Rydberg-derived processes, which generally occur only in tetrasubstituted alkenes.[4] It thus appears that neither the π,π^* nor π,R(3s) state leads to migration. It is perhaps significant that σ strain in cycloalkenes and alkylidenecycloalkanes leads to low-lying $\pi \rightarrow \sigma^*$ transitions.[3] Thus the emergence of the migration process in alkylidenecyclopentanes may be due, at least in part, to the emergence of the π,σ^* state as the lowest lying singlet excited state. Work continues on identification of the excited state involved.

It must be cautioned, however, that not all light-induced positional isomerizations of alkenes involve exclusively an intramolecular hydrogen shift. Thus, although 1-methylcyclohexene (**13**) affords the positional isomers **14** and **15** on irradiation in ether or hydrocarbon solvent (13 and 6%, respectively), formation of **14** has been found to occur with substantial loss of deuterium from the labeled derivative **13**-d_3 (Scheme II). The difference in this case is almost surely associated with the now familiar tendency of cyclohexenes to undergo photoreaction via a highly strained twisted intermediate and probably involves initial cis $\rightarrow$ trans isomerization followed by hydrogen atom abstraction as shown. The partial retention of deuterium in **14**, accompanied by the formation of **15**, indicates that [1,3]-sigmatropic hydrogen shifts occur in competition with the intermolecular pathway.[12]

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(5) Irradiations were conducted on 115-ml pentane or octane solutions containing 20 mmol of olefin using a 450-W Hanovia mercury arc and quartz immersion well. Yields were determined by gas chromatographic analysis of aliquots removed from the irradiation mixture, calculated relative to an internal hydrocarbon standard, and based on consumed starting material.
(6) The expected carbene-derived products analogous to **3** and **4** were also isolated from irradiation of **5** and **6** in combined yields of 67 and 52%, respectively. Mixtures containing two or more products were isolated from irradiation of olefins **7–10** in total yields of 7, 18, 16, and 13%, respectively. These products were not identified because of their low yields and difficulties in separation. 3-Ethylcyclopentene (5%) and substantial amounts of a yellow polymer were also obtained from **8**.
(7) There was no significant change in product ratios as a function of time. Control studies showed that the disubstituted olefinic products related to **2** and **12** and the carbene-derived products from **1**, **6**, and **7** are photostable under the irradiation conditions. However, the trisubstituted photoproducts related to **11** are somewhat photolabile and undergo partial reversion to the starting olefin. Thus, for example, irradiation of 1-ethylcyclopentene afforded the 3-isomer (21%) accompanied by **8** (9%).
(8) S. S. Hixson, J. C. Tausta, and J. Borovsky, *J. Am. Chem. Soc.*, **97**, 3230 (1975), have recently reported that 4-methyl-1,1,4-triphenyl-1-pentene undergoes photoisomerization to the 2-isomer via a carbene intermediate. Such a double bond migration process is not related to that reported here.
(9) By contrast, on direct irradiation the double bond migration products 3,4-dimethyl-2-hexene and 2-ethyl-3-methyl-1-pentene are formed, along with the expected carbene-derived products.[4]
(10) Similarly 2,6-dimethyl-2,6-octadiene, which undergoes double bond migration on irradiation at shorter wavelengths, exhibits only cis $\rightleftarrows$ trans isomerization on irradiation at 254 nm.
(11) For example, 3,5-dimethyl-3-heptene undergoes isomerization to the 2-isomer and 2-ethyl-4-methyl-1-hexene on irradiation in ether solution. Isomerization of 2-butene to the 1-isomer has been previously reported: H. Yamazaki and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **91**, 520 (1969).
(12) By contrast, on sensitized irradiation in hydrocarbon media **13** undergoes isomerization only to **14** via an intermolecular process; see P. J. Kropp and H. J. Krauss, *J. Am. Chem. Soc.*, **89**, 5199 (1967). This is the expected behavior in the triplet manifold, in which only the π,π^* state is available.
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Synthesis and Crystal Structure of a Novel Electron-Rich Nido Trimetallocarborane

Sir:

Recent work in these laboratories has established the ability of both borane and monocarbon carborane ligands to stabilize formal $\{C_5H_5Ni\}^{3+}$ vertices in metallocarborane polyhedra.[1-6] These studies have shown that $\{C_5H_5Ni\}$ may replace $\{CH\}$ in a heteroborane environment, with retention of the major chemical features of the polyhedral framework (including the capacity to undergo polyhedral rearrangement[7]), as previously demonstrated[8] for $\{C_5H_5Co\}$ and $\{BH\}$. We have investigated the reaction of 2-carba-*nido*-hexaborane(9), CB_5H_9, with nickelocene and report here the synthesis and x-ray crystal structure of the first trimetallocarborane containing nickel,[9] $(C_5H_5Ni)_3CB_5H_6$.

The reaction of CB_5H_9[10] with nickelocene and sodium amalgam in tetrahydrofuran afforded a mixture of products. Diamagnetic, air stable $(C_5H_5Ni)_3CB_5H_6$ (I) was isolated in low yield by column chromatography on silica gel. The mass spectrum exhibited a cutoff at *m/e* 448 corresponding to the $^{12}C_{16}{}^{1}H_{21}{}^{11}B_5{}^{60}Ni_3{}^+$ ion. Anal. Calcd: C, 43.33; H, 4.77; Ni, 39.71. Found: C, 42.70; H, 5.00; Ni, 40.32. The 60-MHz ^{1}H NMR spectrum (acetone-d_6) contained sharp singlets of relative area 2:1 at τ 4.85 and 5.07, respectively, which were assigned to the cyclopentadienyl moieties. The 80.5-MHz ^{11}B NMR spectrum contained resonances of area 1:2:2 at −78.5, −26.2, and +9.5 ppm, relative to $Et_2O\cdot BF_3$. Ambiguous NMR data and the novel electron-rich nature (vide infra) of this metallocarborane led us to determine the structure via a single-crystal x-ray diffraction study.

A well-formed green-black crystal of the compound was mounted on a Syntex P$\bar{1}$ automated diffractometer. The complex was found to crystallize in the centrosymmetric orthorhombic space group *Pnma* with unit cell dimensions a = 7.518 (1), b = 14.740 (2), and c = 15.711 (3) Å at 26 °C. The measured density of 1.70 (2) g cm^{-3} agreed with the calculated density of 1.692 g cm^{-3} for $Z = 4$.

A total of 1840 reflections (Mo Kα radiation) with intensities greater than three times their standard deviations was used in the solution and refinement of the structure. Conventional Patterson, Fourier, and least-squares techniques have resulted in R = 3.16%, R_w = 3.93%. All the hydrogen atoms were located and refined. A final difference Fourier map showed no significant features. Full details of the refinement procedure will be discussed in a subsequent publication. Table I summarizes important polyhedral bond distances and angles. The cyclopentadienyl rings were found to be planar within experimental error and showed no unusual features (average Ni–C = 2.13 (3) Å, average C–C = 1.415 (9) Å). Complex I is the first crystallographically characterized trimetallocarborane, and represents the only example of the synthesis of a trimetallocarborane by the direct insertion of three transition metal atoms into a nido carborane.

The molecular units are bisected by crystallographic mirror planes, in congruence with the molecular plane of sym-

Table I. Bond Distances (Å) and Angles (deg)

Ni6–Ni7	2.404 (1)	B2–B3	1.916 (5)
Ni6–Ni8	3.250 (1)	B2–B5	1.798 (9)
Ni6–B2	2.077 (4)	B2–B9	1.735 (6)
Ni6–B3	2.051 (4)	B3–B4	1.977 (8)
Ni6–B9	2.043 (3)		
Ni7–B3	2.070 (3)		
Ni7–B9	2.991 (5)	Ni6–Ni7–Ni8	85.07 (2)
Cl–B2	1.634 (6)	Ni6–B9–Ni8	105.4 (2)
Cl–B3	1.618 (5)	B9–Ni6–Ni7	84.1 (1)

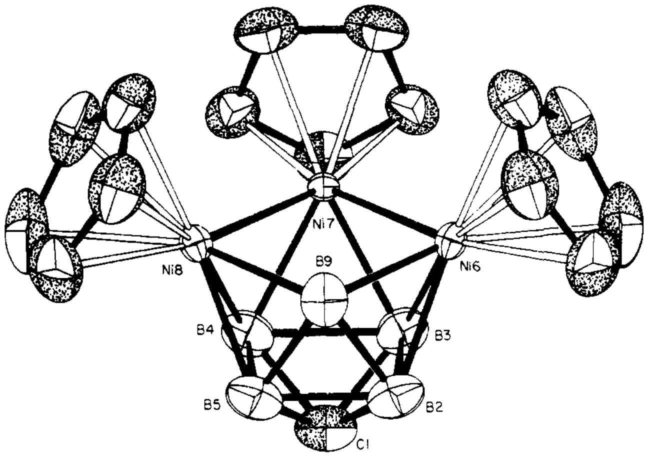

Figure 1. Molecular geometry of *nido*-$(C_5H_5Ni)_3CB_5H_6$. Hydrogen atoms have been omitted.

metry established from the NMR data. The structure (Figure 1) consists of a nine-vertex "opened", or nido, polyhedron, which can be derived from a tricapped trigonal prism by elongation of the Ni7–B9 polyhedral edge. The polyhedron is best described as a distorted monocapped square antiprism. Figure 2 shows a top view of the four-membered open face, composed of Ni6, Ni7, Ni8 and B9.

Because $\{C_5H_5Ni\}$ is formally isoelectronic with $\{CH\}$ (with regard to the number of electrons donated to polyhedral bonding[7]), I is analogous to the hypothetical species $C_4B_5H_9$. Thus the trimetallocarborane possesses two more electrons than required for a closo geometry, and is predicted[7,11] to be nido, as crystallographically observed. However, the nido configuration is achieved through the theoretical elongation of the Ni7–B9 polyhedral edge to generate a four-membered open face, rather than by the elongation of two edges (such as Ni7–B3 and Ni7–B4) to generate a five-membered open face. This latter nido geometry has been predicted[11a] for $C_4B_5H_9$, postulated[12] for the known borane anion, $B_9H_{12}^-$, and crystallographically shown[13] for $C_2B_7H_9(CH_3)_2$, and was not found here. It is interesting that molecular orbital calculations[14] performed on $B_9H_9^{2-}$ indicated that upon two-electron reduction the preferred structure would be the C_{4v} monocapped square antiprism. Presented here is the first confirmed example of this geometry in polyhedral borane chemistry. These observations may be pertinent to the determination of how the closo nine-vertex polyhedron opens upon the addition of two electrons. In fact, we have observed[15] that $B_9H_9^{2-}$ opens in the presence of $[C_5H_5NiCO]_2$ to produce the previously reported[6] metalloborane anion $[1\text{-}(C_5H_5)\text{-}1\text{-}NiB_9H_9]^-$. We note that I contains all three nickel atoms at low-coordinate polyhedral vertices, further evidence of the ability,[2-4] and even preference,[6] of $\{C_5H_5Ni\}$ to reside in a low coordinate position.

Complex I can formally be constructed from the known metallocarborane[16] $(C_5H_5Ni^{III})_2C_2B_5H_7$ by the replacement of a $\{CH\}^{3+}$ vertex with an "isoelectronic" (vide supra) $\{C_5H_5Ni\}^{3+}$ vertex. Thus it can be regarded as a formal mixed valence Ni(III)–Ni(III)–Ni(IV) complex. The near-infrared spectrum showed a broad band in the range 800–1400 nm (λ_{max} 850 nm, ϵ 700), indicating the possibility of mixed valence charge transfer.[17] Estimates of the interaction parameter,[17] α, indicate that significant mixed valence interactions have been induced in this metallocarborane. Further studies are in progress to determine the extent of the valence delocalization. These crystallographic results imply that $(C_5H_5Ni)_2C_2B_5H_7$ would also possess a nido geometry, rather than the proposed closo structure. Based on the NMR data,[16] a probable structure would then be 8,9-$(C_5H_5Ni)_2$-6,7-$C_2B_5H_7$, using the numbering system in Figure 1. It is unfortunate that no electronic spectral data for $(C_5H_5Ni)_2C_2B_5H_7$ are available for comparison.

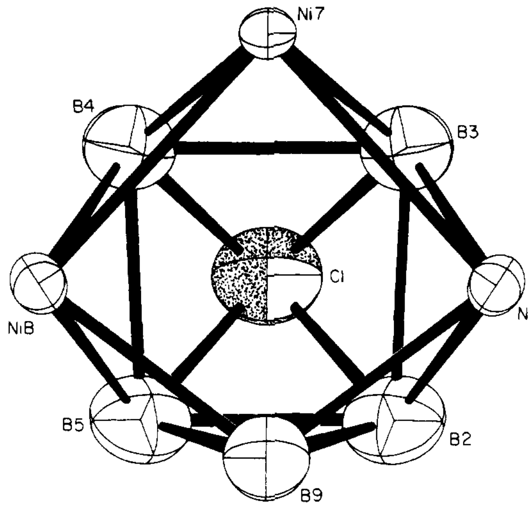

Figure 2. A view of the polyhedron approximately normal to the nido face. Cyclopentadienyl groups and hydrogen atoms have been omitted.

Electron-rich metallocarboranes of the formula $[Cu(C_2B_9H_{11})_2]^{n-}$ (n = 1, 2) were found to possess "slipped sandwich" structures[18] containing weak Cu–C interactions of length ~2.52 Å. Our results indicate that electronic effects upon geometry are more pronounced in the smaller polyhedral systems, as fewer atoms are available to disperse excess electron density.

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