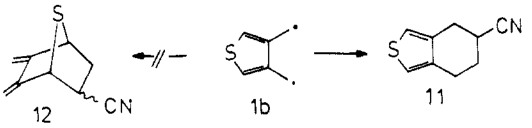
determining step in the thermal reaction is the unimolecular formation of a reactive intermediate **1a** and that only one spin state of **1a** is trapped.[14]

The trapping reaction with olefins is highly stereospecific (see Scheme I), which by reference to trimethylenemethane chemistry[15] is more readily interpreted in terms of the singlet rather than the triplet **1a** as the reactive species.

The generation and behavior of 3,4-dimethylenethiophene **1b** are analogous to those of **1a**, with one conspicuous exception: trapping of **1b** gives exclusively the *fused* thiophene derivative **11**, rather than the bridged isomer(s) **12**.



Photolysis (310 < λ < 380 nm) of a frozen glassy solution of **4a** in toluene, 2-methyltetrahydrofuran (MTHF), Et_2O, or EtOH at <80 K causes the rapid appearance of an intense purple color. The UV–vis absorption spectrum shows three new maxima at 338, 348, and 560 nm ($\epsilon > 10^3$) (Figure 1). Further irradiation at <80 K and then thawing of the glass cause the three bands to grow and diminish, respectively, at the same rate. Melting the matrix causes the color to vanish and ^1H NMR resonances characteristic of the dimers **5** and **6** to appear.[14] Similar phenomena are observed in the sulfur series, where the transient formed by photolysis of **4b** shows λ_{max} 572 nm ($\epsilon > 10^4$). In higher melting media (polycrystalline toluene for **4a**, Carbowax 400 for **4b**), the purple color of either transient is stable at 160 K. The transient from **4b** is not affected by irradiation at λ > 420 nm. We believe that the colored species from **4a** and **4b** are biradicals **1a** and **1b**, respectively.

Laser flash photolysis (355 nm) of a nitrogen-purged $CDCl_3$ solution of diazene **4a** at 10 °C gives rise within 25 ps to a transient, λ_{max} 560 nm, which is long-lived on the picosecond scale. When generated by a 351-nm 10-ns flash and monitored at 555 nm, the species has an apparent lifetime of about 3–4 μs in a nitrogen-purged solution. Whether this value is intrinsic to the biradical or merely measures the rate of capture by adventitious residual O_2 cannot yet be stated confidently. That the transient (or a species rapidly derived from it) reacts readily with O_2 is apparent from the time-dependent decrease in intensity of the 560-nm band (~20% after 50 ns, ~60% after 125 ns) when it is generated by picosecond flashes in O_2-saturated solution.

Photolysis (310 < λ < 380 nm) of **4a** or **4b** in MTHF glass at 12–80 K in the microwave cavity of an EPR spectrometer (Varian E-9) generates an intense purple color but does not give rise to a detectable triplet signal, even after prolonged irradiation.[16]

Although assignments of the lowest energy spin states of **1a** and **1b** are still tentative, all of the present evidence is consistent with a singlet in each case. The apparent experimental confirmation of the predicted[8-11] violation of Hund's rule supports the practical value of both semiempirical INDO/S-CI[8,9] and ab initio[10,11] quantum-mechanical calculations in guiding the search for non-Kekulé molecules with low-spin ground states.

Acknowledgment. We thank the National Science Foundation for grants (CHE8418611 and CHE8506590) in support of this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Professor W. T. Borden for advance word of his theoretical results (ref 11) and Drs. Robert von Treba and Tad Koch for help with the nanosecond experiments.

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(14) (a) 3,4-Cyclobutafuran, the ring-closure product of **1a**, is a known compound.[7,14b] Control experiments now show that it does not react with acrylonitrile in $CDCl_3$ solution at 25 °C and is not formed in the solution or solid-phase reactions of **4a**. Flash vacuum pyrolysis of **4a** gives about 5% of the cyclobutane. (b) Vollhardt, K. P. C.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1973**, 214.

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Quantitation of $^2H/^1H$ NMR Isotope Effects on ^{13}C Chemical Shifts. Linear Correlations Associated with Hybridization and Charge Density Changes in Norbornenyl Systems

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A common serious limitation to the study of compounds possessing distorted double bonds is a lack of crystallinity suitable for three-dimensional X-ray analysis. An extreme sensitivity to air oxidation[3] and/or dimerization[4] is also not easily accommodated. Our continuing interest in this class of molecules has led us to search for a new experimental method capable of determining *in solution phase* the extent of deformation at the olefinic center. As a first step toward this goal, we here report the discovery of both a hybridization and a charge density dependence to deuterium-induced ^{13}C NMR shifts for norbornene, norbornadiene, and structurally related molecules.

Günther et al. recently disclosed that one-bond ^2H isotope effects on the chemical shifts of carbon atoms in monodeuteriated ethane, ethylene, and acetylene vary linearly with the s character of the carbon atoms involved.[5] To our mind, the significance of this find would be appreciably enhanced if similar relationships could be shown to hold at positions of increasing distance from the isotopic label. We therefore chose initially to examine **1–3**, systems which share in common the rigid norbornane framework. Importantly, this series also offers a gradual progression in the hybridization at C5/C6, as determined by $^1J_{(C-H)}$ measurements.

Norbornene-2-*d* was prepared by Shapiro degradation of norbornanone (phenylsulfonyl)hydrazone and quenching of the intermediate vinyl anion with methanol-*d*.[6] To gain access to tricycle **2**, norbornenone ethylene ketal was cyclopropanated, deprotected, and subjected to a comparable Shapiro procedure.[7] Norbornadiene-*2-d* (**3**)[8] was made available by the method of De Lucchi et al.[9] using monodeuteriated (*Z*)-bis(phenylsulfonyl)ethylene (**6**)[10] as dienophile. For reasons to be discussed subsequently, the deltacyclene **4** and benzonorbornadiene **5** were also synthesized. Whereas **4** was obtained by extending the use of **6** to a Diels–Alder reaction with norbornadiene,[9] followed by sodium

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(1) Postdoctoral fellowship awardee of the Deutsche Forschungsgemeinschaft, 1985–1986.

(2) Campus Chemical Instrumentation Center, The Ohio State University.

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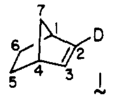
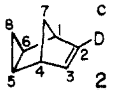
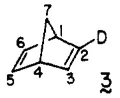
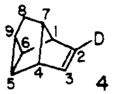
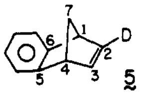
Table I. $^2H/^1H$ Isotope Effects ($\Delta\delta_{Ci}$) on ^{13}C Chemical Shifts (ppb)[a,b]

compd	C1	C2[c]	C3	C4	C5	C6	C7
 **1**	107.4	275.0	151.8	16.1	−10.4	−2.7	−11.4
 **2** c	112.9	269.9	147.0	22.6	−15.7	−7.1	−15.7
 **3**	108.3	273.3	147.4	20.3	−16.8	−8.0	−28.7
 **4**	111.5	267.3	153.8	20.3	−15.2	−14.8	−18.7
 **5**	103.9	273.2	139.6	20.0	−22.7	−14.5	−23.7

[a] Isotope effects are defined as $\Delta\delta_{Ci} = \delta_{Ci}^{RH} - \delta_{Ci}^{RD}$; positive values are therefore shifts to higher field. [b] Experimental error limits are ±0.5 ppb. [c] $\Delta\delta_{C8}$ = −4.7 ppb. Relevant $^1J_{C,D}$ coupling constants: **1**, 25.2 Hz; **2**, 26.0 Hz; **4**, 25.6 Hz; **5**, 27.0 Hz.

amalgam reduction, **5** was prepared by halogen–metal exchange/deuterolysis[11] of 2-bromobenzonorbornadiene.[12]

Carbon spectra of mixtures of the deuterio and protio hydrocarbons were recorded at 303 K as CD_2Cl_2 solutions at 125.759 MHz under ^1H WALTZ-16 decoupling.[13] Those resonances due to C5, C6, and C7 were also recorded individually to assure a digital resolution of up to 0.031 Hz/point. Lorentz to Gaussian line-shape transformations[14] were also utilized to enhance spectral resolution.

^{13}C shifts for **1**, **2**, **3**, and **5** were derived from literature data,[15] as were the values of $^1J_{(C6,7\text{-}H)}$ for **1** and **3**.[16] The assignments for deltacyclene were arrived at on the basis of its proton-coupled ^{13}C spectrum and confirmed by the splitting patterns observed for **4**. The $^1J_{(C6,7\text{-}H)}$ values for **2** and **4** were culled from their coupled carbon spectra.[17]

The isotope effects on individual carbon resonances are collected in Table I. The distinction between positions C5 and C6 has its origins in the normal sequencing $^1J_{(C,D)} > {}^3J_{(C,D)} > {}^2J_{(C,D)} > {}^4J_{(C,D)}$,[16,18] a fact that gives rise to appreciable line broadening at C6 compared to C5 in all five compounds studied. Two particularly striking generalizations emerge: (i) carbon atoms C5, C6, and C7 are consistently shifted to lower field in the labeled systems and (ii) the δ-position is uniformly more strongly perturbed than the corresponding γ-position, i.e., $|\Delta\delta_{C5}| > |\Delta\delta_{C6}|$. The latter finding can be rationalized on the basis that a dual pathway is possible for C5, whereas C6 receives essentially a three-bond effect ($2 \times {}^4\Delta > {}^3\Delta$; ${}^5\Delta \sim 0$).

Our data also reveal the existence of a linear relationship between the δ- and γ-isotope effects ($\Delta\delta_{C5}$, $\Delta\delta_{C6}$) and the one-bond C–H coupling constants at these positions (Table II). Equations 1 and 2

Table II. δ- and γ-Deuterium Isotope Effects and $^1J_{(C5,6\text{-}H)}$ Values

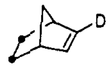
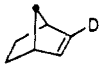
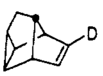
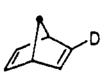
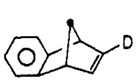
	$\Delta\delta_{C5}$, ppb	$\Delta\delta_{C6}$, ppb	$^1J_{(C5,6\text{-}H)}$, Hz
	−10.4	−2.7	133
	−15.7	−7.1	168
	−16.8	−8.0	173

Table III. $\Delta\delta_{C7}$ and δ_{C7} Values

	$\Delta\delta_{C7}$, ppb	δ_{C7}, ppm
	−11.4	48.5
	−18.7	58.4
	−28.7	75.5
	−23.7	70.6

$$\Delta\delta_{C6}\ (\text{ppb}) = (14.61 - 0.13)^1J_{(C,H)} \qquad (1)$$

$$\Delta\delta_{C5}\ (\text{ppb}) = (10.48 - 0.16)^1J_{(C,H)} \qquad (2)$$

are adhered to, with a correlation coefficient of 0.999 in both instances. One may legitimately ask how general these relationships are. Since inclusion of the data for **4** already lowers the quality of the correlations considerably [$^1J_{(C5,6\text{-}H)}$ = 177 Hz], the deuterium-induced shift at C5/C6 obviously does not follow changes in the C–H coupling constants above a certain level. The interconnective methylene carbon in deltacyclene increases the inherent strain in the system and enlarges the magnitude of the coupling constants while leaving the isotope effect essentially unchanged. This observation is consistent with earlier findings where an acceptable correlation between deuterium-isotope effects and a second structural parameter was found only within very closely related series of compounds.[5,18,19]

Enhanced steric interaction can also cause observable deviation from otherwise well-defined trends. If one considers, for example, the series represented by **1**, **3**, **4**, and **5**, a good linear correlation (eq 3, r = 0.989)

$$\Delta\delta_{C7}\ (\text{ppb}) = (17.29 - 0.59)\delta_{C7} \qquad (3)$$

is found between $\Delta\delta_{C7}$ and the chemical shift of C7 (Table III). Where **2** is concerned, however, nonbonded interactions between the endo C8 cyclopropyl proton and the syn-related hydrogen at position 7 strongly influence the chemical shift of C7.[20]

The results presented above demonstrate for the first time that quantitative relationships do exist between the ^{13}C NMR parameters at positions C5, C6, and C7 in norbornenes and a deuterium perturber at C2. The remarkable dependencies on structure augur well for the future application of these or related parameters to the detailed analysis of π-bond distortion, and we hope to report on this matter in the near future. As for the physical cause of the observed effects, it must be kept in mind that the isotope shift is fundamentally vibrational in origin, such that electronic potential energy surfaces are not affected (Born–Op-

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(20) $\Delta\delta_{C3}$ also correlates with $^1J_{(C5,6\text{-}H)}$. The equation is $\Delta\delta_{C3}(\text{ppb}) = (167.70 - 0.12)^1J_{(C,H)}$ with a correlation coefficient of 0.982.

penheimer approximation). Rather, as Jameson has noted,[21] the chief contribution to $\Delta\delta$ arises from the anharmonic segment of the expression for chemical shielding. The effect of a shorter C-D bond is to deshield C5, C6, and C7 because these atomic centers are particularly responsive to the charge redistribution that accompanies the difference in zero-point vibrational energy.

Acknowledgment. We are indebted to the National Institutes of Health for generous financial support of our research (Grant CA-12115).

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Synthesis and X-ray Structure of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ Cluster: An Extended Fragment of the $Cr_{23}C_6$ Lattice Stabilized in a Molecular Carbonyl Nickel Cluster

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Although close structural ties between molecular carbide clusters and interstitial carbide alloys were earlier pointed out,[1-5] owing to a greater degree of freedom of the former,[6] the above structural analogy is generally restricted to the stereochemistry of the interstitital carbide atom. We wish to report here the synthesis and structural characterization of $[HNi_{38}(CO)_{42}C_6]^{5-}$, which to our knowledge represents the first example of stabilization with carbonyl ligands of an extended fragment of a metal-carbide lattice, such as that shown by $Cr_{23}C_6$.[7]

The $[HNi_{38}(CO)_{42}C_6]^{5-}$ pentaanion has been obtained by reaction of $[NBu_4]_2[Ni_6(CO)_{12}]$ with hexachloropropene in a ca. 1.7:1 molar ratio in tetrahydrofuran (THF) and under a nitrogen atmosphere. After evaporation to dryness of the resulting suspension, the residue was thoroughly washed with water, methanol, and THF; subsequent extraction of the residue with acetone gives a dark brown solution containing $[HNi_{38}(CO)_{42}C_6]^{5-}$ in a fairly pure state.[8] Isolation of a hexacarbide cluster in the above conditions is in keeping with the previously reported synthesis of tetracarbide clusters, viz., $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ (n = 6, 5) and $[Ni_{16}(CO)_{23}(C_2)_2]^{4-}$,[9,10] in addition to the $[Ni_{10}(CO)_{16}C_2]^{2-}$ dicarbide,[11] in the related reaction of $[Ni_6(CO)_{12}]^{2-}$ salts with C_2Cl_6.

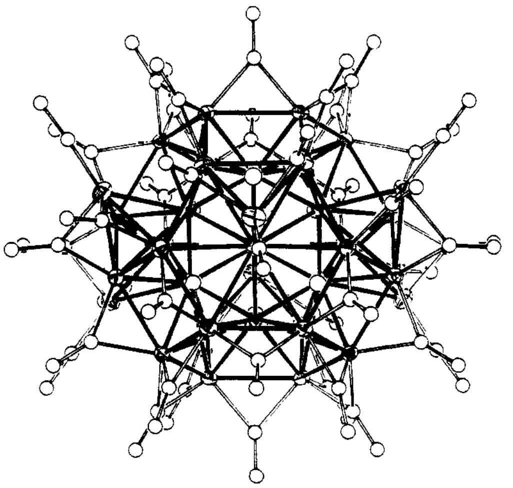

Figure 1. ORTEP drawing of the $[HNi_{38}(CO)_6(\mu_2\text{-}CO)_{36}C_6]^{5-}$ anion.

As in the case of $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$,[9] the presence of a hydride atom in $[HNi_{38}(CO)_{42}C_6]^{5-}$ is only suggested by the reversible protonation-deprotonation equilibrium (1).[8] Crystals of

$$[Ni_{38}(CO)_{42}C_6]^{6-} \underset{Me_2SO}{\overset{H^+,\ MeCN}{\rightleftharpoons}} [HNi_{38}(CO)_{42}C_6]^{5-} \qquad (1)$$

$[NBu_4]_5[HNi_{38}(CO)_{42}C_6]$ were grown from acetone by precipitation with isopropyl alcohol and the structure was determined by X-ray diffraction studies.[12]

The overall structure of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ pentaanion, which shows idealized D_{3d} and crystallographic $\bar{1}$ symmetry, is shown in Figure 1. Figure 2 shows the $Ni_{38}C_6$ core of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ cluster (Figure 2b), as well as the truncated octahedral $Ni_{32}C_6$ moiety contained in the above (Figure 2a). The inner core of the cluster consists in a Ni_8 empty cube ($Ni\text{-}Ni_{av}$ = 2.402 Å) capped onto the six square faces by six carbide atoms which are at the corners of a nonbonded C_6 octahedron (range of interatomic C...C separations = 3.25-3.32 Å). The six carbide atoms are caged into six Ni_8 square-antiprismatic moieties (Figure 2a, $Ni\text{-}C_{av}$ = 2.061, $Ni\text{-}Ni_{interlayer(av)}$ = 2.633 Å), originating from the inner cube and giving rise to an outer truncated octahedron of frequency 1[13] with an average edge length of 2.459 Å. The outer polyhedron recalls the structure of $[H_2Pt_{38}(CO)_{44}]^{2-}$,[1,14] but in contrast to the latter the $Ni_{32}C_6$ moiety does not have a close-packed inner core. Moreover, the central nickel atom of each hexagonal face, which belongs to the inner Ni_8 cube, lies well underneath the Ni_6-ring plane and, as a result, the eight hexagonal faces are clearly concave. The remaining six nickel atoms are μ_3-capping six out of the above eight hexagonal faces ($Ni\text{-}Ni_{av}$ = 2.488 Å), giving rise to a D_{3d} idealized symmetry (Figure 2b; the idealized threefold axis comprises the central nickel atoms of the two uncapped hexagonal faces).

As shown in Figure 1, of the 42 carbonyl groups six are terminally bound to the six μ_3-capping nickel atoms, whereas the remaining 36 are μ_2-edge-bridging ligands. This carbonyl stereochemistry is probably maintained in solution and is likely to be shown also by the $[Ni_{38}(CO)_{42}C_6]^{6-}$ hexaanion, as suggested by the close resemblance of the IR pattern of the two anions and

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(12) Crystal data: $[N(C_4H_9)_4]_5[HNi_{38}(CO)_{42}C_6]$, FW = 4692.86, monoclinic, space group $P2_1/c$, a = 29.208 (17) Å, b = 18.436 (9), Å, c = 32.821 (7) Å, β = 104.14 (4)°, V = 17138 (24) $Å^3$, Z = 4, Mo Kα radiation (λ = 0.71073 Å), μ(Mo Kα) = 41.50 cm^{-1}, D_{calcd} = 1.819 g cm^{-3}. The structure was solved by direct methods (MULTAN) and refined by full-matrix least squares (with anisotropic thermal factors for Ni atoms) on the basis of 7462 absorption-corrected reflections having $I \geq 4\sigma(I)$, in the 2θ range of 3-46°. R and R_w are 0.047 and 0.059, respectively. The asymmetric unit contains two crystallography independent "half"-anions located on inversion centers. No significant differences are observed between corresponding molecular parameters of the two independent anions.

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