that $[Ni(CO)_4]$ readily condenses at room temperature with $[Ni_5(CO)_{12}]^{2-}$ to give $[Ni_6(CO)_{12}]^{2-}$ [equation (3)]; this equilibrium is shifted to the right under a nitrogen atmosphere and to the left under a CO atmosphere (25 °C, 1 atm *). Further condensation

$$[Ni_5(CO)_{12}]^{2-} + [Ni(CO)_4] \rightleftharpoons [Ni_6(CO)_{12}]^{2-} + 4CO \quad (3)$$

of $[Ni_6(CO)_{12}]^{2-}$ with $[Ni(CO)_4]$ has been reported to occur under vacuum at 40 °C to give $[Ni_9(CO)_{18}]^{2-}$ [equation (4)].[10] We have now been able to show that equation (4)

$$[Ni_6(CO)_{12}]^{2-} + 3[Ni(CO)_4] \rightleftharpoons [Ni_9(CO)_{18}]^{2-} + 6CO \quad (4)$$

$$[Ni_6(CO)_{12}]^{2-} + [Ni(CO)_4] \rightleftharpoons [Ni_7(CO)_{15}]^{2-} + CO \quad (5)$$

$$[Ni_7(CO)_{15}]^{2-} + 2[Ni(CO)_4] \rightleftharpoons [Ni_9(CO)_{18}]^{2-} + 5CO \quad (6)$$

is the result of at least two additional equilibria, (5) and (6).

The intermediate occurrence of $[Ni_7(CO)_{15}]^{2-}$ in equilibrium (4) has been proved by i.r. measurements both during the condensation of $[Ni(CO)_4]$ with $[Ni_6(CO)_{12}]^{2-}$ [equation (5)] as well as during the degradation of $[Ni_9(CO)_{18}]^{2-}$ by CO [equation (6)] by carefully monitoring the volume of CO added to $[Ni_9(CO)_{18}]^{2-}$. However, while it was impossible in the degradation of $[Ni_9(CO)_{18}]^{2-}$ [equation (6)] to avoid

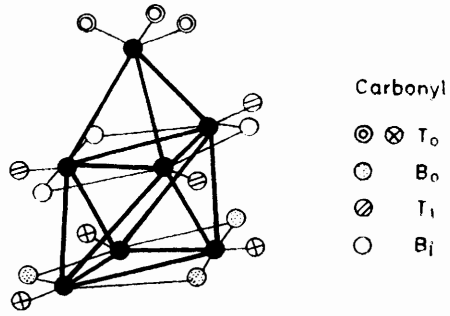

FIGURE 5 Schematic structure of $[Ni_7(CO)_{15}]^{2-}$

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* Throughout this paper: 1 atm = 101 325 Pa.

the concomitant equilibria (5) and (3), it has been possible to prepare a fairly pure sample of $[Ni_7(CO)_{15}]^{2-}$ *via* equation (5) without involving the subsequent condensation [equation (6)]. Thus, dropwise addition of a solution of $[Ni(CO)_4]$ in diethyl ether to a solution of $[Ni_6(CO)_{12}]^{2-}$ at 40 °C while monitoring the i.r. spectrum allowed the isolation of a pure sample of $[Ni_7(CO)_{15}]^{2-}$ by simple evaporation of solvent.

Fairly pure $[Ni_7(CO)_{15}]^{2-}$ has also been obtained *via* the redistribution reaction (7). Unfortunately, however, we

$$[Ni_9(CO)_{18}]^{2-} + [Ni_5(CO)_{12}]^{2-} \longrightarrow 2[Ni_7(CO)_{15}]^{2-} \quad (7)$$

have presently been unable to isolate crystals of $[Ni_7(CO)_{15}]^{2-}$ for *X*-ray analysis since under the conditions required for crystallisation the disproportionation (8) occurs.

$$3[Ni_7(CO)_{15}]^{2-} \rightleftharpoons [Ni_9(CO)_{18}]^{2-} + 2[Ni_6(CO)_{12}]^{2-} + 3CO \quad (8)$$

DISCUSSION

All the nickel carbonyl clusters investigated have low-temperature ^{13}C n.m.r. spectra which show the carbonyls to be static. The exchange process of lowest activation energy involves bridge–terminal carbonyl exchange on the *outer* layers of the cluster and when a similar process occurs on the inner layer {*e.g.* in $[Ni_{12}(CO)_{21}H_2]^{2-}$} there appears to be no randomisation of carbonyls between layers, over the temperature range studied. This behaviour should be contrasted with that found for $[Pt_n(CO)_{2n}]^{2-}$ (n = 6, 9, or 12) which did not exhibit bridge–terminal carbonyl exchange but instead showed rotation of the intact $Pt_3(CO)_3(\mu\text{-}CO)_3$ units about the pseudo-three-fold axis.[7] In this present work we cannot be sure of the eclipsed,staggered arrangement of the Ni_3 triangles present in $[Ni_6(CO)_{12}]^{2-}$, $[Ni_7(CO)_{15}]^{2-}$, or $[Ni_9(CO)_{18}]^{2-}$ in solution, although as pointed out earlier the metal polyhedron in $[Ni_9(CO)_{18}]^{2-}$ is probably more symmetrical in solution than in the solid state and may or may not involve rotation of $Ni_3(CO)_3(\mu\text{-}CO)_3$ units as found for the platinum analogue.

The formulation of a new cluster as $[Ni_7(CO)_{15}]^{2-}$ is entirely consistent with both chemical and spectroscopic studies and provides another link in the already complicated processes involved in agglomeration and demolition of nickel carbonyl cluster anions. This formulation with a capped trigonal-antiprismatic structure (Figure 5), however, is electron-rich (102 electrons), since most other capped octahedral structures have 98 or 100 valence-shell electrons.[16,17] The additional electrons probably result in lengthening of specific Ni–Ni bonds which would account for the high reactivity of the cluster. A similar behaviour is found in M_5 clusters where electron-rich clusters adopt an elongated trigonal-bipyramidal array of metal atoms whereas the electron-precise clusters adopt a more regular array. We feel the alternative capped trigonal-prismatic structure of $[Ni_7(CO)_{15}]^{2-}$, which would be electron-precise, is less probable since, apart from $[Pt_6(CO)_{12}]^{2-}$, metal-atom configurations with this geometry have only been found for clusters containing encapsulated atoms, *e.g.* $[M_6(CO)_{15}C]^{2-}$ [18] and $[M_6(CO)_{15}N]^{-}$ [19] (M = Co or Rh).

EXPERIMENTAL

Carbon-13 n.m.r. spectra were obtained using a JEOL PS-100 spectrometer operating in the pulsed Fourier-transform mode using a ^{13}C probe tuned to 25 MHz. The probe was capable of operation between ±100 °C, with the desired radiofrequency being generated by a Schomandl ND100M frequency synthesiser. Probe temperatures were measured with a Comark 1605 electronic thermometer using a Cr/Al thermocouple and are considered accurate to ±2 °C.

Such spectra were routinely measured using *ca.* 45° (10 μs) pulses and a repetition time of 1 s. Deuterioacetone or deuterioacetonitrile solutions (*ca.* 0.1 mol dm^{-3}), doped with $[Cr(acac)_3]$ (acac = acetylacetonate) at a level of 1 mg per 400 mg, of sample (*ca.* 30—40% ^{13}C-enriched) contained in tubes of 10 mm diameter, were used for all the measurements.

Since most of the nickel carbonyl anions are rapidly and irreversibly degraded by CO (25 °C, 1 atm) [9,10,20] it was not possible to carry out isotopic enrichment by direct exchange with ^{13}CO. Nevertheless, even though $[Ni_5(CO)_{12}]^{2-}$ reacts with CO to give a mixture of $[Ni(CO)_4]$ and a presently uncharacterised more reduced species as shown by the change in colour of the solution and by i.r. spectroscopy, it has been used as the starting material for the preparation of all the other isotopically enriched clusters, since it can be quantitatively recovered by simply evacuating the carbon monoxide. Because of its extreme lability, the solvents and ^{13}CO were rigorously dried and oxygen-free and typical procedures, which are slight modifications of the original syntheses,[9,10] are described below.

Enrichment of $[N(CH_3)_4]_2[Ni_5(CO)_{12}]$ with ^{13}CO.—The salt $[N(CH_3)_4]_2[Ni_5(CO)_{12}]$ (0.281 g) was dissolved in anhydrous tetrahydrofuran (thf) (10 cm^3) in a flask of total volume 110 cm^3. The flask was cooled, evacuated, and filled with ^{13}CO (100 cm^3, 95% ^{13}C). The yellow-brown solution became red-violet and the solution was stirred for 3 d at room temperature. The ^{13}CO was removed by a freeze–pump–thaw cycle and the flask refilled with nitrogen. On stirring for 3 h at room temperature the solution became yellow-brown. Evaporation of the solvent *in vacuo* left a residue of ^{13}CO-enriched $[N(CH_3)_4]_2[Ni_5(CO)_{12}]$ which was used directly to prepare the other nickel carbonyl anions.

$[N(CH_3)_4]_2[Ni_6(CO)_{12}]$.—The ^{13}CO-enriched $[N(CH_3)_4]_2[Ni_5(CO)_{12}]$ (0.25 g) was dissolved in rectified methanol (10 cm^3) under a nitrogen atmosphere. On stirring for 6 h the solution turned red-orange and red crystals of $[N(CH_3)_4]_2[Ni_6(CO)_{12}]$ separated out. Precipitation was completed by adding water (10 cm^3) to the stirred solution. The precipitate was filtered off, washed with water, and dried in vacuum, yield 0.14 g.

$[As(C_6H_5)_4]_2[Ni_9(CO)_{18}]$.—The ^{13}C-enriched $[N(CH_3)_4]_2[Ni_5(CO)_{12}]$ (0.175 g) was dissolved in methanol (10 cm^3) under nitrogen and acetic acid (0.15 cm^3) was added. The initial yellow-brown solution immediately became red and a red microcrystalline precipitate of $[N(CH_3)_4]_2[Ni_6(CO)_{12}]$ separated out. After stirring for 3 h the precipitate dissolved and the solution became dark red due to the formation of $[Ni_9(CO)_{18}]^{2-}$. The solution was filtered and tetraphenylarsonium chloride (0.3 g) was added to the stirred filtrate. The resulting crystalline precipitate of $[As(C_6H_5)_4]_2[Ni_9(CO)_{18}]$ was filtered off, washed with water, and dried in vacuum, yield 0.165 g.

$[N(CH_3)_4]_2[Ni_{12}(CO)_{21}H_2]$.—(*a*) The ^{13}C-enriched $[N(CH_3)_4]_2[Ni_5(CO)_{12}]$ (0.281 g) was dissolved in thf (10 cm^3) under nitrogen and 0.3 cm^3 of a solution containing H_3PO_4

(2 $\mathrm{cm^3}$, 48%) in thf (10 $\mathrm{cm^3}$) was added. The solution immediately turned red and some $[\mathrm{N(CH_3)_4}]_2[\mathrm{Ni_6(CO)_{12}}]$ precipitated out but redissolved on stirring for 1 h to give a red-violet solution and some white precipitate. The solution was filtered and then evaporated to dryness *in vacuo*. The resulting residue was suspended in methanol (10 $\mathrm{cm^3}$) and the precipitation of $[\mathrm{N(CH_3)_4}]_2[\mathrm{Ni_{12}(CO)_{21}H_2}]$ was completed by adding, with stirring, a solution of tetramethylammonium chloride (0.4 g) in water (20 $\mathrm{cm^3}$). The precipitate was filtered off, washed with water, and dried *in vacuo*, yield 0.183 g.

(*b*) Dissolution of ^{13}C-enriched $\mathrm{Na_2[Ni_5(CO)_{12}]}\cdot x\mathrm{thf}$ (0.45 g) in water gave a red solution and a white precipitate which was filtered off. The red solution was evaporated *in vacuo* for a few minutes and then treated, under nitrogen, with $\mathrm{H_3PO_4}$ (0.5 $\mathrm{cm^3}$, 48%) and a saturated aqueous solution of KBr (3 $\mathrm{cm^3}$). The resulting precipitate of $\mathrm{K_2[Ni_{12}(CO)_{21}H_2]}\cdot x\mathrm{H_2O}$ was filtered off, dried *in vacuo* for a few minutes, and then extracted with methanol. Addition of tetramethylammonium chloride (0.5 g) in water (20 $\mathrm{cm^3}$) to the red-violet methanolic solution produced microcrystals of $[\mathrm{N(CH_3)_4}]_2[\mathrm{Ni_{12}(CO)_{21}H_2}]$ which was filtered off and dried *in vacuo* (yield 0.12 g).

$[\mathrm{N(CH_3)_4}]_3[\mathrm{Ni_{12}(CO)_{21}H}]$.—^{13}C-Enriched $[\mathrm{N(CH_3)_4}]_2[\mathrm{Ni_{12}(CO)_{21}H_2}]$ (0.25 g) was suspended in methanol (10 $\mathrm{cm^3}$) and solid Na[OH] (2.5 g) was slowly added. After stirring for 24 h, a brown solution with brown microcrystals of $[\mathrm{N(CH_3)_4}]_3[\mathrm{Ni_{12}(CO)_{21}H}]$ was obtained. Addition of tetramethylammonium chloride (0.5 g) and water (10 $\mathrm{cm^3}$) completed the precipitation and the precipitate was filtered off, washed with water, and dried *in vacuo* (yield 0.205 g).

$[\mathrm{As(C_6H_5)_4}]_2[\mathrm{Ni_7(CO)_{15}}]$.—Equimolar amounts of ^{13}CO-enriched $[\mathrm{As(C_6H_5)_4}]_2[\mathrm{Ni_5(CO)_{12}}]$ and $[\mathrm{As(C_6H_5)_4}]_2[\mathrm{Ni_9(CO)_{18}}]$ were dissolved in acetone (10 $\mathrm{cm^3}$) at −70 °C. The resulting red solution was warmed to room temperature and evaporated to dryness *in vacuo*.

We thank the CNR/British Council and S.R.C. for supporting this work. Some experimental assistance from Dr. L. Longhetti is gratefully acknowledged.

[9/1754 *Received*, 31*st October*, 1979]

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