the d_{xz} and d_{yz} orbitals and the e_{1g} set may require that two electron pairs remain nonbonding and essentially ligand electrons reside in the e_{1g} orbital set. Finally, either the combination of s and d_{z^2} AO's or the s orbital alone may interact with the a_g LO to form a bonding interaction of σ symmetry.

Preliminary reactivity studies indicate that **2** is sufficiently stable to undergo a conventional carborane cage nucleophilic derivatization reaction at carbon. Treatment of **2** with 2 molar equiv of *n*-butyllithium in benzene at 25 °C resulted in precipitation of white solid presumed to be dilithio-**2**. Subsequently, reaction of this material with D_2O resulted in formation of $[Si(C_2B_9H_{10}D)_2]$[8] in ca. 30% yield, as shown in Figure 2. The relatively low yield of this reaction may be a consequence of competing nucleophilic attack by the *n*-butyl reagent at silicon. The reactivity of **2** with respect to nucleophilic and electrophilic substitution and hydrolysis is currently under investigation.

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Registry No. 2, 103303-90-8; $[HNMe_3][nido\text{-}7,8\text{-}C_2B_9H_{12}]$, 12543-22-5; $SiCl_4$, 10026-04-7.

Supplementary Material Available: Tables of positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[8] IR (cm^{-1}; NaCl, Nujol mul) 3047 (m, C–H stretch), 2276 (m, C–D stretch); mass spectrum, parent at *m/e* 298, $^{12}C_4{}^{11}B_{18}H_{20}D_2{}^{28}Si^+$.

Synthesis and Structural Characterization of the $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ (n = 6, 5) and $[Ni_{35}(CO)_{39}C_4]^{6-}$ Clusters: Molecular Models for Carbidized Metal Crystallites

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We wish here to report a series of nickel polycarbide clusters of formula $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ (n = 6, 5) and $[Ni_{35}(CO)_{39}C_4]^{6-}$, whose structural features can be of relevance in envisioning the structural changes which may occur in compactly packed metal crystallites[1] on carbidization.[2,3] In contrast to previously reported nickel polycarbides, e.g., $[Ni_{10}(CO)_{16}C_2]^{2-}$ and $[Ni_{16}(CO)_{23}(C_2)_2]^{4-}$,[4,5] the new compounds contain four isolated carbide atoms imbedded in a complex metal framework derived from the fusion of compact, simple-hexagonal, pentagonal-bipyramidal, and polytetrahedral metal packing[6] moieties.

The $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ (n = 6, 5) derivatives are obtained directly from reactions of tetrasubstituted ammonium salts ($[NEt_4]^+$, $[NMe_3CH_2Ph]^+$, $[NBu_4]^+$) of $[Ni_6(CO)_{12}]^{2-}$ with C_2Cl_6 in a ca. 2:1 molar ratio in acetonitrile or acetone. The reactions afford variable mixtures of $[Ni_{10}(CO)_{16}C_2]^{2-}$,[4] $[Ni_{16}(CO)_{23}(C_2)_2]^{4-}$,[5] $[HNi_{34}(CO)_{38}C_4]^{5-}$, and $[Ni_{34}(CO)_{38}C_4]^{6-}$ clusters. Sequential extraction of the residue, on total evaporation of the reaction mixture, in tetrahydrofuran and acetone allows separation of the less soluble $[Ni_{34}(CO)_{38}C_4]^{6-}$ salts.

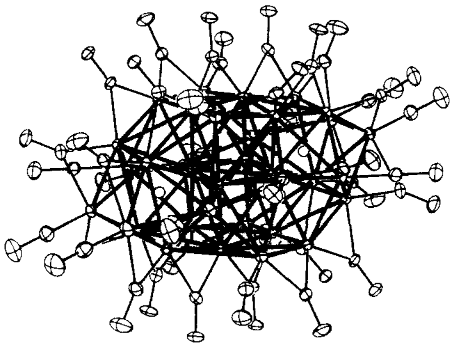

Figure 1. ORTEP drawing of $[HNi_{34}(CO)_{10}(\mu_2\text{-}CO)_{26}(\mu_3\text{-}CO)_2C_4]^{5-}$.

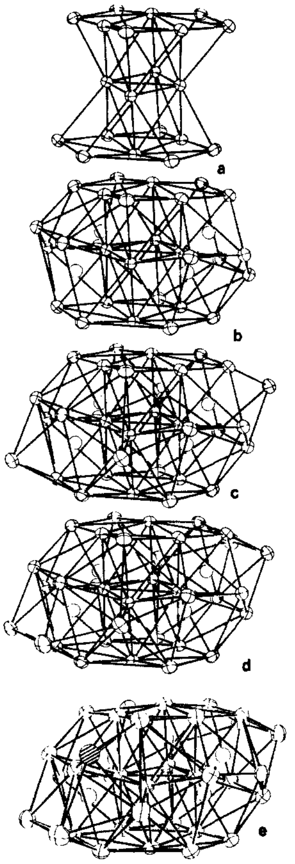

Figure 2. ORTEP drawing of the cluster frame of $[HNi_{34}(CO)_{38}C_4]^{5-}$ (d) and $[Ni_{35}(CO)_{39}C_4]^{6-}$ (e; the additional nickel atom is shown as hatched circle). Parts a–c represent a formal stepwwise building procedure of the two clusters, as described in the text.

As shown in (1), the $[HNi_{34}(CO)_{38}C_4]^{5-}$ cluster is obtained by protonation of the hexaanion with dilute H_3PO_4 in acetonitrile.[7]

$$[Ni_{34}(CO)_{38}C_4]^{6-} \underset{Me_2SO}{\overset{H^+,\ CH_3CN}{\rightleftharpoons}} [HNi_{34}(CO)_{38}C_4]^{5-} \qquad (1)$$

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[1] Davis, S. C.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153–208.

[2] Vannice, M. A. *Catal.: Sci. Technol.* **1982**, *3*, 139–198.

[3] Dry, M. E. *Catal.: Sci. Technol.* **1981**, *1*, 159–255.

[4] Ceriotti, A.; Longoni, G.; Resconi, L.; Manassero, M.; Masciocchi, N.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 181–182.

[5] Ceriotti, A.; Longoni, G.; Piro, G.; Resconi, L.; Manassero, M.; Masciocchi, N.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1402–1403.

[6] Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, England, 1975.

[7] Infrared carbonyl absorptions of $[Ni_{34}(CO)_{38}C_4]^{6-}$ in CH_3CN at 1992 s and 1853 s cm^{-1}. Analytical results for $[NEt_4]_6[Ni_{34}(CO)_{38}C_4]$: Found $[NEt_4]^+$ 19.92, Ni 51.02, $[NEt_4]^+$:Ni = 1:5.67. Calcd $[NEt_4]^+$ 20.06; Ni 51.13; $[NEt_4]^+$:Ni = 1:5.66. Infrared carbonyl absorptions of $[HNi_{34}(CO)_{38}C_4]^{5-}$ in acetone at 2008 s and 1862 s cm^{-1}. Analytical results for $[NMe_3CH_2Ph]_5[HNi_{34}(CO)_{38}C_4]$: Found $[NMe_3CH_2Ph]^+$ 19.27; Ni 51.43; $[NMe_3CH_2Ph]^+$:Ni = 1:6.82. Calcd $[NMe_3CH_2Ph]^+$ 19.44; Ni 51.72; $[NMe_3CH_2Ph]^+$:Ni = 1:6.8. Infrared carbonyl absorptions of $[Ni_{35}(CO)_{39}C_4]^{6-}$ in CH_3CN at 1998 s, 1864 s, and 1850 sh cm^{-1}. Analytical results for $[NEt_4]_6[Ni_{35}(CO)_{39}C_4]$: Found $[NEt_4]^+$ 19.12; Ni 51.32; $[NEt_4]^+$:Ni = 1:5.94. Calcd $[NEt_4]^+$ 19.63; Ni 51.69; $[NEt_4]^+$:Ni = 1:5.83.

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The $[Ni_{35}(CO)_{39}C_4]^{6-}$ cluster was isolated from the decomposition products obtained by refluxing $[NEt_4]_2[Ni_6(CO)_{12}]$ in CH_2Cl_2.[7]

Crystals of $[NMe_3CH_2Ph]_5[HNi_{34}(CO)_{38}C_4]$ and $[NEt_4]_6[Ni_{35}(CO)_{39}C_4]$ were grown from acetonitrile and diisopropyl ether, and their structure was determined by X-ray diffraction studies.[8,9] An ORTEP drawing of the $[HNi_{34}(CO)_{10}(\mu_2\text{-}CO)_{26}(\mu_3\text{-}CO)_2C_4]^{5-}$ pentaanion is given in Figure 1. The 38 carbonyl groups are divided in three sets: 10 terminal (Ni–C$_{av}$ = 1.70; C–O$_{av}$ = 1.17 Å), 26 edge bridging (Ni–C = 1.75 (3)–2.12 (3); C–O$_{av}$ = 1.17 Å) and two triply bridging (Ni–C$_{av}$ = 2.01; C–O = 1.17 Å), although the above assignment is often not clear-cut due to the presence of unsymmetrical and semibridging ligands.[10] As shown in Figure 2, which for the sake of clarity also reports a formal stepwise building procedure, the metal frame consists of a cubic-close-packed Ni_{20} core (Figure 2a). The four carbide atoms are bound to the four square faces of the above nickel moiety and, through condensation of two nickel atoms above each square face, become caged interstitially in four trigonal-prismatic cavities. The resulting $Ni_{28}C_4$ fragment is shown in Figure 2b. Four additional nickel atoms cap the two pentagonal and two of the four adjacent square faces, so that the C_i symmetry is maintained (Figure 2c). This generates a stepped surface owing to the presence of two concave surfacial "butterfly" moieties. The last two nickel atoms condense onto those "butterfly" moieties, rather than on the two uncapped square faces, and give rise to the whole metal skeleton of $[HNi_{34}(CO)_{38}C_4]^{5-}$ shown in Figure 2d. The preferential coordination of nickel on stepped rather than uncapped square faces is confirmed by the structure of $[Ni_{35}(CO)_{39}C_4]^{6-}$, as shown in Figure 2e. The structure is derived from that of $[HNi_{34}(CO)_{38}C_4]^{5-}$ by condensation of an extra Ni(CO) moiety over one of the four stepped faces (Figure 2d,e).[11]

As a result, in both clusters two carbide atoms are caged in trigonal-prismatic cavities, whereas the other two are encapsulated in two distorted capped trigonal prisms and show seven Ni–C interactions, as in the previously reported $[Ni_{10}(CO)_{16}C_2]^{2-}$.[4] The Ni–Ni distances are scattered (2.350 (2)–2.975 (2) Å) and comparable in the two clusters.

High nuclearity metal carbonyl clusters often adopt structures which derive from fragmentation of a close-packed metal lattice.[12-14] The very complicated metal frameworks of $[HNi_{34}(CO)_{38}C_4]^{5-}$ and $[Ni_{35}(CO)_{39}C_4]^{6-}$ are unusual and probably result from the swelling brought about by encapsulation of the four carbide atoms.[15] Related structural changes may also be expected to occur upon carbidization[2,3] in metal crystallites of first-row transition metals.

Acknowledgment. We thank the M.P.I. for a grant and the "Centro per lo Studio della Sintesi e della Struttura" for the use of equipment.

Supplementary Material Available: A list of atomic coordinates and thermal factors of $[NMe_3CH_2Ph]_5[HNi_{34}(CO)_{38}C_4]$ (Table I) and $[NEt_4]_6[Ni_{35}(CO)_{39}C_4]$ (Table II) (14 pages). Ordering information is given on any current masthead page.

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[8] Crystal Data for $[NMe_3CH_2Ph]_5[HNi_{34}(CO)_{38}C_4]$: monoclinic, space group $P2_1/c$, a = 16.779 (4) Å, b = 23.898 (6) Å, c = 18.886 (7) Å, β = 93.70 (2)°, V = 7557 (7) Å^3, D_c = 1.697 g·cm^{-3} for Z = 2, μ(Mo Kα) = 42.03 cm^{-1}, $F(000)$ = 3848. The structure has been solved by direct methods and Fourier syntheses and refined by full matrix least squares on the basis of 5591 independent absorption-corrected reflections having $I \geq 3\sigma(I)$. Current R and R_w are 0.057 and 0.084, respectively.

[9] Crystal data for $[NEt_4]_6[Ni_{35}(CO)_{39}C_4]$: monoclinic, space group $C2/c$, a = 25.443 (33) Å, b = 16.812 (6) Å, c = 32.811 (13) Å, β = 109.35 (6)°, V = 13242 (32) Å^3, D_c = 1.995 g·cm^{-3} for Z = 4, μ(Mo Kα) = 49.38 cm^{-1}, $F(000)$ = 8000. The structure has been solved by direct methods and Fourier syntheses and refined by full matrix least squares on the basis of 2776 independent absorption-corrected reflections having $I \geq 3\sigma(I)$. Current R = 0.070 and R_w = 0.096.

[10] Cotton, F. A. *Prog. Inorg. Chem.* **1974**, *21*, 1–28.

[11] Actually, the $[Ni_{35}(CO)_{39}C_4]^{6-}$ anion shows an overall statistical C_i symmetry due the 35th Ni atom (hatched in Figure 2e) being disordered over two centrosymmetrically related positions, of which only one is shown in Figure 2e for the sake of clarity. The carbonyl stereochemistry of $[Ni_{35}(CO)_{10}(\mu_2\text{-}CO)_{27}(\mu_3\text{-}CO)_2C_4]^{6-}$ is very close to that of $[HNi_{34}(CO)_{38}C_4]^{5-}$; the major difference brought about by the entrance of a Ni(CO) group consists in conversion into edge bridging of a formerly terminal ligand.

[12] Martinengo, S.; Ciani, G.; Sironi, A. *J. Am. Chem. Soc.* **1980**, *102*, 7564–7566.

[13] Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37–61 and references therein.

[14] Ceriotti, A.; Longoni, G.; Marchionna, M.; Piva, G.; Demartin, F.; Manassero, M.; Sansoni, M. *Angew. Chem.* **1985**, *97*, 708–709.

[15] In nickel carbide molecular clusters the preference of isolated carbide atoms for cavities larger than octahedral, such as found in Ni_3C,[16] is also shown by the structures of $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$.[17]

[16] Nakagura, S. *J. Phys. Soc. Jpn.* **1957**, *12*, 482.

[17] Ceriotti, A.; Longoni, G.; Perego, M.; Manassero, M.; Sansoni, M. *Inorg. Chem.* **1985**, *24*, 117–120.

Octaphenyl[4]radialene

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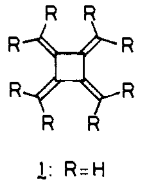
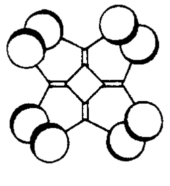
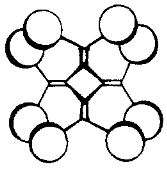
[4]Radialene (tetramethylenecyclobutane) (**1**) is of considerable theoretical and synthetic interest[1,2] because of its potentially destabilizing cyclobutadienoid topology and its unique π-electron system. In particular, octaphenyl[4]radialene (**2**) bearing a potential screw-shaped geometry such as **3** was discussed several decades ago,[3,5] but the synthetic methodology available to attain the compound is still very limited.



1: R=H
2: R=Ph



screw-shaped, **3**



puckered, **4**

In conjunction with our program to develop methods for transition-metal-catalyzed syntheses of radialenes,[7] we have found a one-pot synthesis of the sterically crowded octaphenyl[4]radialene (**2**) by coupling of copper carbenoid complex **11**. The structure of **2** possesses a puckered form like **4** instead of the screw-shaped molecule **3**.

Lithium carbenoid **6** derived from 1,1-dibromo-2,2-diphenylethylene (**5**) is known to give diphenylacetylene (**9**) via (diphenylmethylidene)carbene (methylidenecarbene to acetylene rearrangement).[8,9] On the other hand, the reactions of **5** with

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[1] (a) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 692. (b) Hess, B. A., Jr.; Schaad, L. J. *Ibid.* **1971**, *93*, 305. (c) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750.

[2] (a) Griffin, G. W.; Peterson, L. I. *J. Am. Chem. Soc.* **1963**, *85*, 2268. (b) Miller, F. A.; Brown, F. R.; Rhee, K. H. *Spectrochim. Acta, Part A* **1972**, *28A*, 1467. (c) Bally, T.; Buser, U.; Hasebach, E. *Helv. Chim. Acta* **1978**, *61*, 38. (d) Trabert, L.; Hopf, H. *Liebigs Ann. Chem.* **1980**, 1786.

[3] Tetraphenylbutatriene (**10**) dimerizes photochemically in the solid state. The dimer of **10** was reported to be octaphenyl[4]radialene (**2**).[4a] However, the photodimer was proven to be 1,3-bis(diphenylvinylidene)-2,2,4,4-tetraphenylcyclobutane on the basis of X-ray analysis.[4b]

[4] (a) Uhler, R. O; Shechter, H.; Tiers, G. V. D. *J. Am. Chem. Soc.* **1962**, *84*, 3397. (b) Berkovitch-Yellin, Z.; Lahav, M.; Leiserowitz, L. *Ibid.* **1974**, *96*, 918.

[5] Heptaphenyl[4]radialene was synthesized by Tanaka and Toda by a stepwise route, but the attempted synthesis of **2** failed because of steric hindrance between the phenyl groups.[6]

[6] (a) Tanaka, K.; Toda, F. *Tetrahedron Lett.* **1980**, *21*, 2713. (b) Hart, H.; Ward, D. L.; Tanaka, K.; Toda, F. *Ibid.* **1982**, *23*, 2125.

[7] Iyoda, M.; Tanaka, S.; Nose, M.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1983**, 1058.

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