Inorg. Chem. **1985**, *24*, 117–120

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Nickel Carbide Carbonyl Clusters. Synthesis and Structural Characterization of $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$

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Received April 30, 1984

Several carbide carbonyl clusters of group 8 transition metals (Fe, Ru, Os, Co, and Rh)[1,2] and rhenium[3] have been reported. In contrast, there has been no report of carbide carbonyl clusters of metals of the nickel subgroup other than mixed-metal derivatives such as $[Fe_4Ni_2(CO)_{14}C]^{2-}$,[4] $Fe_5Ni(CO)_{16}C$,[4] $[Fe_5Ni(CO)_{15}C]^{2-}$,[4] $Fe_5Pd(CO)_{16}C$,[4] $[Fe_5Pt(CO)_{15}C]^{2-}$,[5] and $[Co_3Ni_9(CO)_{20}C]^{3-}$.[5,6] The absence in the literature of nickel carbide carbonyl clusters was rather surprising, considering the existence of a Ni_3C bulk phase.[1]

Known methods for introducing a carbide atom in a metal cluster involve either the thermally induced disproportionation of a coordinated carbon monoxide group or the reaction of a small organic molecule, such as CCl_4, $CHCl_3$, or CS_2, with a neutral or anionic cluster.[1,2] More recently, cleavage under mild conditions of dual-coordinated CO has been applied to the synthesis of cobalt and iron carbide clusters.[5,7,8]

Thermal treatment of nickel carbonyl anions was inconclusive, probably because of decomposition to $Ni(CO)_4$ and Ni metal at temperatures well below those generally necessary to achieve thermally induced disproportionation of coordinated carbon monoxide.[9] On the contrary, an investigation of the reaction of $[Ni_6(CO)_{12}]^{2-}$ with CCl_4 resulted in isolation of the first nickel carbide clusters, namely the $[Ni_{10}(CO)_{18}C]^{2-}$, $[Ni_9(CO)_{17}C]^{2-}$, and $[Ni_8(CO)_{16}C]^{2-}$ dianions; the latter two compounds have been structurally characterized by X-ray diffraction studies.

Experimental Section

All the operations were carried out under a well-ventilated hood owing to the high toxicity of $Ni(CO)_4$ and carbon monoxide. Syntheses were performed under inert atmosphere with standard Schlenk equipment. Analyses were obtained as previously described.[9]

1. Synthesis of $[NBu_4]_2[Ni_9(CO)_{17}C]$. $[NBu_4]_2[Ni_6(CO)_{12}]$ (2.2 g) was suspended in tetrahydrofuran (40 mL) under a nitrogen atmosphere. A solution of CCl_4 in THF (5.5 mL, 0.17 M) was added dropwise over a period of 3 h, while the suspension was rapidly stirred. The resulting red-brown solution was evaporated to dryness, and the residue was suspended in methanol (40 mL). Precipitation of $[NBu_4]_2[Ni_9(CO)_{17}C]$ was completed by addition of $[NBu_4]Br$ (1 g) in water (10 mL). The precipitate was filtered, washed with water and 2-propanol, and dried under vacuum overnight. Yield: 1.5 g (79.9% based on Ni). The salt is soluble in THF, acetone, and acetonitrile and sparingly soluble or insoluble in alcohols, water, and nonpolar solvents. Crystals were obtained by dissolving the precipitate in THF and precipitating with cyclohexane.

Anal. Calcd for $[NBu_4]_2[Ni_9(CO)_{17}C]$: $[NBu_4]^+$, 32.26; Ni, 35.21; CO, 31.73; $[NBu_4]^+$:Ni:CO = 1:4.5:8.5. Found: $[NBu_4]^+$, 32.7; Ni, 35.0; $[NBu_4]^+$:Ni = 1:4.41. Infrared carbonyl absorptions in THF: 2000 (s), 1855 (ms), 1800 (m, br) cm^{-1}.

Table I. Crystallographic Data for $[NBu_4]_2[Ni_8(CO)_{16}C]$ and $[NBu_4]_2[Ni_9(CO)_{17}C]$

formula	$[NBu_4]_2[Ni_8(CO)_{16}C]$	$[NBu_4]_2[Ni_9(CO)_{17}C]$
mol wt	1414.8	1501.5
cryst system	tetragonal	tetragonal
space group	*P*4/*nnc* (No. 126) from systematic absences	*P*4*nc* (No. 104) after refinement
a, Å	13.664 (4)	14.115 (3)
c, Å	17.013 (6)	16.195 (4)
V, Å³	3176 (3)	3227 (3)
Z	2	2
D_{calcd}, $g \cdot cm^{-3}$	1.48	1.55
cryst size, mm	0.20 × 0.30 × 0.35	0.20 × 0.25 × 0.35
μ(Mo Kα), cm^{-1}	23.9	26.4
reciprocal space explored	$+h,+k,\pm l$ (with $h \leqslant k$)	$+h,+k,\pm l$ (with $h \leqslant k$)
2θ range, deg	6–46	6–48
no. of reflcns measd	2496	3105
no. of unique data used ($I \geqslant 3\sigma(I)$)	552	1330
scan type	ω–2θ	ω–2θ
scan speed, $deg \cdot min^{-1}$	3	3
scan range, deg	$1.5 + 0.35 \tan \theta$	$2.2 + 0.35 \tan \theta$
bkgrd time	$^1/_2$ total scan time	$^1/_2$ total scan time
abs cor	ψ-scan method	ψ-scan method
rel transmission factors	1–0.88	1–0.81
stds	3 every 150 reflcns	3 every 150 reflcns
decay cor factors (on intensities)	1–1.24	1–1.12
no. of variables refined	81	171
R	0.057	0.055
R_w[a]	0.084	0.063
GOF[b]	1.71	1.52

[a] For both refinements $R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = \sigma^{-2}(F_o)$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (PI)^2]^{1/2}/Lp$, and *P*, the ignorance factor, is 0.06. [b] GOF = $[\Sigma w(F_o - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

2. Synthesis of $[NMe_4]_2[Ni_{10}(CO)_{18}C]$. $[NMe_4]_2[Ni_6(CO)_{12}]$ (2.32 g) was dissolved in acetonitrile (25 mL) under a nitrogen atmosphere, and a solution of CCl_4 in CH_3CN (3.5 mL, 0.2 M) was added dropwise over a period of 2 h, while the solution was rapidly stirred and the reaction atmosphere was purged with a slow stream of nitrogen. The resulting red-brown solution was evaporated to dryness, and the residue was extracted with THF (25 mL). Precipitation by addition of cyclohexane (50 mL) to the filtered red-brown solution afforded 0.72 g of $[NMe_4]_2[Ni_{10}(CO)_{18}C]$ as dark red crystals (yield 34.5% based on Ni).

The compound is soluble in THF, acetone, and acetonitrile and sparingly soluble or insoluble in alcohols, water, and nonpolar solvents. Anal. Calcd for $[NMe_4]_2[Ni_{10}(CO)_{18}C]$: $[NMe_4]^+$, 11.83; Ni, 46.92; CO, 40.28; $[NMe_4]^+$:Ni:CO = 1:5:9. Found: $[NMe_4]^+$, 11.7; Ni, 45.2; $[NMe_4]^+$:Ni = 1:4.87. Infrared carbonyl absorptions in THF: 2005 (s), 1800 (ms) cm^{-1}.

3. Synthesis of $[NBu_4]_2[Ni_8(CO)_{16}C]$. $[NBu_4]_2[Ni_9(CO)_{17}C]$ (1.5 g) was dissolved in THF (20 mL) under a nitrogen atmosphere. The solution was evacuated and saturated with carbon monoxide. After 1-h of stirring, the resulting orange-red solution was evaporated to dryness to eliminate $Ni(CO)_4$. The residue was dissolved in THF (20 mL) under carbon monoxide and precipitated by slow diffusion of cyclohexane (50 mL). Yield: 1.1 g (69.2% based on Ni).

Anal. Calcd for $[NBu_4]_2[Ni_8(CO)_{16}C]$: $[NBu_4]^+$, 34.24; Ni, 33.22; CO, 31.69; $[NBu_4]^+$:Ni:CO = 1:4:8. Found: $[NBu_4]^+$, 33.9; Ni, 33.4; $[NBu_4]^+$:Ni = 1:4.06. Infrared carbonyl absorptions in THF: 1995 (s), 1850 (s) cm^{-1}.

4. X-ray Crystallographic Measurements. Intensity data for $[NBu_4]_2[Ni_8(CO)_{16}C]$ and $[NBu_4]_2[Ni_9(CO)_{17}C]$ were collected on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Most parameters pertaining to data collection, structure solution, and refinement are reported in Table I.

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Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
		$[NBu_4]_2[Ni_8(CO)_{16}C]$		
Ni	0.7020 (1)	0.6311 (1)	0.1836 (1)	6.12 (4)
C	0.750	0.750	0.250	5.4 (6)
C(1)	0.657 (1)	0.514 (1)	0.1923 (9)	8.3 (4)
O(1)	0.629 (1)	0.4358 (9)	0.1978 (8)	13.4 (5)
C(2)	0.809 (1)	0.613 (1)	0.1112 (9)	7.7 (4)
O(2)	0.8278 (8)	0.5699 (9)	0.0554 (7)	10.8 (3)
N	0.750	0.250	0.000	8.0 (6)*
C(3A)	0.812 (2)	0.279 (3)	0.071 (2)	10 (1)*
C(4A)	0.874 (3)	0.317 (3)	0.030 (3)	13 (1)*
C(5A)	0.948 (4)	0.327 (3)	0.137 (4)	17 (2)*
C(6A)	1.037 (4)	0.306 (3)	0.134 (3)	15 (2)*
C(3B)	0.775 (3)	0.144 (2)	−0.017 (2)	10 (1)*
C(4B)	0.590 (3)	0.201 (3)	0.074 (2)	12 (1)*
C(5B)	0.512 (3)	0.125 (3)	0.096 (3)	13 (1)*
C(6B)	0.449 (4)	0.130 (3)	0.137 (3)	15 (2)*
		$[NBu_4]_2[Ni_9(CO)_{17}C]$		
Ni(1)	0.6184 (1)	0.4615 (1)	0.000	5.46 (4)
Ni(2)	0.5561 (1)	0.3884 (1)	−0.1382 (1)	5.22 (3)
Ni(3)	0.500	0.500	−0.2499 (2)	5.52 (5)
C	0.500	0.500	−0.077 (2)	4.9 (4)
C(1)	0.7354 (9)	0.424 (1)	−0.013 (1)	6.6 (4)
O(1)	0.8116 (7)	0.4066 (8)	−0.0183 (9)	10.1 (3)
C(2)	0.608 (1)	0.281 (1)	−0.137 (1)	8.2 (4)
O(2)	0.6452 (9)	0.2050 (8)	−0.135 (1)	13.5 (4)
C(3)	0.500	0.500	−0.354 (2)	6.0 (5)
O(3)	0.500	0.500	−0.420 (1)	8.4 (4)
C(4)	0.564 (1)	0.371 (1)	0.0757 (9)	7.4 (4)
O(4)	0.5877 (9)	0.3281 (8)	0.1310 (9)	10.0 (3)
C(5)	0.639 (1)	0.447 (1)	−0.213 (1)	7.0 (4)
O(5)	0.7038 (7)	0.4282 (7)	−0.2583 (6)	7.6 (3)
N	0.000	0.500	0.186 (1)	7.6 (4)*
C(6A)	−0.051 (2)	0.495 (3)	0.271 (2)	8.7 (9)*
C(6B)	−0.098 (3)	0.455 (3)	0.220 (3)	11 (1)*
C(7)	−0.157 (2)	0.469 (2)	0.266 (1)	12.6 (7)*
C(8)	−0.231 (3)	0.428 (3)	0.313 (3)	21 (1)*
C(9)	−0.305 (2)	0.436 (2)	0.340 (2)	18 (1)*
C(10A)	0.031 (2)	0.456 (2)	0.118 (2)	7.1 (7)*
C(10B)	0.040 (2)	0.395 (2)	0.174 (2)	9.0 (9)*
C(11)	0.086 (2)	0.362 (2)	0.123 (2)	14.6 (8)*
C(12)	0.109 (2)	0.278 (2)	0.072 (2)	17 (1)*
C(13)	0.153 (2)	0.212 (2)	0.067 (2)	16.5 (9)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Both compounds crystallized as dark red tetragonal bipyramids and were fairly stable toward air oxidation during data collection; only a moderate decay was observed and taken into account in both cases (see Table I). $h,k,+l$ and $h,k,-l$ reflections are symmetry equivalent, and were therefore averaged, only for the centrosymmetric $[NBu_4]_2[Ni_8(CO)_{16}C]$. Both structures were solved by direct methods and subsequent difference-Fourier synthesis. Refinement by full-matrix least squares progressed to the reported R's. Two structure enantiomorphs were refined for the noncentrosymmetric $[NBu_4]_2[Ni_9(CO)_{17}C]$; no statistically significant differences were present in the final molecular parameters of the two refined models, and the reported one is that associated with a very slightly lower value of R_w (0.069 vs. 0.070). In both compounds the cations lie on space group special positions. The orderly located nitrogen atoms show crystallographic S_4 and C_2 site symmetries in $[NBu_4]_2[Ni_8(CO)_{16}C]$ and $[NBu_4]_2[Ni_9(CO)_{17}C]$, respectively. The carbon atoms of the n-butyl chains show different degrees of disorder, which in both compounds was rationalized; therefore, some carbon atoms in Table II are split into pairs of half-atoms.

All calculations were performed on a PDP-11/34 computer using the Enraf-Nonius structure determination package SDP (including MULTAN for direct methods and ORTEP for drawings) and the physical constants tabulated therein.

Results and Discussion

Table III. Selected Interatomic Distances (Å)

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

Ni–Ni′ 2.477 (2), Ni–Ni″ 2.612 (2), Ni–Ni‴ 2.641 (2), Ni–C 2.084 (1), Ni–C(1) 1.72 (1), Ni–C(2) 1.93 (1), Ni′–C(2), 1.91 (1), C(1)–O(1) 1.14 (1), C(2)–O(2) 1.15 (1)

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

Ni(1)–Ni(1)′ 2.485 (2), Ni(1)–Ni(2) 2.617 (2), Ni(1)–Ni(2)′ 2.608 (2), Ni(2)–Ni(2)′ 2.493 (2), Ni(2)–Ni(3) 2.526 (3), Ni(1)–C 2.15 (2), Ni(2)–C 2.03 (2), Ni(3)···C 2.81 (3), Ni(1)–C(1) 1.75 (2), Ni(2)–C(2) 1.69 (2), Ni(3)–C(3) 1.69 (3), Ni(1)–C(4) 1.93 (2), Ni(1)′–C(4) 1.90 (2), Ni(2)–C(5) 1.88 (2), Ni(2)′–C(5) 1.99 (2), Ni(3)–C(5) 2.18 (2), C(1)–O(1) 1.11 (2), C(2)–O(2) 1.19 (2), C(3)–O(3) 1.07 (3), C(4)–O(4) 1.13 (3), C(5)–O(5) 1.20 (2)

The enneanuclear $[Ni_9(CO)_{17}C]^{2-}$ dianion is directly obtained by reaction of $[NBu_4]_2[Ni_6(CO)_{12}]$[9] with CCl_4 in tetrahydrofuran (THF) under a nitrogen atmosphere, according to the formal stoichiometry given in (1). Reaction 1 is complete after dropwise

$$2[Ni_6(CO)_{12}]^{2-} + CCl_4 + (CO) \xrightarrow{THF,\ N_2} [Ni_9C(CO)_{17}]^{2-} + 2Ni(CO)_4 + Ni^{2+} + 4Cl^- \quad (1)$$

addition of 0.4–0.5 mol of CCl_4/mol of $[NBu_4]_2[Ni_6(CO)_{12}]$; a stronger excess of CCl_4 readily results in progressive oxidation to $Ni(CO)_4$ and Ni^{2+} salts. The dark red $[Ni_9(CO)_{17}C]^{2-}$ dianion is isolated in good yield (ca. 60% based on nickel) as the tetrabutylammonium salt by evaporation to dryness of the reaction solution, washing with water–alcohol mixtures, and crystallization from THF and cyclohexane. As shown by IR monitoring, isolation of $[Ni_9(CO)_{17}C]^{2-}$ from reaction 1 probably results from the reaction sequence shown in (2)–(4); thus, reaction of $[Ni_6(CO)_{12}]^{2-}$

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

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

$$[Ni_{10}(CO)_{18}C]^{2-} + 2CO + Cl^- \rightarrow [Ni_9(CO)_{17}C]^{2-} + [Ni(CO)_3Cl]^- \quad (4)$$

with CCl_4 initially gives rise to $[Ni_{10}(CO)_{18}C]^{2-}$ according to reaction 2. Concomitantly, the evolving carbon monoxide causes the controlled degradation of most $[Ni_{10}(CO)_{18}C]^{2-}$ to $[Ni_9(CO)_{17}C]^{2-}$, probably according to reaction 3 and/or 4. Desultory formation of $[Ni(CO)_3Cl]^-$ is shown by appearance of a carbonyl absorption band at ca. 1950 cm^{-1}.[10]

The $[Ni_{10}(CO)_{18}C]^{2-}$ anion is isolated in a fairly pure state only when CCl_4 in diluted CH_3CN solution is added to a solution of $[NMe_4]_2[Ni_6(CO)_{12}]$, while the reaction atmosphere is purged from the evolving carbon monoxide with a slow stream of nitrogen, and when the addition of CCl_4 is stopped while unreacted $[Ni_6(CO)_{12}]^{2-}$ is still present. The two dianions are separated owing to the differential solubility of their tetramethylammonium salts in THF.

The octanuclear $[Ni_8(CO)_{16}C]^{2-}$ dianion is synthesized from either preformed $[Ni_9(CO)_{17}C]^{2-}$ or $[Ni_{10}(CO)_{18}C]^{2-}$ by degradation under carbon monoxide; equilibrium reaction 5 is com-

$$[Ni_9(CO)_{17}C]^{2-} + 3CO \xrightleftharpoons{CO,\ 1\ atm} [Ni_8(CO)_{16}C]^{2-} + Ni(CO)_4 \quad (5)$$

pletely shifted to the right under a carbon monoxide atmosphere (25 °C, 1 atm). The red-orange $[Ni_8(CO)_{16}C]^{2-}$ dianion has been isolated in the solid state by evaporation of the reaction solution and crystallization of the residue in THF–cyclohexane.

The molecular structures of the $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$ dianions, in their tetrabutylammonium salts, were established by X-ray diffraction studies. Crystallographic data

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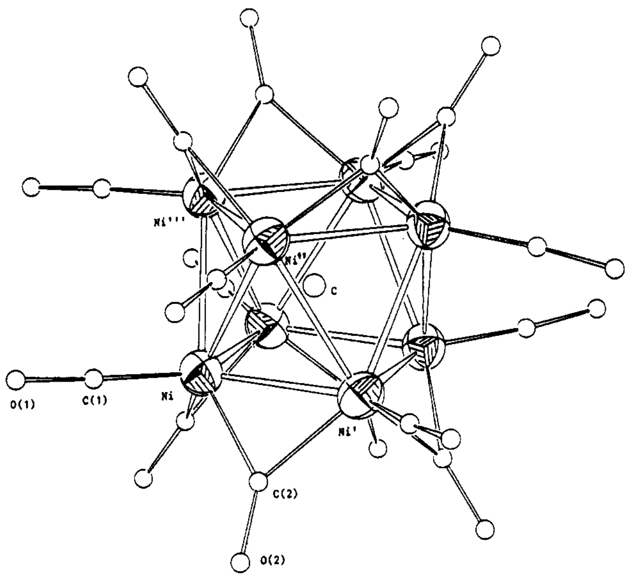

Figure 1. ORTEP drawing of the $[Ni_8(CO)_{16}C]^{2-}$ dianion. Carbon and oxygen atoms are shown as small circles for clarity.

and positional parameters are collected in Table I and II; selected interatomic distances are listed in Table III for both anions.

As shown in Figure 1, the octanuclear $[Ni_8(CO)_8(\mu\text{-}CO)_8C]^{2-}$ dianion, of crystallographic D_4 and idealized D_{4d} symmetries, originates from two square $Ni_4(CO)_4(\mu\text{-}CO)_4$ moieties condensed along the C_4 axis in a staggered conformation so as to give rise to an elongated square-antiprismatic metal framework. The Ni–Ni intralayer distance (2.477 (2) Å) is shorter than the mean interlayer one (2.627 Å), in keeping with the presence of bridging carbonyl ligands on the intralayer edges.

The structure of the $[Ni_9(CO)_9(\mu\text{-}CO)_4(\mu_3\text{-}CO)_4C]^{2-}$ dianion, of crystallographic C_4 and idealized C_{4v} symmetries, derives from that of $[Ni_8(CO)_{16}C]^{2-}$ by capping a square face with a Ni(CO) fragment and by converting into triply bridging groups four formerly edge-bridging carbonyl groups (Figure 2).

The structure determination of the $[Ni_{10}(CO)_{18}C]^{2-}$ dianion could not be undertaken owing to the poor quality of the crystalline samples of both its tetramethyl- and tetrabutylammonium salts; its infrared spectrum, which shows the presence only of terminal and triply bridging carbonyls (see the Experimental Section), suggests a μ_4-Ni bicapped square-antiprismatic structure with a carbonyl distribution closely related to the upper part of the $[Ni_9(CO)_{17}C]^{2-}$ dianion.

The enneanuclear $[Ni_9(CO)_{17}C]^{2-}$ shows a metal frame quite close to that of the interstitial phosphide $[Rh_9(CO)_{22}P]^{2-}$ cluster,[11] and the two compounds are isoelectronic in both having $6N + 11$ filled cluster valence molecular orbitals (CVMO). The octanuclear $[Ni_8(CO)_{16}C]^{2-}$ also has $6N + 11$ CVMO's but is unique in showing a fairly regular square-antiprismatic metal skeleton. Previously reported octanuclear carbide clusters include the bicapped octahedral $[Re_8(CO)_{24}C]^{3-}$ [12] and $Os_8(CO)_{21}C$[13] (both having $6N + 7$ CVMO), the bicapped trigonal-prismatic $Rh_8(CO)_{19}C$[14] ($6N + 9$ CVMO), and the distorted square-antiprismatic $[Co_8(CO)_{18}C]^{2-}$ [15] ($6N + 9$ CVMO). The last cluster shows a rhombic distortion of the two square faces and an apparent preference of the interstitial carbide atom for tetrahedral coordination, which is absent in $[Ni_8(CO)_{16}C]^{2-}$.

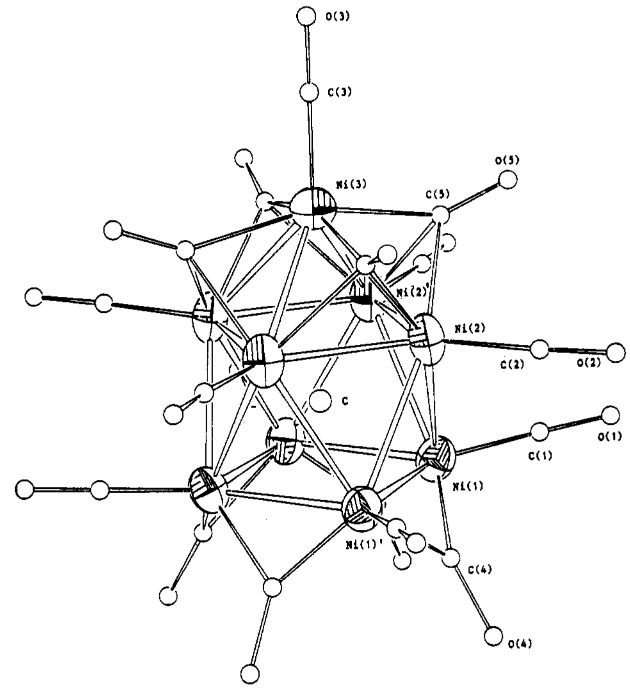

Figure 2. ORTEP drawing of the $[Ni_9(CO)_{17}C]^{2-}$ dianion. Carbon and oxygen atoms are shown as small circles for clarity.

A perfectly regular square-antiprismatic metal skeleton has been recently found in a post-transition-metal naked cluster, namely Bi_8^{2+},[16] which significantly is isoelectronic with $[Ni_8(CO)_{16}C]^{2-}$. It is, therefore, shown that departure from a D_{4d} square-antiprismatic metal geometry, as respectively represented by the structural behaviors of $[Ni_8(CO)_{16}C]^{2-}$ and $[Co_8(CO)_{18}C]^{2-}$, could be associated with a reduction in the number of CVMO's from $6N + 11$ to $6N + 9$.

It is worth mentioning that although carbido-centered hexanuclear clusters of the first transition series do exist, either with octahedral geometry (e.g. $[Fe_6(CO)_{16}C]^{2-}$ [17] or $[Co_6(CO)_{14}C]^{-}$ [18]) or with trigonal-prismatic geometry (e.g. $[Co_6(CO)_{15}C]^{2-}$ [19]), so far we do not have any evidence of the existence of a related hexanuclear species in the case of nickel. It may be speculated that in molecular clusters of group 8 metals of the first transition series a decrease in the formal covalent radii on moving from iron to nickel may be expected, as a result of an increasing bridging-to-terminal carbonyl ratio; this would progressively destabilize the isolated octahedral and trigonal-prismatic geometries, because of the size of the interstitial carbide atom. In contrast, a larger polyhedral frame, such as the square antiprism, would in addition allow attainment of shorter M–M contacts. It appears significant that in both title compounds the average Ni–Ni distance (2.55 Å for both compounds) is intermediate between that observed in the bulk metal (2.50 Å) and that observed in the Ni_3C binary phase (2.62 Å).[20]

Characterization of other nickel carbide derivatives, resulting from chemical transformation of the present series of nickel carbides, is currently underway.

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Acknowledgment. We thank the MPI for a grant and the Centro per lo Studio della Sintesi e della Struttura dei composti dei metalli di transizione nei bassi stati di ossidazione, 20133 Milano, Italy, for the use of equipment.

Registry No. $[NBu_4]_2[Ni_9(CO)_{17}C]$, 90051-78-8; $[NMe_4]_2[Ni_{10}(CO)_{18}C]$, 93756-03-7; $[NBu_4]_2[Ni_8(CO)_{16}C]$, 85190-61-0; $[NBu_4]_2[Ni_6(CO)_{12}]$, 93756-04-8; $[NMe_4]_2[Ni_6(CO)_{12}]$, 60464-19-9; CCl_4, 56-23-5.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes and anisotropic thermal parameters for $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$ (15 pages). Ordering information is given on any current masthead page.

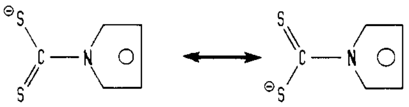
Additions and Corrections

1984, Volume 23

J. E. J. Schmitz and J. G. M. van der Linden*: Reaction Entropies of Redox Reactions of Transition-Metal Complexes with Sulfur Donor Ligands.

Page 3298. In footnote 9, the correct formula for pdtc$^-$ = pyrrole-*N*-carbodithioate should read $C_4H_4NCS_2^-$.

Page 3301. Formulas X and XI should read



X XI

Page 3302. In the second column, line 19 should read as follows: "We expect r_B(bis) < r_B(tris)" etc.—*J. G. M. van der Linden*

David W. Abbott and Clifton Woods*: Carbon-13, Phosphorus-31, and Proton NMR Studies of the Interactions of the Carbonylbis(triphenylphosphine)rhodium(I) Cation with Base Pairs of 6-Mercaptoguanosine and 8-Mercaptoguanosine with Cytidine.

Page 3627. The axis in Figure 1 is labeled incorrectly: it should read δ (ppm from 85% H_3PO_4).—Clifton Woods