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.

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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.

(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.

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(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.

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(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.

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Octaphenyl[4]radialene

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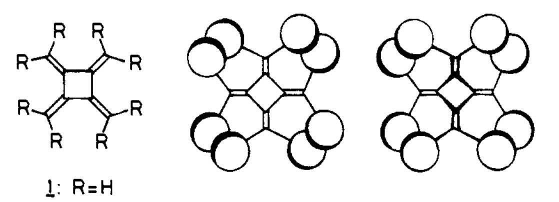
[4]Radialene (tetramethylenecyclobutane) (**1**) is of considerable theoretical and synthetic interest[1,2] because of its potentially destabilizing cyclobutadienoid topology and its unique π-electron system. In particular, octaphenyl[4]radialene (**2**) bearing a potential screw-shaped geometry such 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

(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]

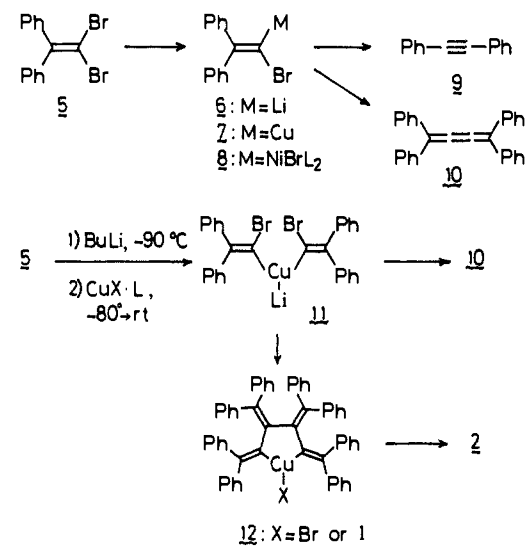
(4) (a) Uhler, R. O; Shechter, H.; Tiers, G. V. D. *J. Am. Chem. Soc.* **1962**, *84*, 3397. (b) Berkovitch-Yellin, Z.; Lahav, M.; Leiserowitz, L. *Ibid.* **1974**, *96*, 918.

(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.

Scheme I



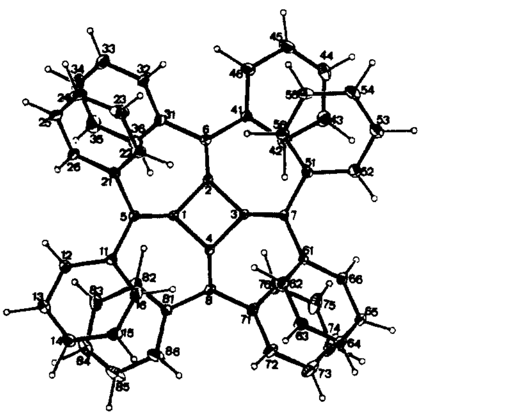


Figure 1. Molecular structure of compound **2** by ORTEP drawing with thermal ellipsoids at 20% probability level for non-hydrogen atoms and the spheres with 1.0-Å^2 temperature factor for hydrogen atoms.

Table I. Thermal Reactions of Copper Carbenoid **11** (Scheme I)[a]

entry	Cu^{I} complex	**5**:BuLi:Cu^{I}	% yield[b] **2**	**10**	**9**
1	CuI·PBu$_3$	1:1:1	traces	39	
2	CuI·PBu$_3$	2:2:1	34	40	
3	CuI·PBu$_3$	4:2:1	48[c]	29[c]	
4	CuBr·SMe$_2$[d]	4:2:1	44[e]	26[e]	
5	CuCN	2:2:1	traces	41	
6	CuI	2:2:1			86

[a] For the reaction procedures, see the text. [b] Isolated yields. [c] Based on the recovered **5** (19%). [d] In the presence of excess amounts of dimethyl sulfide. [e] Based on the recovered **5** (23%).

metallic copper and nickel(0) complexes produce tetraphenylbutatriene (**10**) via the copper and nickel carbenoids **7** and **8** (dimerization) (Scheme I).[10] In view of these results, we investigated the coupling of the ate-type complex **11** of the copper carbenoid. A THF solution of **5** (1.5 mmol in 10 mL of THF) was treated with 0.5–1 equiv of butyllithium in hexane at −90 °C. After the solution was allowed to stir at −90 °C for 1 h, 0.25–1 equiv of copper(I) complex was added in one portion, and the reaction mixture was stirred at −80 °C for 1 h. The mixture was allowed to warm to room temperature and stirred for 20 h. Results are summarized in Table I.

Treatment of **6**, derived from **5**, with 0.5 equiv of CuI·PBu$_3$ gave octaphenyl[4]radialene (**2**)[11] in 34% yield, together with **10** (40%) (entry 2). However, similar treatment of **6** with 1 equiv of CuI·PBu$_3$ afforded **10** in 39% yield with only trace amounts of **2** (entry 1). These results show that oligomerization of the ate complex **11** plays an important part for the formation of **2**, and the final step can be explained by assuming reductive elimination of copper halide from the metallacyclic intermediate **12**. Interestingly, the yield of **2** increased to 48% when the reaction was carried out in the presence of **5** (entry 3). Similar results were obtained using CuBr·SMe$_2$ as the copper(I) complex (entry 4). With CuCN, however, the main product was **10** (41%), together with trace amounts of **2** (entry 5). Although CuI is usually employed for the preparation of Gilman reagents, the use of CuI resulted in the formation of diphenylacetylene (**9**) via (diphenylmethylidene)carbene, presumably owing to a poor solubility of CuI in THF at low temperatures (entry 6). The [4]radialene **2** thus obtained is stable to light and air in spite of the fairly large ring strain.

The molecular structure of **2** determined by X-ray diffraction method is shown in Figure 1.[12] **2** has an approximate D_{2d} symmetry which is different from the screw-shaped geometry **3**. The noteworthy structural feature is the very large puckered angle of 34.7° in the four-membered ring, which relieves the steric repulsion between the phenyl groups in this molecule. The corresponding puckered angles are reported as 26.5°, 19.2°, and 19.1° for perchloro-,[14] heptaphenyl-,[6b] and tetrakis(4,5-dicarbomethoxy)-1,3-dithiol-2-ylidene)[4]radialene,[15] respectively. The out-of-plane deformation angles of the exocyclic double bonds have an average value of 13.5°, which is comparable with that in perchloro derivative, 14.2°, and larger than those in heptaphenyl, 8.4°, and tetrakis(4,5-dicarbomethoxy-1,3-dithiol-2-ylidene), 11.7°, derivatives. The endo- and exocyclic carbon–carbon bond distances are 1.504 and 1.347 Å, which are the localized C_{sp^2}–C_{sp^2} single- and double-bond distances, respectively.

In agreement with these results, **2** exhibits characteristic electronic and NMR spectra, the former showing a very broad absorption tailing up to 600 nm. The ^{1}H NMR spectrum (CDCl$_3$) indicates an upper field shift of the phenyl protons as a broad singlet at δ 6.80 due to the shielding effect of the closely situated neighboring benzene ring, and the ^{13}C NMR spectrum reflects the highly symmetrical structure [δ 132.0 (methylene carbon) and 139.3 (ring carbon)].

In summary, we have developed a new method for the synthesis of sterically crowded radialenes employing an unusual cyclization of the ate-type complex of a copper carbenoid. Further investigations of these reactions and their mechanisms are now in progress.

Supplementary Material Available: Full list of fractional atomic coordinates and interatomic bond distances and angles in **2** (4 pages). Ordering information is given on any current masthead page.

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(11) **2**: deep red needles (Et$_2$O), yellow prisms (CH$_2$Cl$_2$–hexane), mp 276.5–277.5 °C; mass spectrum, m/e 712 (M$^+$, base peak); ^{1}H NMR (CDCl$_3$) δ 6.80 (br s); ^{13}C NMR (CDCl$_3$) δ 142.5, 139.3, 132.0, 129.3, 127.5, 126.1; UV–vis (cyclohexane) λ_{max} (log ε) 295 (4.49), 348 (4.42), 440 sh (3.96) nm. Carbon and hydrogen analyses were within 0.30% of theory.

(12) Crystal data of **2**: $C_{56}H_{40}$, M_r 712.9, triclinic, space group $P\bar{1}$, a = 11.896 (2) Å, b = 16.831 (4) Å, c = 11.942 (4) Å, α = 113.42 (2)°, β = 104.93 (2)°, γ = 68.54 (2)°, U = 2024.3 (9) Å^3, Z = 2, D_x = 1.17 g cm^{-3}. Diffraction intensities were measured on a Rigaku four-circle diffractometer with graphite monochromatized Mo Kα radiation. A total of 7120 reflections was collected up to 2θ = 50°, among which 4343 were observed reflections. The structure was solved by the direct method (MULTAN-78)[13] and refined by the full-matrix least squares to the R index of 0.073 for observed reflections (non-hydrogen atoms anisotropically, hydrogen atoms isotropically).

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