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Carbonylnickelates. 3. Synthesis and Chemical Characterization of the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3, 4) Clusters

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The hydrolysis of the $[Ni_6(CO)_{12}]^{2-}$ dianion under buffered conditions results in the synthesis of the interstitial hydride derivatives $[Ni_{12}(CO)_{21}H_2]^{2-}$ and $[Ni_{12}(CO)_{21}H]^{3-}$. The two compounds are related by an easily reversible protonation–deprotonation equilibrium. In contrast, deprotonation of $[Ni_{12}(CO)_{21}H]^{3-}$ to the corresponding $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion is possible only under severe conditions. The tetraanion has been obtained as a byproduct of the synthesis of $[Ni_6(CO)_{12}]^{2-}$ by reduction of $Ni(CO)_4$ in KOH-saturated methanolic solution. The $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3, 4) derivatives have been isolated in pure crystalline form with a variety of tetrasubstituted ammonium or phosphonium cations. All these dodecanuclear nickel carbonyl clusters are rapidly degraded by carbon monoxide (25 °C, 1 atm) and possess limited thermal stability. Degradation of $[Ni_{12}(CO)_{21}H_2]^{2-}$ by carbon monoxide in THF solution affords the binuclear hydride derivative $[Ni_2(CO)_6H]^-$ and $Ni(CO)_4$. Degradation of $[Ni_{12}(CO)_{21}H]^{3-}$, in addition to the former products, gives rise to $[Ni_5(CO)_{12}]^{2-}$, which becomes the only product, together with $Ni(CO)_4$, when starting from $[Ni_{12}(CO)_{21}]^{4-}$.

Introduction

The synthesis and structural characterization of $[M_6(CO)_{12}]^{2-}$ (M = Ni, Pt)[1-4] and $[M_9(CO)_{18}]^{2-}$ (M = Ni, Pt)[3-5] established a contact point between nickel and platinum carbonyl cluster chemistry. However, while oxidation of $[Pt_9(CO)_{18}]^{2-}$ afforded a series of inorganic oligomers of general formula $[Pt_3(CO)_6]_n{}^{2-}$ with n ranging from 4 to ca. 10,[3,4] the analogous oxidation of $[Ni_9(CO)_{18}]^{2-}$ resulted in decomposition to $Ni(CO)_4$ and Ni metal.[5] Nevertheless, evidence of the probable existence of higher nuclearity nickel carbonyl clusters was obtained when reacting $[Ni_3(CO)_6]_n{}^{2-}$ (n = 2, 3) with acids.[2,5] Two compounds tentatively formulated on the basis of their elemental analysis as $[Ni_{11}(CO)_{21}H_2]^{2-}$ and $[Ni_8(CO)_{14}H_2]^{2-}$ in a preliminary report[6] were subsequently shown by X-ray and neutron-diffraction studies[7] to be interstitial hydrides of stoichiometry $[Ni_{12}(CO)_{21}H_2]^{2-}$ and $[Ni_{12}(CO)_{21}H]^{3-}$, respectively. An apparently unrelated brown anionic species, isolated as a byproduct of the synthesis of the $[Ni_6(CO)_{12}]^{2-}$ dianion,[2] has been later structurally characterized by X-ray analysis and shown to be the missing $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion.[8]

We report here the synthesis and chemical characterization of this series of isostructural dodecanuclear nickel carbonyl clusters having the general formula $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3, 4).

Results and Discussion

1. Synthesis of $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3) by Hydrolysis of $[Ni_6(CO)_{12}]^{2-}$. The $[Ni_6(CO)_{12}]^{2-}$ dianion has previously been described as stable to hydrolysis because, contrary to the behavior of $[Ni_5(CO)_{12}]^{2-}$, it can be recovered substantially unchanged even after prolonged standing in aqueous solution.[2] However, this apparent stability is probably the result of the drop in H^+ concentration after limited hydrolysis such as that represented in eq 1. In agreement with this suggestion, addition of $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ to deoxygenated water raises the pH of the soluton rapidly to ca. 9–10; after several days of standing the pH is in the range 10–11, and the red color of the solution is unchanged.

$$2[Ni_6(CO)_{12}]^{2-} + H_2O \rightarrow [Ni_{12}(CO)_{21}H]^{3-} + 3CO + OH^- \quad (1)$$

Precipitation of the carbonylnickelates present in solution by addition of tetramethylammonium chloride allows recovery of $[NMe_4]_2[Ni_6(CO)_{12}]$ containing only minor traces of $[NMe_4]_3[Ni_{12}(CO)_{21}H]$. In contrast, addition of $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ to a solution buffered at pH 6–7 with NH_4Cl, or with a mixture of Na_2HPO_4 and NaH_2PO_4, gives an initial red solution, which turns green-brown owing to the formation of significant amounts of $[Ni_{12}(CO)_{21}H]^{3-}$. At pH 7, the transformation according to eq 1 requires about 2 weeks, whereas in slightly acidic conditions (pH 6) it is completed in a couple of days. At pH 6 the yield of $[NMe_4]_3[Ni_{12}(CO)_{21}H]$ is ca. 50–60% owing to formation of $Ni(CO)_4$ and nickel metal as byproducts. Formation of $Ni(CO)_4$ is not surprising since both $[Ni_{12}(CO)_{21}H]^{3-}$ and the parent $[Ni_6(CO)_{12}]^{2-}$ are easily degraded by carbon monoxide at atmospheric pressure, but the concomitant formation of nickel metal indicates that the hydrolysis process is more complicated than represented in eq 1.

The corresponding $[Ni_{12}(CO)_{21}H_2]^{2-}$ dianion has been obtained by hydrolysis of $[Ni_6(CO)_{12}]^{2-}$ under acidic conditions. Thus, addition of dilute phosphoric or sulfuric acid to a stirred aqueous solution of $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ results in the separation of a silky red-violet precipitate, as the pH drops to ca. 3–4. Samples precipitated from different reactions present variable Ni/K ratios ranging from 6 to 9, although they show infrared spectra in methanol solution invariably corresponding to that of $[Ni_{12}(CO)_{21}H_2]^{2-}$. This results from coprecipitation of the potassium and hydronium $[Ni_{12}(CO)_{21}H_2]^{2-}$ salts. The pure hydronium salt has been obtained by extraction into ether. As previously found for the hydronium salt of $[Co_6(CO)_{15}H]^-$,[9] the corresponding hydronium salt of $[Ni_{12}(CO)_{21}H_2]^{2-}$ in the solid state shows a limited stability and when it stands under nitrogen it decomposes to a mixture of $Ni(CO)_4$ and nickel metal. In contrast the tetrasubstituted ammonium or phosphonium salts of $[Ni_{12}(CO)_{21}H_2]^{2-}$ are indefinitely stable under nitrogen both in the solid state and in solution. The $[Ni_{12}(CO)_{21}H_2]^{2-}$ dianion is also the final product of the controlled protonation of $[Ni_6(CO)_{12}]^{2-}$ with dilute H_3PO_4 and H_2SO_4 either in methanol or in THF. Monitoring by IR and ^1H NMR under these experimental conditions shows that the

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Table I. Infrared Carbonyl Absorption Frequencies (±5 cm^{-1}) of the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ ($n = 2, 3, 4$) Anions

compd	color	solvent	ν_{CO}
$[Ni_{12}(CO)_{21}]^{4-}$	brown	CH_3CN	1980 (s), 1800 (s)
$[Ni_{12}(CO)_{21}H]^{3-}$	green-brown	CH_3CN	1990 (s), 1830 (s)
		CH_3OH	2005 (s), 1830 (s)
$[Ni_{12}(CO)_{21}H_2]^{2-}$	red-violet	THF	2020 (s), 1985 (mw), 1865 (s), 1860 (s)
		CH_3OH	2030 (s), 1990 (mw), 1870 (s)

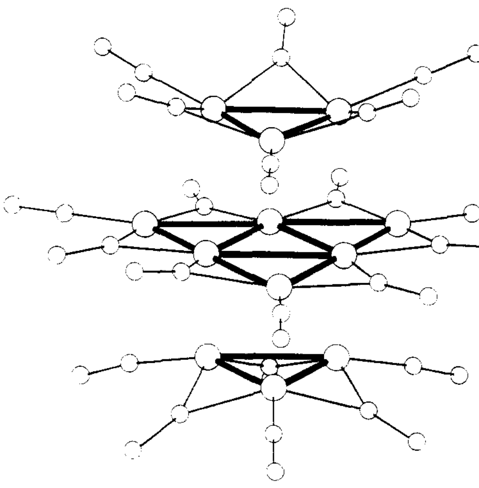

Figure 1. Schematic representation of the structure of the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3,[7] 4[8]) anions.

reaction of $[Ni_6(CO)_{12}]^{2-}$ with acids is more complicated than represented in eq 1 and apparently occurs through the sequence of reactions given by eq 2–4. Reactions 2 and 3 probably

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

$$2[Ni_9(CO)_{18}]^{2-} + H^+ \rightarrow [Ni_{12}(CO)_{21}H]^{3-} + 3Ni(CO)_4 + 3Ni + 3CO \quad (3)$$

$$[Ni_{12}(CO)_{21}H]^{3-} + H^+ \rightleftarrows [Ni_{12}(CO)_{21}H_2]^{2-} \quad (4)$$

result from facile redox condensation processes[6] between the starting material and a more oxidized species generated in solution by protonation. If the reaction is carried out in methanol by stepwise addition of acetic acid (rather than H_3PO_4 or H_2SO_4) and is monitored by IR, the hydrolysis of $[Ni_6(CO)_{12}]^{2-}$ is limited mainly to reaction 2. The subsequent condensation reaction (3) has also been observed by reacting preformed $[Ni_9(CO)_{18}]^{2-}$ with dilute H_2SO_4 in THF, although it is difficult to stop protonation at $[Ni_{12}(CO)_{21}H]^{3-}$ in the presence of strong acids owing to equilibrium 4. Addition of too large an excess of acid results in complete decomposition to $Ni(CO)_4$ and Ni^{2+} salts. It is conceivable that the above sequence of reactions may also be responsible for the formation of $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3) in aqueous solution, as suggested by the formation of nickel metal and $Ni(CO)_4$ also under those experimental conditions.

The synthesis of both $[Ni_{12}(CO)_{21}H]^{3-}$ and $[Ni_{12}(CO)_{21}H_2]^{2-}$ has also been carried out in one step starting from $Ni(CO)_4$. The tetracarbonylnickel is reduced with potassium hydroxide in dimethylformamide (DMF) or dimethyl sulfoxide (Me_2SO) to a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$, and the resulting solutions are quenched with water to convert the former into the latter, as previously described.[2] $[Ni_{12}(CO)_{21}H]^{3-}$ is then obtained by buffering these solutions at pH 6–7, whereas the alkali and hydronium salts of $[Ni_{12}(CO)_{21}H_2]^{2-}$ are coprecipitated by addition with stirring of acid down to pH 3–4. The low solubility in acidic water of both the potassium and hydronium salts of $[Ni_{12}(CO)_{21}H_2]^{2-}$ makes this anion more readily and selectively available. Therefore, $[Ni_{12}(CO)_{21}H]^{3-}$ may also be conveniently synthesized by complete hydrolysis of $[Ni_6(CO)_{12}]^{2-}$ to $[Ni_{12}(CO)_{21}H_2]^{2-}$, followed by deprotonation of the latter with alkali hydroxides in methanol or potassium *tert*-butoxide in acetone.

Both $[Ni_{12}(CO)_{21}H_2]^{2-}$ and $[Ni_{12}(CO)_{21}H]^{3-}$ have also been isolated in the solid state by addition of excess tetrasubstituted ammonium, phosphonium, or arsonium halides to their aqueous or methanolic solutions. All their salts are generally very soluble in polar organic solvents, but in some cases, limited stability has been observed (see later). For this reason the $[Ni_{12}(CO)_{21}H_2]^{2-}$ salts have been exclusively crystallized from acetone–isopropyl alcohol or THF–toluene, whereas the corresponding $[Ni_{12}(CO)_{21}H]^{3-}$ salts have been crystallized from either acetone–isopropyl alcohol or acetonitrile–diisopropyl ether.

A schematic drawing of the structure of $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3, 4)[7,8] is shown in Figure 1. The pattern of the infrared spectra of these anions shows only minor modifications on changing either the counterion or the solvent. The infrared data are collected in Table I. The proton NMR spectra of the mono- and dihydride derivatives show sharp high-field resonances at τ 34.2 and 28.3, respectively, which are invariant on changing the temperature from +40 to −80 °C. Integration of these resonances with respect to the signal of the cation (see Experimental Section) gives a ca. 1:3 and 1:1 ratio, respectively. It is worth noting that the hydride atom of $[Ni_{12}(CO)_{21}H]^{3-}$ is probably fluxional and rapidly migrates at least within the two octahedral cavities, as suggested by the equivalence of the outer carbonyl groups in the ^{13}C NMR spectrum.[10]

2. Synthesis of $[Ni_{12}(CO)_{21}]^{4-}$. The $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion has been obtained as a byproduct of the synthesis of $[Ni_6(CO)_{12}]^{2-}$ from $Ni(CO)_4$ and potassium hydroxide in methanol.[2] Thus, reduction of $Ni(CO)_4$ with KOH-saturated methanolic solution under a nitrogen atmosphere over a period of 36–48 h results in a red-brown suspension. The solution generally contains a variable mixture of $[Ni_5(CO)_{12}]^{2-}$, $[Ni_6(CO)_{12}]^{2-}$, and minor amounts of $[Ni_{12}(CO)_{21}]^{4-}$. Removal of the methanol followed by dissolution of the residue in water results in a nearly complete conversion of $[Ni_5(CO)_{12}]^{2-}$ into $[Ni_6(CO)_{12}]^{2-}$.[2] $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_{12}(CO)_{21}]^{4-}$ may be then separated owing to differential solubilities of their potassium salts in water and of their tetrasubstituted ammonium salts in polar organic solvents such as THF and acetone. Thus, most of the $[Ni_6(CO)_{12}]^{2-}$ dianion may be precipitated out from the aqueous solution by saturation with KBr, while $[Ni_{12}(CO)_{21}]^{4-}$ precipitates out only on addition of a bulkier cation such as tetramethylammonium. $[NMe_4]_4[Ni_{12}(CO)_{21}]$ has been further purified by extracting the last traces of $[NMe_4]_2[Ni_6(CO)_{12}]$ with acetone and has been crystallized from acetonitrile–diisopropyl ether. Under these experimental conditions the yield of $[NMe_4]_4[Ni_{12}(CO)_{21}]$ calculated on the starting $Ni(CO)_4$ never exceeds ca. 5%. Exhaustive reduction of $Ni(CO)_4$ in an attempt to increase the yield results in complete decomposition. The $[NMe_4]_4[Ni_{12}(CO)_{21}]$ salt is sparingly soluble or insoluble in most organic solvents such as alcohols, THF, acetone, and ethers and is fairly soluble in acetonitrile and Me_2SO.

The $[Ni_{12}(CO)_{21}]^{4-}$ tetraanion is readily protonated by acids to the corresponding mono- and dihydride derivatives, according to the right-hand side of equilibria 4 and 5, both in

$$[Ni_{12}(CO)_{21}]^{4-} + H^+ \rightleftarrows [Ni_{12}(CO)_{21}H]^{3-} \quad (5)$$

aqueous solution and in organic solvents. In contrast, deprotonation of $[N_{12}(CO)_{21}H]^{3-}$ to $[Ni_{12}(CO)_{21}]^{4-}$ is not ob-

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[10] Longoni, G.; Heaton, B. T.; Chini, P. *J. Chem. Soc., Dalton Trans.* **1980**, 1537–1541.

tained even by saturated methanol solutions of alkali-metal hydroxides. Low yields of $[Ni_{12}(CO)_{21}]^{4-}$ (ca. 10%) have been obtained only by working in highly ionizing solvents such as DMF or Me_2SO and in the presence of an excess of strong bases such as potassium *tert*-butoxide. However, concomitant degradation of $[Ni_{12}(CO)_{21}H]^{3-}$ to $[Ni_6(CO)_{12}]^{2-}$ and yet unknown species make rather difficult the subsequent separation and purification of the $[Ni_{12}(CO)_{21}]^{4-}$ salts. As a result this two-step synthesis of $[Ni_{12}(CO)_{21}]^{4-}$ is hardly an improvement over the original procedure. It should be noted that a similar Brønsted acid–base chemistry has been previously reported for other transition-metal carbonyl clusters.[6]

It may be argued that condensation of $[Ni_6(CO)_{12}]^{2-}$ to $[Ni_{12}(CO)_{21}H]^{3-}$, as represented in eq 1, and subsequent deprotonation of the latter to $[Ni_{12}(CO)_{21}]^{4-}$ provide a possible pathway for the formation of the tetraanion in the original procedure. However, this appears unlikely in view of the stability of $[Ni_6(CO)_{12}]^{2-}$ in alkaline conditions and the resistance to deprotonation of $[Ni_{12}(CO)_{21}H]^{3-}$. It is more conceivable that $[Ni_{12}(CO)_{21}]^{4-}$ results from a redox condensation process induced by nucleophilic attack of OR^- (R = H, CH_3) onto a nickel carbonyl anionic species present in solution, e.g. $[Ni_9(CO)_{18}]^{2-}$, $[Ni_6(CO)_{12}]^{2-}$, or $[Ni_5(CO)_{12}]^{2-}$.

Although thermal decomposition is a well-documented synthetic route to higher nuclearity clusters,[6] attempts to synthesize the $[Ni_{12}(CO)_{21}]^{4-}$ salts by thermally induced condensation of $[Ni_6(CO)_{12}]^{2-}$, according to eq 6, were not

$$2[Ni_6(CO)_{12}]^{2-} \not\rightarrow [Ni_{12}(CO)_{21}]^{4-} + 3CO \qquad (6)$$

successful even under UV radiation and/or a continuous flow of nitrogen. At temperatures above 120 °C complete decomposition to $Ni(CO)_4$ and nickel metal was observed.

3. Chemical Behavior of the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3, 4) Anions. The salts of the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2, 3, 4) anions are air sensitive both in solution and in the solid state; air oxidation results in decomposition to nickel carbonate and some $Ni(CO)_4$. The two hydride derivatives $[Ni_{12}(CO)_{21}H_2]^{2-}$ and $[Ni_{12}(CO)_{21}H]^{3-}$ also display a limited thermal stability both in solution and in the solid state, $[Ni_{12}(CO)_{21}H]^{3-}$ being the most stable. Thus, $[Ni_{12}(CO)_{21}H_2]^{2-}$ in THF solution is readily converted into $[Ni_9(CO)_{18}]^{2-}$ according to eq 7, on

$$4[Ni_{12}(CO)_{21}H_2]^{2-} \xrightarrow[50\text{–}60\,°C]{THF} 4[Ni_9(CO)_{18}]^{2-} + 3Ni(CO)_4 + 9Ni + 4H_2 \qquad (7)$$

warming at 50–60 °C. Analogously, the $[Ni_{12}(CO)_{21}H]^{3-}$ monohydride derivative 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 (8).

$$4[Ni_{12}(CO)_{21}H]^{3-} \xrightarrow[80\text{–}90\,°C]{CH_3CN} 6[Ni_6(CO)_{12}]^{2-} + 3Ni(CO)_4 + 9Ni + 2H_2 \qquad (8)$$

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 in nickel metal and $Ni(CO)_4$ at temperatures above 120 °C. The lability of these compounds is also shown by their decomposition reactions in certain solvents at room temperature and under strict anaerobic conditions. Thus, $[Ni_{12}(CO)_{21}H_2]^{2-}$ is stable in alcohols, acetone, and THF but cannot be handled in solvents such as acetonitrile, DMF, and Me_2SO owing to concomitant autodeprotonation and autodecomposition reactions, which afford a mixture of $Ni(CO)_4$, $[Ni_{12}(CO)_{21}H]^{3-}$, and yet uncharacterized species. All the reactions described above are generally not affected by the counterion; in contrast the stability of $[Ni_{12}(CO)_{21}H]^{3-}$ may depend on the countercation. For example, its tetrabutylammonium salt is stable in most organic solvents (alcohols, acetone, THF, acetonitrile, DMF, and Me_2SO), while several other salts, e.g. NMe_4^+, PPh_4^+, $AsPh_4^+$, and $N(PPh_3)_2^+$, on dissolution in THF at room temperature disproportionate according to the apparent stoichiometry (9).

$$2[Ni_{12}(CO)_{21}H]^{3-} \xrightarrow[25\,°C]{THF} [Ni_9(CO)_{18}]^{2-} + 2[Ni_6(CO)_{12}]^{2-} + 3Ni + H_2 \qquad (9)$$

The disproportionation reaction (9) is probably induced by precipitation of the corresponding $[Ni_6(CO)_{12}]^{2-}$ salts, leaving essentially $[Ni_9(CO)_{18}]^{2-}$ in solution. As a result reaction 9, as well as reaction 7, represents an alternate synthesis of $[Ni_9(CO)_{18}]^{2-}$, which has been previously isolated by oxidation of $[Ni_6(CO)_{12}]^{2-}$ with $Ni(EtOH)_xCl_2$.[5]

In agreement with the behavior of most nickel carbonyl anionic compounds so far characterized,[2,5] and in keeping with a Ni–Ni bond energy low in comparison with the Ni–CO bond energy,[6] all three dodecanuclear clusters are rapidly and irreversibly degraded by carbon monoxide at atmospheric pressure and at room temperature according to the eq 10–12,

$$[Ni_{12}(CO)_{21}]^{4-} + 11CO \rightarrow 2[Ni_5(CO)_{12}]^{2-} + 2Ni(CO)_4 \qquad (10)$$

$$[Ni_{12}(CO)_{21}H]^{3-} + 17CO \rightarrow [Ni_5(CO)_{12}]^{2-} + [Ni_2(CO)_6H]^- + 5Ni(CO)_4 \qquad (11)$$

$$[Ni_{12}(CO)_{21}H_2]^{2-} + 23CO \rightarrow 2[Ni_2(CO)_6H]^- + 8Ni(CO)_4 \qquad (12)$$

respectively, as shown by IR and NMR monitoring. It may be speculated that formation of $[Ni_5(CO)_{12}]^{2-}$ in reaction 10 is probably the result of the extreme reactivity of more reduced carbonyl species toward $Ni(CO)_4$ and/or trace amounts of oxygen or moisture.[2] Reaction 12 represents the most reproducible synthesis so far available for the colorless dinuclear $[Ni_2(CO)_6H]^-$ anion, which has been previously characterized by X-ray crystallography.[11]

Both $[Ni_{12}(CO)_{21}H_2]^{2-}$ and $[Ni_{12}(CO)_{21}H]^{3-}$ are stable under a hydrogen atmosphere. However, when hydrogen is replaced by deuterium, proton NMR monitoring shows the disappearance of the hydride signals over a period of 24 h. The signals can be restored to their original intensities by putting the solution back under a hydrogen atmosphere. Despite the occurrence in solution of equilibrium 13 at atmospheric

$$[Ni_{12}(CO)_{21}H_{4-n}]^{n-} \underset{H_2}{\overset{D_2}{\rightleftarrows}} [Ni_{12}(CO)_{21}D_{4-n}]^{n-} \qquad (13)$$
$$n = 2, 3$$

pressure, neither hydrogenation nor hydroformylation of 1-pentene has been observed, even under hydrogen pressure (50 atm). Like most nickel carbonyl anions, these dodecanuclear clusters are precursors for acetylene polymerization catalysts.[12]

Attempts to oxidize the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ derivatives with oxygen, iodine, or Ni(II) salts under controlled conditions result in complete decomposition with no detectable intermediate by IR analysis. In contrast, when Ag^+ salts ($AgNO_3$, $AgBF_4$) are used as oxidizing agents, the following intermediate equilibrium has been observed:

$$[Ni_{12}(CO)_{21}H_{4-n}]^{n-} + Ag(S)_x^+ \rightleftarrows [(S)_xAgNi_{12}(CO)_{21}H_{4-n}]^{(n-1)-} \qquad (14)$$

S = solvent
n = 2, green, ν_{CO} 2050 (s), 1885 (s) cm^{-1}
n = 3, green-brown, ν_{CO} 2020 (s), 1840 (s) cm^{-1}

Owing to the need of excess Ag^+ salts to shift the equilibrium

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(11) Longoni, G.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1979**, *174*, C41–C44.

(12) Ceriotti, A.; Longoni, G.; Chini, P. *J. Organomet. Chem.* **1979**, *174*, C27–C28.

(14) to the right with subsequent decomposition to silver and nickel metal as well as $Ni(CO)_4$, these silver adducts have not been further investigated. A reaction similar to (14) has been previously observed on starting from $[Ni_9(CO)_{18}]^{2-}$ and $[Rh_6C(CO)_{15}]^{2-}$.[5,13] The analogous reaction of $[Rh_6C(CO)_{15}]^{2-}$ with Cu^+ salts afforded $(CH_3CN)_2Cu_2Rh_6C(CO)_{15}$, which has been isolated and structurally characterized by X-ray diffraction.[14]

4. Concluding Remarks. In view of the previously suggested similarity between $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_4(CO)_9]^{2-}$,[2] it may be speculated that the $[Ni_{12}(CO)_{21}H]^{3-}$ trianion here reported corresponds to the $[Ni_4(CO)_9H]^-$ reported in the literature;[15] the analytical results reported for the two compounds are in good agreement, and their synthesis and reported chemical behavior are similar. However, in the absence of spectroscopic data for the purported $[Ni_4(CO)_9H]^-$ anion it is difficult to substantiate this suggestion.

Experimental Section

Owing to the well-known toxicity of $Ni(CO)_4$, all the operations were carried out under a hood in a well-ventilated room. All the reactions were performed under nitrogen in purified and deoxygenated solvents. During the reduction of $Ni(CO)_4$, all the reaction vessels were equipped with a condenser cooled at −30 °C to minimize losses of $Ni(CO)_4$ due to the stripping action of the evolving carbon monoxide. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer using calcium fluoride cells. The proton NMR spectra were recorded on a Varian XL-60 instrument. The analytical data were obtained by following the procedures given elsewhere.[2]

1. Synthesis of $[PPh_4]_2[Ni_{12}(CO)_{21}H_2]$ from $Ni(CO)_4$. $Ni(CO)_4$ (5 mL) and NaOH (1.5 g) in dimethyl sulfoxide (20 mL) were stirred 12 h under a nitrogen atmosphere. The resulting yellow-brown solution was cooled at 0 °C and quenched with water (50 mL). After 3 h of standing, phosphoric acid (20%, 5 mL) was added dropwise to the solution with vigorous stirring. The resulting silky violet precipitate was filtered off, washed with acidified water, and dried in vacuo. The solid was extracted into methanol (30 mL) and $[Ni_{12}(CO)_{21}H_2]^{2-}$ precipitated by dropwise addition of tetraphenylphosphonium chloride (2 g) in methanol (10 mL) and water. The resulting microcrystalline precipitate was filtered, washed with isopropyl alcohol, and crystallized either from acetone–isopropyl alcohol or from THF–toluene to give 3.4 g of $[PPh_4]_2[Ni_{12}(CO)_{21}H_2]$. Anal. Calcd: PPh_4, 34.37; Ni, 35.71; CO, 29.81; PPh_4:Ni:CO:H = 1:6:10.5:1. Found: PPh_4, 34.9; Ni, 35.3; CO, 28.7; PPh_4:Ni:CO:H = 1:5.84:9.98:0.94.[16] The corresponding $[NMe_4]^+$, $[NMe_3CH_2Ph]^+$, $[AsPh_4]^+$, and $[N(PPh_3)_2]^+$ salts have been analogously synthesized and crystallized.

2. Synthesis of $[PPh_3CH_2Ph]_2[Ni_{12}(CO)_{21}H_2]$ from $K_2[Ni_6(CO)_{12}]\cdot xH_2O$. $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ (1.72 g) was dissolved in deaerated water (25 mL) to give a deep red solution. Phosphoric acid (20%, 3 mL) was added dropwise to the solution with vigorous stirring. The resulting silky violet precipitate of $K_2[Ni_{12}(CO)_{21}H_2]\cdot xH_2O$ was filtered off and immediately extracted with methanol (20 mL). Addition of excess triphenylbenzylphosphonium chloride and water resulted in a microcrystalline precipitate of $[PPh_3CH_2Ph]_2[Ni_{12}(CO)_{21}H_2]$, which was recrystallized from THF–toluene; yield 1.2 g. Anal. Calcd: PPh_3CH_2Ph, 35.3; Ni, 35.2; CO, 29.4; PPh_3CH_2Ph:Ni:CO:H = 1:6:10.5:1. Found: PPh_3CH_2Ph, 34.5; Ni, 31.4; CO 27.3; PPh_3CH_2Ph:Ni:CO:H = 1:5.48:9.97:0.98.[16]

3. Synthesis of $[PPh_4]_3[Ni_{12}(CO)_{21}H]\cdot CH_3COCH_3$ from $Ni(CO)_4$. $Ni(CO)_4$ (5 mL) and NaOH (1.3 g) in dimethyl sulfoxide (20 mL) were stirred 12 h under a nitrogen atmosphere. The resulting yellow-brown solution was filtered, quenched with water (50 mL) with stirring at 0 °C, and buffered with a solution of NH_4Cl (3.5 g) in water (40 mL). During 72 h under nitrogen the solution rapidly turned red and then slowly green-brown. The solution was filtered, and $[Ni_{12}(CO)_{21}H]^{3-}$ was precipitated by addition of tetraphenylphosphonium chloride (1.5 g) in methanol (5 mL). The resulting brown precipitate was filtered off, washed with water and 2-propanol, and dried in vacuo. The solid was crystallized from acetone–isopropyl alcohol to give 4.2 g of $[PPh_4]_3[Ni_{12}(CO)_{21}H]\cdot CH_3COCH_3$. Anal. Calcd: PPh_4, 42.94; Ni, 29.73; CO, 24.83; PPh_4:Ni:CO:H = 1:4:7:0.33. Found: PPh_4, 41.5; Ni, 28.6; CO, 24.3; PPh_4:Ni:CO:H = 1:3.98:7.08:0.4.[16] The corresponding $[NMe_3CH_2Ph]^+$, $[PPh_3CH_2Ph]^+$, $[AsPh_4]^+$, and $[N(PPh_3)_2]^+$ salts have been analogously synthesized and crystallized.

4. Synthesis of $[NMe_4]_3[Ni_{12}(CO)_{21}H]$ from $[NMe_4]_2[Ni_{12}(CO)_{21}H_2]$. $[NMe_4]_2[Ni_{12}(CO)_{21}H_2]$ (1.2 g) was suspended in a solution of NaOH (0.5 g) in methanol (25 mL). The solution was vigorously stirred under a nitrogen atmosphere for 6 h. $[NMe_4]_3[Ni_{12}(CO)_{21}H]$ was precipitated quantitatively from the resulting green-brown suspension by the addition with stirring of tetramethylammonium chloride (1 g) and water (20 mL). The resulting microcrystalline brown precipitate was filtered off, washed with a mixture of methanol and water (1:3, 20 mL), and dried thoroughly in vacuo; yield 1.15 g.

5. Synthesis of $[NMe_4]_4[Ni_{12}(CO)_{21}]\cdot CH_3CN$ from $Ni(CO)_4$. $Ni(CO)_4$ (8 mL) was added to a solution of KOH (15 g) in methanol (60 mL), and the solution was stirred 48 h under a nitrogen atmosphere. The resulting deep red suspension was evaporated under vacuum to dryness, and the residue was suspended in water (50 mL) and filtered. The $[Ni_6(CO)_{12}]^{2-}$ dianion present in the resulting deep red solution was precipitated quantitatively by addition with stirring of solid KBr (20 g) and further removal in vacuo of the last traces of methanol. The red microcrystalline precipitate of $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ was removed by filtration, and the resulting dark brown solution was treated with tetramethylammonium chloride (1 g) in water (10 mL). The resulting brown precipitate of $[NMe_4]_4[Ni_{12}(CO)_{21}]$ was filtered off, washed with water (30 mL), and dried in vacuo. The compound is unsoluble or sparingly soluble in methanol, isopropanol, THF, and acetone, and subsequent extractions with small portions of these solvents were used to eliminate the last traces of $[NMe_4]_2[Ni_6(CO)_{12}]$. The compound is fairly soluble in acetonitrile and Me_2SO, and well-shaped crystals of $[NMe_4]_4[Ni_{12}(CO)_{21}]\cdot CH_3CN$ were obtained by slow diffusion of diisopropyl ether into its acetonitrile solution; yield 0.43 g. Anal. Calcd: NMe_4, 18.17; Ni, 43.23; CO 36.08; NMe_4:Ni:CO = 1:3:5.25. Found: NMe_4, 18.5; Ni, 43.7; CO, 35.7; NMe_4:Ni:CO = 1:2.98:5.1.

6. Synthesis of $[NMe_4]_4[Ni_{12}(CO)_{21}]$ from $[NMe_4]_3[Ni_{12}(CO)_{21}H]$. $[NMe_4]_3[Ni_{12}(CO)_{21}H]$ (1.77 g) was dissolved in anhydrous Me_2SO (20 mL) in a two-necked round-bottomed flash equipped with a microburet filled with a solution of potassium *tert*-butoxide (1.3 g) in Me_2SO (10 mL). Dropwise addition with stirring of this solution was stopped when IR monitoring showed the disappearance of the absorptions due to $[Ni_{12}(CO)_{21}H]^{3-}$. Addition with stirring of excess tetramethylammonium chloride and water (40 mL) afforded a brown precipitate, which was filtered, washed with water (20 mL), and dried. The precipitate was washed with acetone until the filtering solution became colorless. The residue was dissolved in acetonitrile and reprecipitated by addition of ether to give 0.33 g of crude $[NMe_4]_4[Ni_{12}(CO)_{21}]$.

7. Reaction of $[N(PPh_3)_2]_2[Ni_{12}(CO)_{21}H_2]$ with Carbon Monoxide. Synthesis of $[N(PPh_3)_2][Ni_2(CO)_6H]$. $[N(PPh_3)_2]_2[Ni_{12}(CO)_{21}H_2]$ (2.1 g) was dissolved in THF (30 mL) under a carbon monoxide atmosphere. The initially red-violet solution turned rapidly colorless upon 2 h of stirring. The solution was evaporated to dryness under vacuum, and the residue was dissolved in anhydrous THF (10 mL) under carbon monoxide and precipitated by addition of *n*-heptane (30 mL) to give 0.51 g of $[N(PPh_3)_2][Ni_2(CO)_6H]$ as colorless microcrystals.

Registry No. $[PPh_4]_2[Ni_{12}(CO)_{21}H_2]$, 68169-42-6; $[PPh_3CH_2Ph]_2[Ni_{12}(CO)_{21}H_2]$, 85151-86-6; $[PPh_4]_3[Ni_{12}(CO)_{21}H]$, 85151-87-7; $[NMe_4]_3[Ni_{12}(CO)_{21}H]$, 85151-88-8; $[NMe_4]_4[Ni_{12}(CO)_{21}]$, 85151-89-9; $[N(PPh_3)_2][Ni_2(CO)_6H]$, 71520-91-7; $[NMe_4]_2[Ni_{12}(CO)_{21}H_2]$, 71456-74-1; $Ni(CO)_4$, 13463-39-3; $K_2[Ni_6(CO)_{12}]$, 60464-09-7.

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(16) By integration of the hydride signal with respect to the cation signal in the proton NMR spectrum.