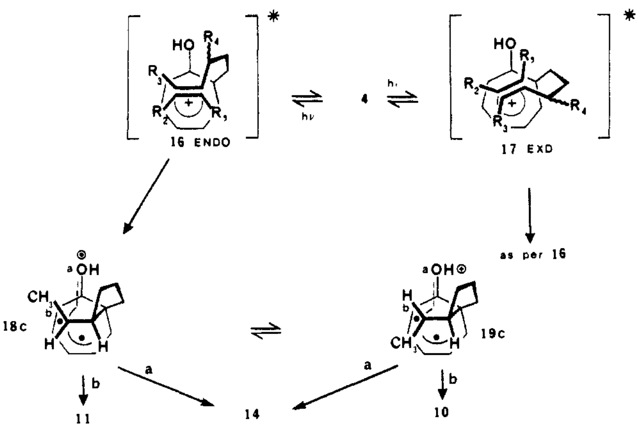
Scheme I



ature with 350-nm light. When GLC analysis indicated consumption of starting material (30–60 min), the cycloadducts were isolated by chromatography on silica gel. Representative results are shown in Table I.

Examination of the cycloadduct structures reveals the regiochemical and stereochemical complexity of this reaction. The regiochemistry of addition (i.e., [6 + 2] vs. [8 + 2]) is sensitive to the location of the methyl substituent on the alkenyl side chain, as exclusive [6 + 2] cyclization results only when $R_1 = CH_3$ (**3a**).

When the stereochemical outcome of the [6π + 2π] cyclization of alkenyl tropones **3a–c** is considered, two issues must be addressed: (1) the endo vs. exo mode of cycloaddition and (2) the loss of alkene stereochemistry upon [6 + 2] cyclization of **3b** and **3c**. Quite surprisingly, the exo mode of addition, which produces the highly strained *trans*-bicyclo[3.3.0]octane adduct **8**,[10] is favored upon irradiation of **3a**. Furthermore, irradiation of either the (*E*)-alkenyl tropone **3b** or the *Z* isomer **3c** resulted in product distributions containing virtually identical ratios of endo [6 + 2] adducts **10** and **11** to [8 + 2] adduct **14**. Control experiments demonstrated that the (*E*)- and (*Z*)-alkenyl tropones do not interconvert under the reaction conditions, indicating that alkene stereochemistry is not lost prior to cycloaddition.

To account for the regiochemical and stereochemical results of this unique tropylium–alkene photocyclization reaction, we suggest a mechanism shown in Scheme I. Our hypothesis features stereochemical control through initial exciplex formation, followed by regiochemical control through eventual diradical collapse with either carbon–carbon or carbon–oxygen bond formation.

We postulate that the ratio of endo (**7**, **10–13**) to exo (**8**, **9**) products of [6π + 2π] cycloaddition reflects the relative populations, and hence stabilities, of the diastereomeric parallel plane exciplexes **16** and **17** formed upon electronic excitation of hydroxytropylium precursor **4**. It is plausible that placing a methyl substituent directly over the cationic ring disrupts the stabilizing solvation by the nucleophilic solvent and raises the energy of that exciplex.[11] Thus, irradiation of **4a** and **4c** would generate exciplexes **16a** and **17c** which both experience this destabilizing interaction. Therefore, the major products of these cycloadditions are derived from the alternative exciplexes **17a** and **16c**, respectively.

For simplicity, the remainder of the scheme is detailed for the endo tropylium exciplex **16c** derived from (*Z*)-alkenyltropone **3c**. Collapse of this endo exciplex would produce diradical **18c** which can lose initial alkene stereochemistry through equilibration with the diastereomeric diradical **19c**. According to our mechanistic hypothesis, the strain inherent in the *trans*-bicyclo[3.3.0]octane portion of adducts **8** and **9** is not imparted until the final bond closure step. The step that determines stereochemistry (collapse of exciplexes **17a** or **17b** with carbon–carbon bond formation) occurs prior to introduction of this strain, and therefore the product stereochemistry is simply a consequence of exciplex stability.

In summary, we have developed an efficient synthesis of functionalized bicyclo[6.3.0]undecane carbocycles through an intramolecular [6π + 2π] photocycloaddition reaction of alkenyltropones. The regiochemical and stereochemical outcome of this reaction can be rationalized through a novel mechanistic pathway. Applications of this [6π + 2π] photocyclization reaction to the synthesis of cyclooctane-containing natural products are in progress.

Acknowledgment. We thank the Syntex-Russell Marker Fund and a Schering-Plough Corporation Grant of Research Corporation of financial support and Dr. M. Parvez for performing the X-ray crystallography analysis of **8**.

Supplementary Material Available: Tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and labeled diagrams for **8** (6 pages). Ordering information is given on any current masthead page.

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(6) The alkenyltropones used in this study were prepared by addition of the corresponding alkenyl Grignard reagents to 2-chlorotropone: **3a**, 80%; **3b**, 26%; **3c**, 42%; **3d**, 30%. Doering, W. v. E.; Hiskey, C. F. *J. Am. Chem. Soc.* **1952**, *74*, 5688.

(7) (a) R_n = H unless otherwise noted. (b) The yields in Table I are reported as GLC yield (isolated yield) percent. Sensitivity of the cycloadducts to chromatographic purification typically resulted in diminished recovered yields.

(8) All new compounds exhibited satisfactory spectral data (^{1}H NMR, ^{13}C NMR, IR, MS, high-resolution MS, UV). The stereochemistry of the cycloadducts could be deduced from an examination of extensive ^{1}H NMR decoupling and difference NOE data. The complete structure and stereochemistry of cycloadduct **8** was determined by single-crystal X-ray analysis. Crystal data for **8**: $C_{13}H_{16}O$; M 188.3; monoclinic; space group $P2_1/n$; a = 13.038 (4) Å, b = 6.437 (1) Å c = 13.004 (3) Å, β = 105.53 (2)°; V = 1051.6 Å^3; Z = 4; D_{calcd} = 1.19 g cm^{-3}; Enraf-Nonius CAD4 diffractometer, MO $K\alpha$ (λ = 0.71073 Å) radiation, μ = 0.68 cm^{-1}; 864 observed reflections [$I > 3\sigma(I)$] refined to a conventional R = 0.072 (R_w = 0.079).

(9) Identical 1:1 mixture of two stereoisomeric [8 + 2] adducts were isolated from irradiation of either **3b** or **3c**. The stereochemical assignments for these isomers is still being investigated. (b) A 1:1 mixture of stereoisomeric [8 + 2] adducts was recovered from irradiation of **3d**. These adducts were not further characterized.

(10) Molecular mechanics calculations suggest that exo adduct **8** is ca 9 kcal/mol less stable than endo adduct **7**.

(11) A similar arguement can be invoked to rationalize the stereochemical outcome of the Diels–Alder cycloaddition between tropylium tetrafluoroborate and cyclopentadiene in water. See: Ito, S.; Itoh, I. *Tetrahedron Lett.* **1971**, 2969. Clemans, G. B.; Dobbins, M. A. *Tetrahedron Lett.* **1982**, 382.

Synthesis of Polyoxygenated Hydrocarbons via Radical-Mediated Oxygenation of Vinylcyclopropanes

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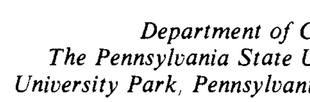
The development of regio- and stereocontrolled methods for introduction of oxygen into unsaturated hydrocarbons has led to the construction of many complex polyoxygenated natural products. For example, recent advances in the epoxidation or hydroxylation of alkenes afford a general solution to the synthesis of the vicinal diol segments common to many antibiotics and carbohydrates.[1] The corresponding oxidation of cyclopropanes (eq 1) has received scant attention,[2] despite its potential for direct



(1)

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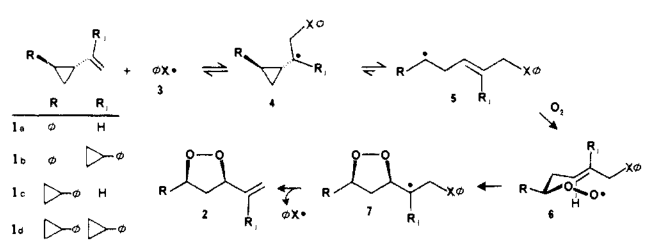
† Author to whom inquiries regarding the X-ray data should be addressed.

(1) (a) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, 3943. (b) Christ, W. J.; Cha, J. K.; Kishi, Y. *Ibid.* **1983**, 3947. (c) Behrens, C. W.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67 and references cited therein.

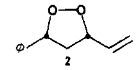
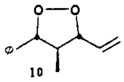
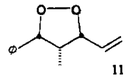
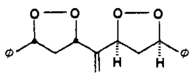
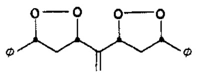
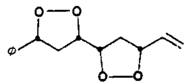
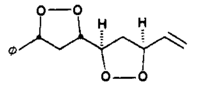
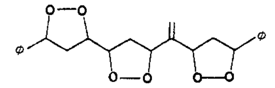
Scheme I



access to the 1,3-diol unit common to many polyacetate-derived natural products. The repetitive nature of the 1,3-diol subunit in many of the polyol macrolide antibiotics, and our interest in developing applications of multicomponent condensations in organic synthesis, suggested to us that sequential oxidation of appropriate polycyclopropane precursors might provide direct entry into such polyol segments. In this paper we report our preliminary results on a conceptually new, stereoselective approach to the direct oxidation of cyclopropane derivatives through radical intermediates in which molecular oxygen ($^3O_2$) serves as the oxidant.

On the basis of the seminal investigations of Beckwith[3a] and Porter,[3b,c] inter alia, we reasoned that a cyclopropane bearing a radical accepting group, such as vinyl, and a radical stabilizing group, such as phenyl, might incorporate a molecule of oxygen as detailed in Scheme I.[3] The expectation that this series of unimolecular and bimolecular radical reactions will occur as outlined could be justified by considering the relative magnitudes of the expected rates of reaction for each step. Specifically, addition of phenylthio radical to substituted vinylcyclopropanes has been demonstrated to occur at a nearly diffusion-controlled rate.[4,5] Cyclopropylcarbinyl radical **4** could trap oxygen directly or open to the homoallylic radical **5**. As the rate of cyclopropyl cleavage is known to be more rapid than the rate of oxygen addition to secondary radicals at low oxygen concentration,[6] we anticipated that homoallylic radical **5** would be the first radical sufficiently long lived to trap oxygen. Cyclization of the 5-hexenylperoxy radical **6** through a conformer which minimizes 1,3-diaxial interactions is well precedented.[6a] Thus, the pseudoequatorial substituent R should anchor **6** as shown, and the syn, 1,2-dioxolane **7** was anticipated.[3,6a,7] Peroxyl radical **7** could partition through three precedented pathways: (1) rearrangement to an epoxyalkoxy radical,[8] (2) trapping by molecular oxygen, or (3) expulsion of thio radical.[9] Again, a consideration of rate constants[6,8,9] suggested the unimolecular expulsion of thio radical should prevail at low oxygen concentration.

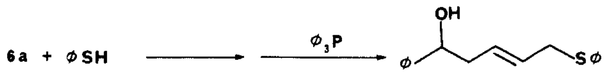
Table I

vinylcyclopropane[10]	react cond[a]	1,2-dioxolane products	yield[11]
1a	a	 2	63
 9	b	 10 2.8 : 1  11	73
1b	c	 12 1 : 1  13	79
1c	d	 14 1 : 1.4  15	48
1d	e	 16	38

^{a}Conditions: (a) 0.1 equiv of $(C_6H_5)_2Se_2$, 0.05 equiv of AIBN, CH_3CN, 0 °C. (b) 1.0 equiv of $(C_6H_5)_2Se_2$, 0.25 equiv of $(C_6H_5)_2$AIBN, CH_3OH, -50 °C. (c) 0.04 equiv of $(C_6H_5)_2Se_2$, 0.02 equiv of AIBN, CH_3CN, 0 °C. (d) 0.4 equiv of $(C_6H_5)_2S_2$, 0.2 equiv of AIBN, CH_3CN, 0 °C. (e) 0.3 equiv of $(C_6H_5)_2S_2$, 0.15 equiv of AIBN, CH_3CN, 0 °C.

In fact, slow addition of an acetonitrile solution of diphenyl disulfide (35 mM) and AIBN (17 mM) to a stirred, ice-cooled 12 mM acetonitrile solution of vinylcyclopropane **1a** under 1 atm of oxygen, with concomitant sunlamp irradiation, produced *exclusively* the syn 1,2-dioxolane **2** in 63% yield after flash chromatography. The other vinylcyclopropanes illustrated in Table I were allowed to react in a similar manner to give the indicated products.

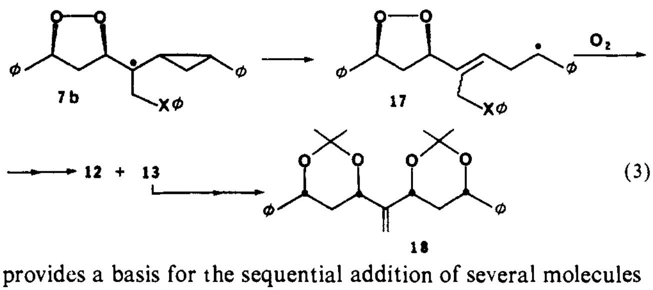
In support of our mechanistic hypothesis, when **1a** was allowed to react with thiophenol, followed by triphenylphosphine reduction of the reaction mixture, a substantial amount (22%) of alcohol **8** was produced (eq 2). This alcohol presumably arises through



8 (2)

hydrogen abstraction from thiophenol by peroxy radical **6a**. Moreover, the formation of **8** was suppressed when diphenyl disulfide was used as the radical source. Omission of any of the components used to generate the initial chalcogen radical (sulfur or selenium radical source, AIBN, sunlamp irradiation) resulted in complete recovery of the vinylcyclopropane, indicating that the cyclopropane ring does not interact directly with molecular oxygen.

Carbon radicals such as **5** or **7** can be diverted from the reaction path illustrated in Scheme I by incorporating additional cyclopropyl substituents in the molecule. For example, **7b** underwent a *second* cyclopropylcarbinyl cleavage with incorporation of an additional molecule of oxygen (eq 3). This repetitive process



(3)

provides a basis for the sequential addition of several molecules of oxygen to the bis- and tris(cyclopropane) derivatives **1b–d**

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(2) (a) For a multistep formal addition of oxygen across a cyclopropane, see: Adam, W.; Birke, A.; Cadiz, C.; Diaz, S.; Rodriguez, A. *J. Org. Chem.* **1978**, *43*, 1153. (b) Adventitious insertion of oxygen across uniquely activated cyclopropanes can be found in: Becker, H. D.; Elebring, T. *J. Org. Chem.* **1985**, *50*, 1319. Askani, R.; Wieduwilt, M. *Chem. Ber.* **1976**, *109*, 1887. Criegee, R.; Askani, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 537.

(3) For mechanistically related processes, see: (a) Beckwith, A. L. J.; Wagner, R. D. *J. Chem. Soc., Chem. Commun.* **1980**, 485. (b) Khan, J. A.; Porter, N. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 217. (c) Roe, A. N.; McPhail, A. T.; Porter, N. A. *J. Am. Chem. Soc.* **1983**, *105*, 1199. (d) O'Connor, D. E.; Mihelich, E. D.; Coleman, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 3577.

(4) Lishanskii, I. S.; Vinogradova, N. D.; Zak, A. G.; Zvyagina, A. B.; Guliev, A. M.; Fomina, O. S.; Khachuturov, A. S. *Zh. Org. Khim.* **1974**, *10*, 493.

(5) The rate constant for phenylthio radical addition to styrene is 1.2 × 10^9 L m^{-1} s^{-1} and to 1-butene is 7 × 10^6 L m^{-1} s^{-1} at 25 °C. Sivertz, C. *J. Phys. Chem.* **1959**, *63*, 34.

(6) (a) Cyclopropylcarbinyl radicals open with a rate constant of $\sim 10^8$ s^{-1}. See: Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073 and references therein. (b) Benzyl radical combines with molecular oxygen with a rate constant of $\sim 3 \times 10^9$ L m^{-1} s^{-1} (25 °C). Maillard, B.; Ingold, K. U.; Scaiano, J. *J. Am. Chem. Soc.* **1983**, *105*, 5095.

(7) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron Lett.* **1985**, 373.

(8) 3-Methylene 1,2-dioxolane radicals rearrange to epoxyalkoxy radicals with a rate constant of 7.5 × 10^4 s^{-1} (25 °C). Porter, N. A.; Nixon, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7116.

(9) The rate constant for the ejection of thio radical from a β-thio alkyl radical can be estimated to be $\geq 10^6$ s^{-1}. Walling, C.; Helmreich, W. *J. Am. Chem. Soc.* **1954**, *81*, 1144. Onyszchuk, M.; Sivertz, C. *Can. J. Chem.* **1957**, *35*, 723. See also ref 6b.

yielding bis- and tris(1,2-dioxolanes) (Table I).

The diastereofacial selectivity of oxygen addition to the carbon radical in mono(dioxolane) **17** under the influence of the distal asymmetric center (1,5 relationship) is negligible, and an equal mixture of syn bis(1,2-dioxolanes) is produced. In the case of bis cyclopropane **1c**, there is modest 1,2-diastereofacial selectivity in the addition of oxygen to the intermediate monodioxolane carbon radical, and a slight preference for the erythro syn bis(1,2-dioxolane) **15** is observed.

The structure and stereochemistry of dioxolanes **12** and **14** were determined by X-ray crystallographic analysis. The syn stereochemistry of the 1,2-dioxolanes contained in **2**, **10**, **11**, **13**, and **15** was deduced from examination of ^{1}H coupling constants in the derived acetonides (lithium aluminum hydride reduction; 2,2-dimethoxypropane, catalytic PPTS in CH_2Cl_2).[10] In summary, we have demonstrated that radical-mediated addition of molecular oxygen to vinyl cyclopropanes is an efficient method for preparing syn 1,2-dioxolanes and that multiple addition of oxygen to polycyclopropanes occurs with some diastereoselectivity. For instance, only two out of eight possible diastereomeric bis(1,2-dioxolanes) are formed from vinylcyclopropane **1c**, while five out of 32 possible tris(1,2-dioxolanes) are formed from **1d**. We are currently examining the scope and limitations of this novel oxygenation process.

Acknowledgment. We thank Drs. DeShong and Weinreb for helpful discussions, Thorsten Fisher for his experimental contributions, and the Syntex-Russell Marker Fund for financial support.

Supplementary Material Available: Tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and labeled diagrams for **12** and **14** (12 pages). Ordering information is given on any current masthead page.

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(10) The syntheses of the vinylcyclopropanes used in this study, and a discussion of the assignment of stereochemistry of the derived 1,2-dioxolanes,[12] will be detailed in a full account of this work.

(11) All yields refer to chromatographically pure compounds. Compounds were characterized by standard spectral methods (^{1}H NMR, ^{13}C NMR, low- and high-resolution mass spectroscopy).

(12) For characterization of a similar structure, see: Beckwith, A. L. J.; Wagner, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 7099 and ref 3a.

Synthesis and Structural Characterization of the $[Ni_9(AsPh)_3(CO)_{15}]^{2-}$ and $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$ Dianions Containing Noncentered Icosahedral $Ni_{12-x}As_x$ Cores (x = 2, 3): Electronically Equivalent Metal Cluster Analogues of the Regular Icosahedral $[B_{12}H_{12}]^{2-}$ Dianion

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Received October 29, 1985

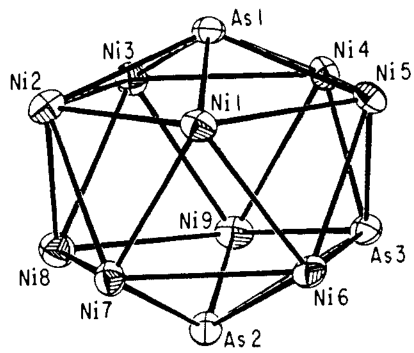

Figure 1. Noncentered icosahedral Ni_9As_3 core in the $[Ni_9(AsPh)_3(CO)_{15}]^{2-}$ dianion (**1**) of crystallographic C_1-1 site symmetry. This core of idealized mirror-plane geometry has *shorter* As(1)···As(2) and Ni(2)···Ni(3) distances of 3.932 (7) and 4.732 (8) Å, respectively, than the other trans Ni···Ni distances of 4.909 (8)–5.031 (8) Å. The eight Ni–Ni distances (range, 2.587 (8)–2.767 (7) Å; mean, 2.680 Å) within the As-capped Ni_5 and Ni_4As pentagons are 0.16 Å *longer* than the 10 interpentagonal Ni–Ni distances (range, 2.452 (7)–2.564 (8) Å; mean, 2.519 Å). The 13 Ni–As distances vary from 2.340 (7) to 2.474 (6) Å; the unique As–As distances is 2.507 (6) Å. A terminal carbonyl ligand is coordinated to each of the nine nickel atoms; four of the other six carbonyl ligands are doubly bridging and the remaining two are triply bridging.

Herein we report the synthesis and structural-bonding analysis of the $[Ni_9(AsPh)_3(CO)_{15}]^{2-}$ dianion (**1**) and the $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$ dianion (**2**). The *noncentered* icosahedral skeletal framework displayed by the nickel–arsenic cores of these high nuclearity clusters is unprecedented for discrete non-boron species; previous molecular examples of this architecture (which is one of the five regular Platonic polyhedra[1]) as a basic structural bonding unit have been limited to the $[B_{12}H_{12}]^{2-}$ dianion,[2] the $[B_{12}X_{12}]^{2-}$ dianions (X = Cl, Br, I),[3] and a number of carboranes and metallocarboranes[4] (with a skeletally substituted carborane containing one, two, or in one example[5] three metal atoms). These *noncentered* 12-atom icosahedral (i.e., bicapped pentagonal antiprismatic) structures represent a marked contrast to the 13-atom icosahedral metal cages with encapsulated atoms observed in several high nuclearity metal clusters including the Au-centered Au_{13} icosahedron in the 162-electron $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ trication,[6] the Sb-centered $Rh_{12}Sb$ icosahedron in the 170-electron $[Rh_{12}Sb(CO)_{27}]^{3-}$ trianion,[7] and the interpenetrating Au-centered $Au_{13}Ag_{12}$ triicosahedra in the $[(Ph_3P)_{12}Au_{13}Ag_{12}Cl_6]^{n+}$ cation.[8] Centered icosahedral transition-metal clusters have been experimentally and theoretically implicated as a structural unit in a wide variety of amorphous materials[9,10] and in the formation and growth of small metal particles.[11]

In addition to their unusual architectures, **1** and **2** provide the first illustration (to our knowledge) of an AsR ligand coordinated equally to *five* metal atoms. A similar mode of pentametal coordination has been previously observed for the electronically equivalent (isolobal[12]) PR ligand.[13]

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(1) Cf.: Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford University Press: London, 1975; pp 60–63.

(2) (a) Lipscomb, W. N.; Wunderlich, J. A. *J. Am. Chem. Soc.* **1960**, *82*, 4427–4428. (b) Mutterties, E. L.; Merrifield, R. E.; Miller, H. C.; Knoth, W. H.; Downing, J. R. *J. Am. Chem. Soc.* **1962**, *84*, 2506–2508.

(3) Muetterties, E. L.; Knoth, W. H. *Chem. Eng. News* **1966**, 88.

(4) (a) Muetterties, E. L.; Knoth, W. H. "Polyhedral Boranes"; Marcel Dekker: New York, 1968; pp 21–31 and references cited therein. (b) Greenwood, N. N.; Earnshaw, A. "Chemistry of the Elements"; Pergamon Press: New York, 1984; pp 206–213. (c) Grimes, R. N. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1984; Vol. I, pp 459–542. (d) Ferguson, G.; Hawthorne, M. F.; Kaitner, B.; Lalor, F. J. *Acta Crystallogr., Sect. C* **1984**, *C40*, 1707–1709. (e) O'Neill, M. E.; Wade, K. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum Press: New York, 1982; pp 1–36.

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(10) Charlot, M.-F.; Kahn, O. *Surf. Sci.* **1979**, *81*, 90–108 and references cited therein.

(11) Renou, A.; Gillet, M. *Surf. Sci.* **1981**, *106*, 27–34 and references cited therein.

(12) (a) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148–1155. (b) Hoffmann, R. *Science (Washington, D.C.)* **1981**, *211*, 995–1002.

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