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Interconversions of nickel carbonyl cluster anions

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Abstract

The dodecacarbonylhexanickelate(2−) dianion, $[Ni_6(CO)_{12}]^{2-}$, has been studied by infrared spectroscopy in tetrahydrofuran and acetonitrile solutions under applied high pressures of carbon monoxide or syngas ($CO/H_2 = 1:2$) both at 25 and 100 °C. The dianion is converted, possibly by fragmentation, to other carbonyl clusters via the dodecacarbonylpentanickelate(2−) dianion, $[Ni_5(CO)_{12}]^{2-}$, under 20 atm. of CO or syngas at 25 °C and primarily to $Ni(CO)_4$ at a pressure of 20 atm. and at 100 °C. The X-ray crystal structure of $[N(PPh_3)_2]_2[Ni_6(CO)_{12}]$ is reported and compared with that of the tetramethylammonium analogue, $[NMe_4]_2[Ni_6(CO)_{12}]$.

Introduction

Cluster chemistry is an expanding area of research that has received increasing attention in the past decade. Despite this effort, the chemistry of carbonyl clusters is still far from being completely understood due in part to the complexity of the systems in which they have been observed. This complexity arises from the facile interconversions that can occur between such clusters via equilibria quite often involving simple monomeric homoleptic carbonyls.

Metal carbonyl clusters have been implicated in many homogeneously catalysed reactions [1]. Identification of the active catalytic species, which is often transient and highly unstable under reaction conditions, presents a great challenge to researchers in this field. A very important non-intrusive physical technique that is used in the *in situ* study of such reactions is high-pressure infrared (HPIR) spectroscopy. This technique has been reviewed by Whyman [2].

The major advantages of HPIR spectroscopy as compared to high-pressure NMR spectroscopy are the speed of acquisition of data and the high sensitivity of the technique (particularly with regard to metal–carbonyl and metal–hydride absorptions). This sensitivity is desirable when working at the low catalyst concentrations often encountered in catalytic processes. HPIR spectroscopy has been useful in the study of various transition metal catalysts under pressures of carbon monoxide and dihydrogen. Some recent examples of liquid phase catalysts studied under varying ratios of CO/H_2 are carbonyl clusters such as $[Rh_4(CO)_{12}]$ [3, 4] and their phosphite derivatives $[Rh_4(CO)_{12-x}L_x]$ ($L = P(OPh)_3$, $x = 1$–4) [5] and olefin hydroformylation catalysts such as $[RhH(CO)_2(PR_3)_2]$ and $[HCo(CO)_4]$ [6]. Heterogeneous catalysts have also been studied by HPIR spectroscopy. A recent example is the reaction of CO and CO/H_2 mixtures with rhodium on SiO_2 for which HPIR spectra provide evidence of linear and bridging carbonyls as intermediates to reaction products such as methane, methanol and ethanol [7].

The salts of nickel carbonyl clusters $[NMe_4]_2[Ni_5(CO)_{12}]$, $[NMe_4]_2[Ni_6(CO)_{12}]$, $[NMe_4]_2[Ni_{12}(CO)_{21}H_2]$ and $[NEt_4]_3[Ni_{12}(CO)_{21}H]$ in acetone have been reported to be sources of efficient catalysts for the polymerisation of acetylene (1 atm., 20 °C) [8]. More recently, deposition of $Na_2[Ni_6(CO)_{12}]$ on a support of La_2O_3 has been shown to produce an effective catalyst for carbon monoxide methanation [9]. Further insights into the interconversions of nickel carbonyl clusters under conditions of high temperature and high pressures are thus of considerable importance in relation to the catalytic applications of these materials.

The salts of all the known nickel carbonyl clusters are air sensitive both in solution and in the solid state. $Ni(CO)_4$ is commonly observed to be a decomposition product resulting from the air oxidation of these cluster species. A solid sample of $[NMe_4]_2[Ni_5(CO)_{12}]$ has been reported to decompose to nickel metal on heating to ~75 °C whereas the more stable $[NMe_4]_2[Ni_6(CO)_{12}]$ salt decomposes over the temperature range 190–230 °C [10]. No intermediate decomposition products of either cluster species have been observed by thermogravimetric analysis [10].

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TABLE 1. Selected IR absorption frequencies of $Ni(CO)_4$ and various carbonylnickelate cluster anions

Molecule	Cation	Solvent	ν(CO) (cm^{-1})	Reference
$Ni(CO)_4$		CCl_4	2044s	11
$[Ni_5(CO)_{12}]^{2-}$	Li^+	THF	1970s, 1920m, 1830w, 1790w, 1710mw	10[a]
	Na^+, K^+	THF	1970s, 1920m, 1822w, 1795w, 1760w, 1740mw	
$[Ni_6(CO)_{12}]^{2-}$	Li^+	THF	1980s, 1810m, 1790m, 1710w	10[a]
	Na^+, K^+	THF	1980s, 1815m, 1795m, 1745mw	
$[Ni_7(CO)_{15}]^{2-}$	PPN^+	MeCN	1990s, 1940w, 1820sh, 1800ms	12[b]
$[Ni_3(CO)_x]^{2-}$[c]	Na^+	THF	1945ms, 1920s	10

s = strong, m = medium, w = weak, ms = medium strong, mw = medium weak, sh = shoulder. [a]Similar spectra have been observed in DMSO, MeCN, DMF and HMPA with various counterions [10]. [b]This dianion has not been structurally characterised. [c]A red trinuclear nickel carbonyl species has been formulated as $[Ni_3(CO)_8]^{2-}$ purely on the basis of analytical data [13–15]. The formulation of the red–violet $[Ni_3(CO)_x]^{2-}$ dianion by Longoni *et al.*, however, was based on IR data, although the number of carbonyl ligands (x) thought to be associated with this trinuclear species was not stated. Due to the absence of IR data on the putative $[Ni_3(CO)_8]^{2-}$ dianion, no connection has been made here between the two species.

The nickel carbonyl species are most conveniently identified in the reaction solution by their characteristic IR carbonyl stretching absorptions which are collected in Table 1. Changes in cation and solvent for the $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ dianions result in slight variations in the IR 'fingerprints' and other examples of these effects are reported in the literature [10].

In the presence of carbon monoxide (1 atm.*, 25 °C) the $[Ni_6(CO)_{12}]^{2-}$ dianion in THF solution is known to be easily converted into $[Ni_5(CO)_{12}]^{2-}$ according to equilibrium (1) [10].

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

It has been established by FTIR spectroscopic monitoring at standard temperature and pressure, that the pentadecacarbonylheptanickelate(2−) dianion, $[Ni_7(CO)_{15}]^{2-}$, is an important intermediate in the condensation of $Ni(CO)_4$ with $[Ni_6(CO)_{12}]^{2-}$ to give the octadecacarbonylnonanickelate(2−) dianion, $[Ni_9(CO)_{18}]^{2-}$ (eqns. (2) and (3)) [12]. The overall reaction is shown in eqn. (4). The IR stretching absorptions for the $[Ni_7(CO)_{15}]^{2-}$ dianion in MeCN are collected in Table 1.

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

$$[Ni_7(CO)_{15}]^{2-} + 2Ni(CO)_4 \rightleftharpoons [Ni_9(CO)_{18}]^{2-} + 5CO \qquad (3)$$

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

We report here an HPIR study of the reactions of solutions of $[Ni_6(CO)_{12}]^{2-}$ as a function of temperature and under elevated pressures of CO and H_2. In the course of this study we have isolated $[Ni_6(CO)_{12}]^{2-}$ as its PPN^+ salt (where $PPN = N(PPh_3)_2$), the structure of which is compared with that of $[NMe_4]_2[Ni_6(CO)_{12}]$ [16].

Experimental

Instrumental design

High-pressure and high-temperature IR spectroscopic measurements were recorded on a Digilab FTS 20/80 spectrometer. The high-pressure configuration is achieved by the use of a Cylindrical Internal Reflectance (CIRCLE) Accessory (Spectra Tech, Inc.). This consists of a stainless steel cylindrical flow-through CIRCLE cell mounted with an optical bench and base plate assembly and contains a 1/4″ diameter zinc selenide internal reflection crystal along the centre axis of the CIRCLE cell. A pressure gauge was positioned outside the spectrometer so that the internal pressure of the system could be recorded (±0.5 atm.) throughout the experiment. Teflon™ or Kalrez™ 'O'-rings provide a temporary pressure-tight seal between the crystal and the inside of the CIRCLE cell.

The high-temperature configuration involves the use of four 1/8″ diameter heater cartridges within a stainless steel jacket which surrounds the CIRCLE cell, thereby allowing the cell to reach temperatures up to 250 °C. The temperature for the present experiments was set and maintained at 100 ± 1 °C by a thermostat. The temperature is measured using a 'K' type thermocouple. The high temperature jacket is insulated from the CIRCLE optics with a ceramic block.

Spectroscopic measurements

The procedure used in the high-temperature high-pressure (HTHP) experiments was as follows. Prior to each experiment, the CIRCLE cell was charged with dinitrogen (20 atm.) and its position on the baseplate

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*Non-SI units employed: 1 atm. = 101 325 Pa.

TABLE 2. Selected IR absorption frequencies for an MeCN solution initially containing $[PPN]_2[Ni_6(CO)_{12}]$ ($[Ni] = 0.079$ M) under dinitrogen and then under applied pressure of carbon monoxide at 25 and 100 °C

Pressure CO (atm.)	Temperature (°C)	Time (min)[a]	ν(CO) (cm^{-1})	Tentative assignment
0	25	0	1982s, 1810w, 1784m	$[Ni_6(CO)_{12}]^{2-}$
1	25	1	2043w 1981s, 1808w, 1784m	$Ni(CO)_4$ $[Ni_6(CO)_{12}]^{2-}$
20	25	1	2043s 1977m 1922w	$Ni(CO)_4$ $[Ni_5(CO)_{12}]^{2-}$ $[Ni_3(CO)_x]^{2-}$[b]
20	25	15	2043s 1946w, 1922m	$Ni(CO)_4$ $[Ni_3(CO)_x]^{2-}$
20	100	5	2043s	$Ni(CO)_4$

[a] The spectrum was recorded at the stated time interval after a change in pressure or temperature. [b] Where x is unknown, see Table 1, footnote c for an explanation.

was finely adjusted to maximise the IR throughput before a background spectrum was recorded. The CIRCLE cell was then flushed (2 min) with the reactant gas (CO or CO/H_2), the liquid sample (1.5 ml) was injected and the IR spectrum of the sample was recorded. As a consequence of the small cell volume and of the cell design, solutions in the CIRCLE cell were unstirred. The cell was then pressurised with the reactant gas to 20 atm. and several spectra were recorded over various time intervals until there was no further change in the spectrum. The pressurised cell was then heated to 100 °C and several spectra were recorded as described above. After the cell had cooled to room temperature and near atmospheric pressure (2 atm.) its IR spectrum was recorded. In the experiment where CO was the reactant gas, the contents of the CIRCLE cell were removed and stored under dinitrogen. The product solution was analysed by IR spectroscopy in a solution NaCl cell immediately after transfer to an atmosphere of dinitrogen and also 12 h later.

The reported spectra were corrected for solvent absorptions by subtraction of reference spectra of THF or MeCN.

Synthesis

All preparative reactions were carried out in an atmosphere of dinitrogen. Solvents were distilled prior to use; tetrahydrofuran (Merck) was distilled from sodium benzophenone ketyl and acetonitrile (Aldrich) was distilled from calcium hydride. Sodium tetraphenylborate was used as received from Merck. Bis(triphenylphosphine)iminium chloride was prepared in methanol according to the method of Ruff and Schlientz [17]. Carbon monoxide and syngas ($CO/H_2 = 1{:}2$) were supplied by The Commonwealth Industrial Gases Limited (Australia) and were used as received.

Preparation of $[PPN]_2[Ni_6(CO)_{12}]$

A THF solution of $[Ni_6(CO)_{12}]^{2-}$ was added to a saturated solution of PPN^+Cl^- to precipitate $[PPN]_2[Ni_6(CO)_{12}]$. The red crystals were filtered, washed several times with methanol, then dried *in vacuo*. The solution IR spectrum in acetonitrile was recorded in a NaCl cell. The carbonyl stretching absorptions given in Table 2 were in close agreement with the literature values (Table 1) [10]. A crystal of $[PPN]_2[Ni_6(CO)_{12}]$ was structurally characterised by X-ray diffraction.

Preparation of a solution of $[PPN]_2[Ni_6(CO)_{12}]$ in acetonitrile for reaction under CO

A sample of $[PPN]_2[Ni_6(CO)_{12}]$ (0.0462 g, 2.62×10^{-5} mol) was dissolved in acetonitrile (2 ml) and an aliquot of this red solution (1.5 ml, $[Ni] = 0.079$ M) was removed for analysis by high-temperature, high-pressure IR spectrometry with carbon monoxide as the reactant gas as described above. After the CIRCLE cell had returned to room temperature and pressure, the product solution was eluted by flushing with extra acetonitrile (5 ml) and a sample removed for IR analysis (NaCl cell).

Preparation of a solution of $[PPN]_2[Ni_6(CO)_{12}]$ in acetonitrile for reaction under CO/H_2

A sample of $[PPN]_2[Ni_6(CO)_{12}]$ (0.0573 g, 3.25×10^{-5} mol) was dissolved in acetonitrile (2 ml) and an aliquot of this red solution (1.5 ml, $[Ni] = 0.098$ M) was removed for analysis by high-temperature, high-pressure IR spectrometry with syngas as the reactant gas as described above.

Preparation of a solution of $Na_2[Ni_6(CO)_{12}]$ in THF

A solution of $Na[BPh_4]$ (0.0980 g, 2.86×10^{-4} mol) in THF (8 ml) was added to solid $[PPN]_2[Ni_6(CO)_{12}]$ (0.129 g, 7.33×10^{-5} mol) and the suspension was stirred until all of the red $[PPN]_2[Ni_6(CO)_{12}]$ had dissolved. The solution IR spectrum recorded in an NaCl cell confirmed the presence of $[Ni_6(CO)_{12}]^{2-}$ with carbonyl stretching absorptions observed at 1980s, 1815m and 1796m cm^{-1}. A sample of this red solution (1.5 ml, $[Ni] = 0.055$ M) was analysed as described above by high-temperature high-pressure IR spectrometry with syngas as the reactant gas.

Structure determination

X-ray diffraction data were recorded using an Enraf-Nonius CAD4-F diffractometer with Mo Kα radiation, $\lambda = 0.71069$ Å.

Cell constants were determined by a least-squares fit to the θ values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD-4 diffractometer with a graphite monochromator. Data were reduced and Lorentz, polarisation and decomposition corrections were applied using the Enraf-Nonius Structure Determination Package [18]. The structure was solved by direct methods within the SHELXS-86 program [19]. Phenyl groups were refined as rigid planar hexagons (C–C 1.395 Å) with individual isotropic temperature factors. All other non-H atoms were refined anisotropically and H atoms were included at calculated sites (C–H 0.97 Å) with group isotropic thermal parameters. Full-matrix least-squares refinement was carried out using the program SHELXS-76 [20]. Scattering factors and anomalous dispersion corrections for Ni were taken from the International Tables [21], and for all others the values supplied in SHELXS-76 were used. Figure 1 was drawn using the program ORTEP [22].

Crystal data

$C_{84}H_{60}N_2Ni_6O_{12}P_4$, $M = 1765.48$, triclinic, space group, $P\bar{1}$, $a = 13.024(2)$, $b = 13.270(2)$, $c = 13.319(3)$ Å, $\alpha = 81.38(2)$, $\beta = 73.68(2)$, $\gamma = 60.94(2)$, $U = 1931$ Å^3, D_c $(Z = 1) = 1.518$ g cm^{-3}, $F(000) = 902$, μ(Mo Kα) = 15.47 cm^{-1}. $N = 3822$, $N_0 = 1432$, range of hkl $-12 \rightarrow 12$, $-12 \rightarrow 12$, $0 \rightarrow 12$, merging $R = 0.03$, $R = 0.069$, $R_w = 0.066$, $w = 2.37/(\sigma^2F_o + 0.0010F_o^2)$, residual extrema $+0.7$ and -0.5 e Å^3.

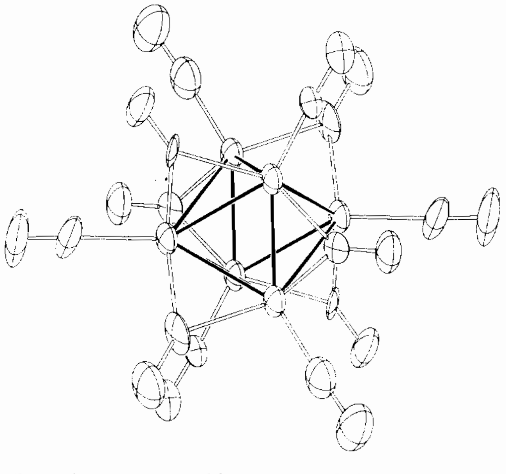


Fig. 1. ORTEP plot (30% probability) of the $[Ni_6(CO)_{12}]^{2-}$ dianion of $[PPN]_2[Ni_6(CO)_{12}]$.

Results and discussion

Comparison of the crystal structure of $[PPN]_2[Ni_6(CO)_{12}]$ with $[NMe_4]_2[Ni_6(CO)_{12}]$ [16]

The gross features of the two dianions are similar as expected. Both dianions adopt an elongated octahedral (or trigonal-antiprismatic) arrangement of their metal atoms. The metal arrangement of the PPN^+ salt can be thought of as two planar $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties with shorter Ni–Ni bond lengths (2.392(5) Å) joined together through longer Ni–Ni interactions (2.789(4) and 2.761(5) Å) (Fig. 1). The corresponding distances quoted for the $[NMe_4]^+$ salt are 2.38 and 2.77 Å, respectively. There are six bridging and six terminal carbonyl ligands in both dianions. The major difference between the two structures is in their crystal symmetry. The dianion with the tetramethylammonium salt has an idealised $\bar{3}2/m$ symmetry whereas the dianion reported in this paper has a centre of symmetry.

HTHP reaction of $[Ni_6(CO)_{12}]^{2-}$ with carbon monoxide

The carbonyl stretching regions of selected spectra obtained by cylindrical internal reflectance (CIR) of an acetonitrile solution of $[PPN]_2[Ni_6(CO)_{12}]$ ($[Ni] = 0.079$ M) before and after pressurising with CO (20 atm.) and heating (100 °C) are shown in Fig. 2. The tentative assignment of the observed absorptions is given in Table 2; these have been made on the basis of comparison with the absorptions reported for known cluster anions which are collected in Table 1. The observed carbonyl absorptions in an NaCl solution cell are given in Table 2; it should be noted that the $[Ni_6(CO)_{12}]^{2-}$ solution was initially under an atmosphere of dinitrogen. However, the CIRCLE cell had been flushed with CO prior to the introduction of the sample. Hence the detection of a small amount of $Ni(CO)_4$ observed in Fig. 2(a) is consistent with the known equilibrium of eqn. (1) where $[Ni_6(CO)_{12}]^{2-}$ is converted into $Ni(CO)_4$ and $[Ni_5(CO)_{12}]^{2-}$ under CO (1 atm.). The $[Ni_5(CO)_{12}]^{2-}$ dianion is not detected until a pressure of CO (20 atm.) is applied as shown in Fig. 2(b). This pressure change is accompanied by the expected predominance of $Ni(CO)_4$. At this stage another reduced species is observed with ν(CO) at 1922 cm^{-1}. HPIR monitoring of the solution over the next 15 min shows the disappearance of absorptions attributed to $[Ni_5(CO)_{12}]^{2-}$ and the distinct presence of a

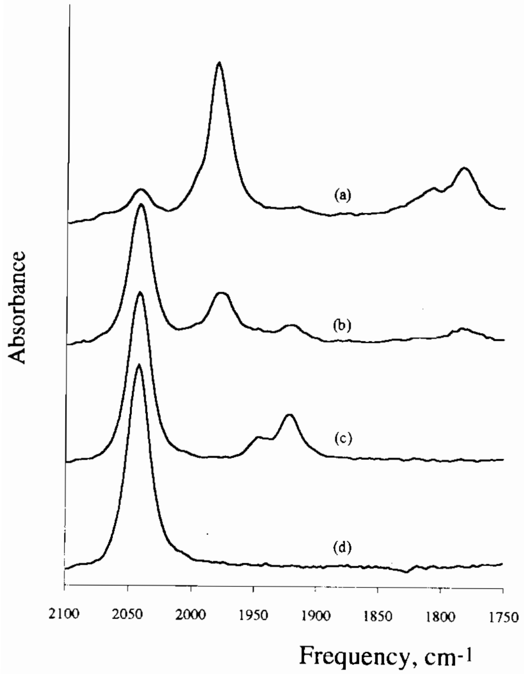


Fig. 2. IR spectra of $[Ni_6(CO)_{12}]^{2-}$ ([Ni] = 0.079 M) in MeCN under: (a) 1 atm. CO, 25°C; (b) 20 atm. CO (1 min), 25 °C; (c) 20 atm. CO (15 min), 25 °C; (d) 20 atm. CO (25 min), 100 °C (5 min).

reduced species as seen in Fig. 2(c). Longoni *et al.* [10] were the first to report the IR absorption bands, collected in Table 1, of a reduced species which they tentatively formulated as an $[Ni_3(CO)_x]^{2-}$ dianion with an undetermined number, x, of presumably terminal carbonyl ligands. The available IR data provide no evidence of the presence of bridging carbonyl ligands although the possibility cannot be excluded since the resonances of bridging ligands may be too weak to be observed at such low concentrations. Although this species has still not been unequivocally characterised, it was originally observed under quite different conditions, for example, when $Ni(CO)_4$ is reduced by sodium sand in the presence of naphthalene or anthracene [10].

Heating the pressurised CIRCLE cell to 100 °C caused the complete disappearance of the absorptions attributed to the reduced species after about 5 min, presumably via oxidation of this species to $Ni(CO)_4$ (Fig. 2(d)). After the cell was allowed to cool to room temperature and near atmospheric pressure of CO (2 atm.), the only $\nu(CO)$ absorption observed in the CIRCLE cell was that of $Ni(CO)_4$. Once the yellow product solution was removed from a carbon monoxide atmosphere, its IR spectrum recorded under dinitrogen in a NaCl cell contained $\nu(CO)$ at 2043s cm^{-1} attributed to $Ni(CO)_4$, and additional resonances at 1978s, 1920w, 1810w and 1781m cm^{-1} assigned to the presence of $[Ni_5(CO)_{12}]^{2-}$. After leaving this solution overnight under dinitrogen it had changed to a red colour and its IR spectrum then contained resonances attributed to $Ni(CO)_4$ (2043s cm^{-1}) and $[Ni_6(CO)_{12}]^{2-}$ (1983s, 1810w and 1785m cm^{-1}). Under one atmosphere of dinitrogen it is known that $[Ni_5(CO)_{12}]^{2-}$ reacts with $Ni(CO)_4$ to form $[Ni_6(CO)_{12}]^{2-}$ and CO according to the equilibrium of eqn. (1). Thus under the present conditions, the overall conversion of $[Ni_6(CO)_{12}]^{2-}$ into $Ni(CO)_4$ was largely reversible.

HTHP reaction of $[PPN]_2[Ni_6(CO)_{12}]$ with syngas ($CO/H_2 = 1:2$)

The tentative assignment of the carbonyl stretching absorptions observed for an MeCN solution of $[PPN]_2[Ni_6(CO)_{12}]$ ([Ni] = 0.098 M) before and after pressurising with syngas (20 atm.) and heating (100 °C) are identical with those given in Table 2 for the same system under applied pressure of CO. The only difference in the IR spectra of the two experiments is that the absorptions attributed to the $[Ni_3(CO)_x]^{2-}$ dianion (1947w and 1922m) are less intense when syngas is the reactant gas. At this lower concentration, the absorption at 1947 cm^{-1} is too weak to observe reliably.

HTHP reaction of $Na_2[Ni_6(CO)_{12}]$ with syngas ($CO/H_2 = 1:2$)

The tentative assignment of the observed absorptions in the carbonyl stretching region of a THF solution prepared from $[PPN]_2[Ni_6(CO)_{12}]$ ([Ni] = 0.055 M) and $Na[BPh_4]$ before and after pressurising with syngas (20 atm.) and heating (100 °C) is given in Table 3. The results of this experiment are very similar to those of the previous two systems in that a solution of $[Ni_6(CO)_{12}]^{2-}$ is converted to $Ni(CO)_4$ via $[Ni_5(CO)_{12}]^{2-}$ and a reduced species, presumably $[Ni_3(CO)_x]^{2-}$, when pressurised with syngas and heated to 100 °C. This system differs from the others in that the PPN^+ salt of $[Ni_6(CO)_{12}]^{2-}$ is insoluble in THF. Addition of $Na[BPh_4]$ resulted in a solution of the dianion in THF. The IR spectrum of this solution both under one atmosphere of dinitrogen and under carbon monoxide (Table 3) contains additional carbonyl resonances which clearly cannot be attributed either to the $[Ni_6(CO)_{12}]^{2-}$ dianion or to $Ni(CO)_4$. The $\nu(CO)$ stretching frequencies at 1995sh and 1946sh cm^{-1} have been tentatively assigned as the $[Ni_7(CO)_{15}]^{2-}$ dianion by comparison with the absorptions reported for this cluster (Table 1). It should be noted that the characteristic resonances reported for $[Ni_7(CO)_{15}]^{2-}$ occurring at 1820sh and 1800ms cm^{-1} are not observed directly in this study due to the overlap of resonances attributed to the $[Ni_6(CO)_{12}]^{2-}$ dianion occurring at 1815m and 1795m cm^{-1}. However, the observed increase in intensity of the resonance at 1815 cm^{-1} (cf. Table 2) can be explained by the presence of $[Ni_7(CO)_{15}]^{2-}$. It is likely

TABLE 3. Selected IR absorption frequencies for a THF solution initially containing $Na_2[Ni_6(CO)_{12}]$ ([Ni] = 0.055 M) under dinitrogen and then under applied pressures of syngas (CO/H_2 = 1:2) at 25 and 100 °C

Pressure CO (atm.)	Temperature (°C)	Time (min)[a]	ν(CO) (cm^{-1})	Tentative assignment
0[b]	25	0	2008sh	unassigned
			1995sh, 1946sh	$[Ni_7(CO)_{15}]^{2-}$
			1981s, 1815m, 1795m	$[Ni_6(CO)_{12}]^{2-}$
			1753w	unassigned
1	25	1	2042s	$Ni(CO)_4$
			1980s, 1808w, 1784m	$[Ni_6(CO)_{12}]^{2-}$
			1993s	$[Ni_7(CO)_{15}]^{2-}$
20	25	1	2042s	$Ni(CO)_4$
			1975m	$[Ni_5(CO)_{12}]^{2-}$
			1959sh	unassigned
			1922w	$[Ni_3(CO)_x]^{2-}$[c]
20	100	5	2042s	$Ni(CO)_4$

[a] The spectrum was recorded at the stated time interval after a change in pressure or temperature. [b] This spectrum was recorded under dinitrogen (1 atm.) in an NaCl cell. [c] Where x is unknown, see Table 1, footnote c for an explanation.

that the new unassigned absorption which appears as a shoulder at 1959 cm^{-1} after the system is pressurised with syngas is a species derived from $[Ni_7(CO)_{15}]^{2-}$ and which is then converted to $Ni(CO)_4$ very soon after heating commences.

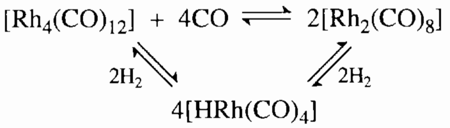
The results presented herein for nickel carbonyl clusters are in contrast with the behaviour reported for the carbonyl clusters of rhodium. For example, $[Rh_4(CO)_{12}]$ is converted to a higher nuclearity cluster, $[Rh_6(CO)_{16}]$, under carbon monoxide pressure at elevated temperatures (>50 °C) [23, 24]. However, on pressurisation with CO or CO/H_2 gas mixtures at low temperatures $[Rh_4(CO)_{12}]$ is also reported to undergo reversible fragmentation to $[Rh_2(CO)_8]$ [24], as shown in eqn. (5). The dirhodium octacarbonyl species is not

$$[Rh_4(CO)_{12}] + 4CO \underset{25\ °C}{\overset{430\ atm.\ CO,\ -19\ °C}{\rightleftharpoons}} 2[Rh_2(CO)_8] \qquad (5)$$

known under normal conditions of temperature and pressure and consequently had proven difficult to characterise. Further fragmentation to the purported mononuclear hydride species $[HRh(CO)_4]$ on pressurisation with CO/H_2 is only observed under extremely high pressures of syngas [25]. This reaction is thought to occur via eqn. (6).

$$[Rh_4(CO)_{12}] + 4CO + 2H_2 \underset{258\text{–}273\ K}{\overset{1522\ atm.\ CO/H_2}{\rightleftharpoons}} 4[RhH(CO)_4] \qquad (6)$$

Recent high-pressure IR studies by Whyman [3] on this system reveal the transient presence, at room temperature, of $[HRh(CO)_4]$ upon addition of dihydrogen to the $[Rh_4(CO)_{12}]/[Rh_2(CO)_8]$ equilibrium mixtures generated under carbon monoxide. Therefore the overall system can be summarised as in Scheme 1 [3].



Scheme 1.

In contrast, under the present conditions we have not detected any IR absorptions attributable to any known nickel hydride or carbide species. There is also no evidence of nickel metal as indicated by the quality of the IR spectra and by observation of the solutions after completion of the experiments.

Conclusions

The reactions of $[Ni_6(CO)_{12}]^{2-}$ in various solvents under applied pressure of CO or CO/H_2 (1:2) and heat (100 °C) ultimately generate $Ni(CO)_4$ as the only product detectable by HPIR spectroscopy. The interconversions under applied pressure alone involve the formation of $Ni(CO)_4$ and the intermediate species $[Ni_5(CO)_{12}]^{2-}$. The pentanuclear cluster is itself converted to a reduced species which has been assigned by Longoni *et al.* as an $[Ni_3(CO)_x]^{2-}$ carbonyl dianion but is otherwise uncharacterised. Another unknown reduced species with a carbonyl stretching absorption at 1959 cm^{-1} is generated when the reaction is carried out in the presence of $Na[BPh_4]$ under applied pressures of syngas. This latter species is also oxidised to $Ni(CO)_4$ upon heating.

The product solution obtained from the reaction of $[Ni_6(CO)_{12}]^{2-}$ in acetonitrile under pressure of CO at 100 °C initially contains $[Ni_5(CO)_{12}]^{2-}$ and $Ni(CO)_4$ as indicated by IR analysis under dinitrogen at room temperature and pressure. After being under dinitrogen overnight, the composition of the product solution changes as the $[Ni_5(CO)_{12}]^{2-}$ dianion is then converted back to the starting material, $[Ni_6(CO)_{12}]^{2-}$. It is assumed that the same reversibility would apply to the syngas systems. Therefore, under the conditions of our experiments, the oxidative fragmentation to $Ni(CO)_4$ is largely reversible. When $[Ni_6(CO)_{12}]^{2-}$ is dissolved in THF as the Na^+ salt, small quantities of $[Ni_7(CO)_{15}]^{2-}$ are also generated in solution.

The relatively slow reaction rates of cluster interconversions under high pressures and heat as compared with reported conversions under ambient conditions may be a consequence of incomplete mixing within the CIRCLE cell.

Supplementary material

Positional parameters of all atoms, thermal parameters, listings of anisotropic thermal parameters, and observed and calculated structure factor amplitudes and tables of bond distances and angles are available from the authors upon request.

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