Acknowledgment. We are grateful for support to K.S. from Carnegie-Mellon University through a grant from Ford Motor Co. and to B.M.C. from the National Institutes of Health (HL20350). We thank Dr. R. F. Stewart for fostering this collaborative effort. Crystallographic calculations were carried out by using the computer programs written or modified by Dr. Shiono. The 300- and 600-MHz NMR spectra (included in the supplementary material) were obtained by using facilities supported by the National Institutes of Health (GM27390, RR00272). We are indebted to Drs. A. A. Bothner-By, M. Llinas, R. Stephens, and J. Lecomte for their help in obtaining the spectra.

Registry No. (±)-**5a**, 85710-89-0; (±)-**6a**, 85710-90-3; (±)-**6b**, 85760-86-7.

Supplementary Material Available: NMR spectra for synthetic substances (19 pages). Ordering information is given on current masthead page.

Reactions of *tert*-Butyl Isocyanide with a Binuclear Niobium(III) Compound

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In the emerging chemistry of niobium and tantalum in their lower oxidation states, but without η^5-C_5R_5 groups, there is already evidence for remarkable reactivity toward nitriles,[1-3] acetylenes,[3-7] olefins,[8] and hydrogen.[8-10] We have now found that very remarkable compounds can be obtained by using isocyanides, e.g., by reaction of t-C_4H_9NC, with $Nb_2Cl_6(SMe_2)_3$ (Nb=Nb),[11] and we here describe two of these. The product yields are strongly influenced by reaction conditions, including the mole ratio of reactants. With an isocyanide/$Nb_2Cl_6(SMe_2)_3$ ratio greater than 7:1 two compounds, having the following apparent stoichiometries, are obtained: $Nb_3Cl_8(t\text{-BuNC})_5$ (**1**) and $Nb_2Cl_6(t\text{-BuNC})_6$ (**2**). These two compounds, neither of which can be converted into the other, probably arise from a common (as yet unidentified) green precursor. Crystalline red-brown compound **1** is obtained (ca. 20% yield) admixed with an amorphous dark solid by very slow interdiffusion of solutions of the reactants, whereas purple compound **2** is formed (ca. 60% yield) by rapid mixing of the solutions. To obtain good crystals of **2**, it was redissolved in 3:1 mixture of Et_2O and CH_3CN and the solution cooled to 0 °C.

Crystal structure determinations were carried out by standard methods, using data from an automated counter-diffractometer.[12,13] In neither case is any crystallographic symmetry imposed on the molecules.

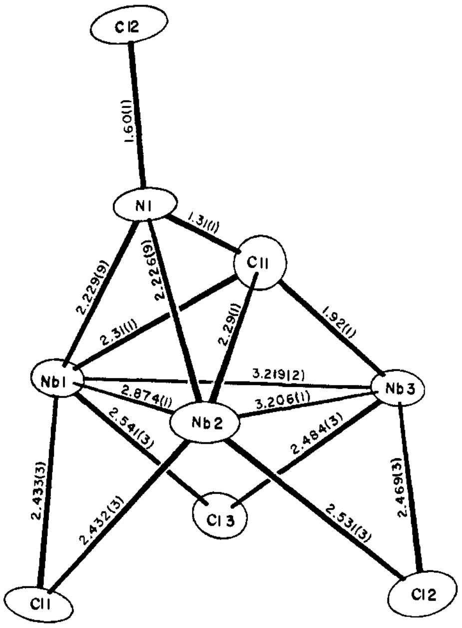
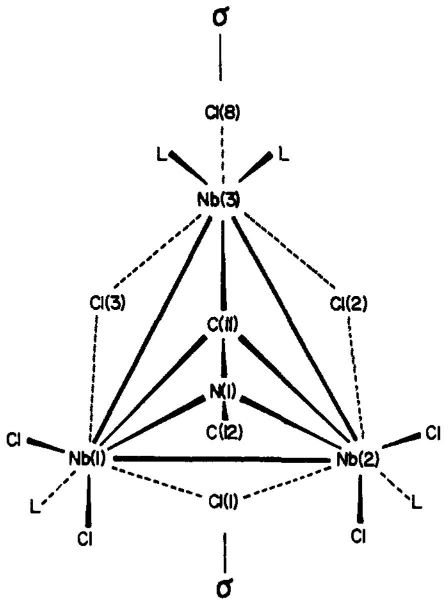


Figure 1. Central portion of the $Nb_3Cl_8(t\text{-BuNC})_5$ molecule, showing important bond lengths.

The $Nb_3Cl_8(t\text{-BuNC})_5$ molecule, shown schematically in I, has an approximate symmetry plane passing through Nb(3), Cl(8), C(11), N(1), C(12), and Cl(1) and bisecting the Nb(1)–Nb(2) bond. The more important bond lengths are shown in the ORTEP view of the central portion of the molecule, Figure 1. The niobium atoms define an isosceles triangle, with a bridging Cl atom below each edge and a rare type of multiply bridging isocyanide above the metal atom triangle. The short metal–metal distance (Nb(1)–Nb(2), 2.874 (1) Å) is suggestive of a two-electron bond, while the interpretation of the other two Nb–Nb distances, which average 3.213 [9] Å, is problematical. Nor is a detailed description of the bonding of the multiply bridging t-BuNC molecule to the Nb_3 cluster unambiguous solely on the basis of structural data.



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(12) Compound **1** crystallizes with two $C_6H_5CH_3$ per Nb_3 unit in space group $P2_1/c$ with unit cell dimensions of a = 23.750 (6) Å, b = 9.099 (2) Å, c = 25.031 (3) Å, β = 95.59 (2)°, and Z = 4 (trinuclear units). Refinement of 375 parameters using 3538 independent reflections with $F^2 \geq 3\sigma(F^2)$ produced reliability indices of R_1 = 0.071 and R_2 = 0.085. Tables of atomic positional and thermal parameters are available as supplementary material.

(13) Compound **2** crystallizes in space group Pn with unit cell dimensions of a = 14.102 (2) Å, b = 13.486 (5) Å, c = 11.157 (4) Å, β = 93.26 (2)°, and Z = 2 (dinuclear units). Refinement of 392 parameters using 2438 independent reflections with $F^2 \geq 3\sigma(F^2)$ produced reliability indices of R_1 = 0.054 and R_2 = 0.073. Tables of atomic positional and thermal parameters are available as supplementary material.

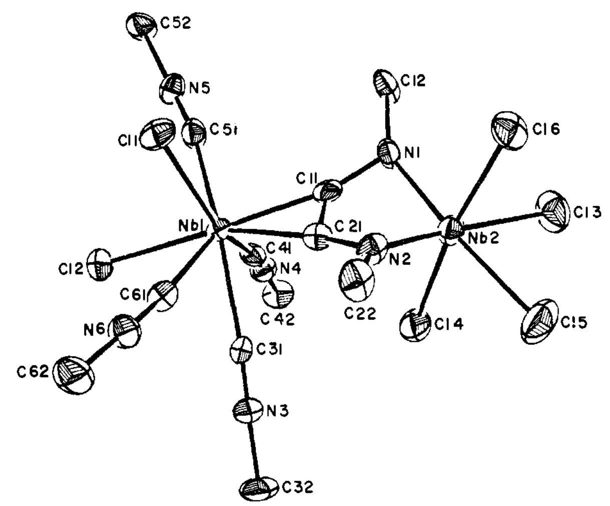

Figure 2. $Nb_2Cl_6(t\text{-}BuNC)_4(\mu\text{-}t\text{-}BuNCCN\text{-}t\text{-}Bu)$ molecule.

We think a reasonable hypothesis, beginning with $t\text{-Bu}{-}^{+}N{\equiv}C^{-}$: is that the two pairs of π electrons are used to form donor bonds to Nb(1) and Nb(2), in much the same way as alkynes form such $RC{\equiv}CR$ to M–M bridging arrangements, while C(11) forms a strong donor bond to Nb(3). It is difficult to assign oxidation numbers unambiguously, and this problem is still under investigation. The compound in solution gives a well-resolved EPR spectrum (9.075 MHz) at room temperature consisting of a symmetrical decet $\langle g\rangle \approx 1.95$ and $\langle A\rangle \approx 130$ G. This is consistent with a spin doublet ground state with the unpaired electron localized on one niobium atom, Nb(3).

The structure and the proposed bonding scheme for **1** are analogous to those recently reported[14] in $Fe_3(CO)_9(CN\text{-}t\text{-}Bu)$, although in this carbonyl compound all metal atoms have 18-electron configurations, whereas in our compound they do not. Formally similar stereoelectronic character is found with a CO ligand in $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_7$[15] and with a CH_3CN ligand in $Fe_3(CO)_9(CH_3CN)$,[16] and compounds with $\mu^2\text{-}\eta^2$-RNC ligands are also relevant.[17]

Compound **2** contains molecules of the type shown in Figure 2. Again there is an approximate plane of symmetry, containing Cl(1), Cl(2), Nb(1), Nb(2), Cl(4), and Cl(6). In this case, there is a unique bridging ligand that has arisen by the coupling of two isocyanide molecules to form a new carbon–carbon bond; there is at least one prior example of such a coupling.[18] Nb(1) has a coordination number of 8, or 7 if the C(11)–C(21) unit is taken as a single ligand. In the latter case the coordination polyhedron is effectively a pentagonal bipyramid. At Nb(2) the coordination is effectively octahedral.

The bonding in the bridging ligand is uncertain: the average C–N distance, 1.35 [2] Å, and the C–C distance, 1.42 (2) Å, as well as planarity at the nitrogen atoms, suggest a delocalized π system with C–C and C–N bond orders exceeding 1.0. If this bridging ligand is regarded as forming two Nb(1)–C single bonds and two Nb(2)←N donor bonds, the niobium atoms would each be in oxidation state IV. Since the NMR spectrum shows that the molecule is diamagnetic,[19] this picture then needs to be supplemented by some means of pairing the two electrons thus left on the metal atoms. We assume that this occurs through the π system of the BuNCCNBu ligand that connects the two metal atoms. It cannot, of course, be ruled out that the oxidation states of the metal atoms should be assigned as III and V, whereby the diamagnetism could also be accounted for.

Acknowledgment. This work was supported by a grant from the Robert A. Welch Foundation.

Registry No. 1, 85552-55-2; **2**, 85533-79-5; $Nb_2Cl_6(Me_2S)_3$, 75038-66-3.

Supplementary Material Available: Tables of atomic positional and thermal parameters for both structures (8 pages). Ordering information is given on any current masthead page.

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[19] The ^1H NMR also shows fluxionality, which is still under study.

A Nondegenerate Mirror-Image Rearrangement: Semibullvalene in the Solid State

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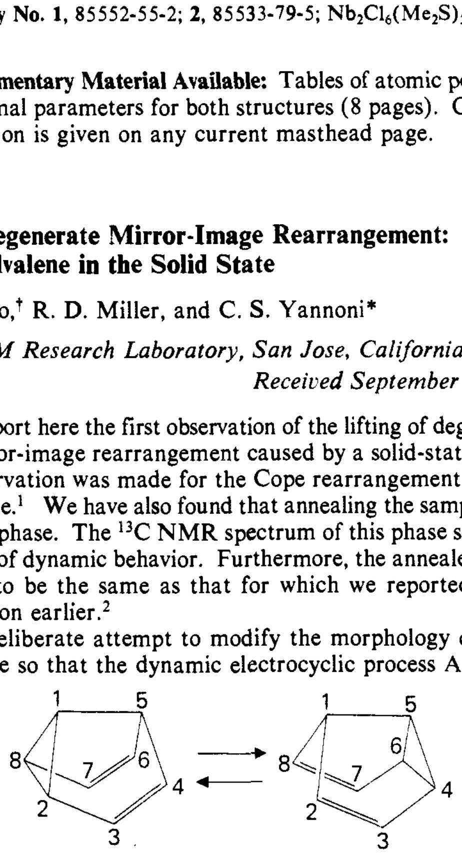
We report here the first observation of the lifting of degeneracy in a mirror-image rearrangement caused by a solid-state effect; this observation was made for the Cope rearrangement of semibullvalene.[1] We have also found that annealing the sample leads to a new phase. The ^{13}C NMR spectrum of this phase shows no evidence of dynamic behavior. Furthermore, the annealed phase appears to be the same as that for which we reported a rate suppression earlier.[2]

In a deliberate attempt to modify the morphology of semibullvalene so that the dynamic electrocyclic process A ⇌ B is observable in the solid state by ^{13}C NMR, we experimented with a number of rapid cooling techniques.[3,4] Spectra obtained from samples prepared by any of these methods are identical and are shown in Figure 1a as a function of temperature. At −185 °C, the classic five-line pattern characteristic of a nonrearranging semibullvalene (A or B) is observed.[1,2] Increase in temperature causes a broadening of the outer lines accompanied by a slight change in the corresponding chemical shifts. At −95 °C, the appearance of the spectrum has changed dramatically, and the individual aliphatic and vinylic carbon resonances have almost merged into two signals, one upfield and one downfield, respectively. This behavior is completely reversible with temperature. It is important to note that the solution-averaged spectrum (see arrows in Figure 1a) was never observed in the accessible temperature range.[5] This interesting spectral behavior can be ra-



A B

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