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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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]

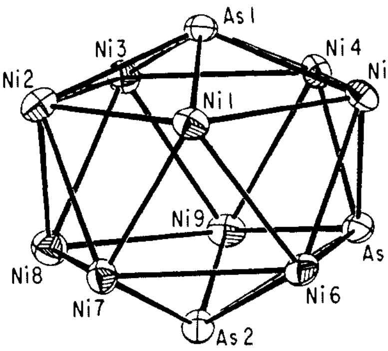

Figure 1. Noncentered icosahedral Ni_9As_3 core in the $[Ni_9(AsPh)_3(CO)_{15}]^{2-}$ dianion (**1**) of crystallographic C_1-1 site symmetry. This core of idealized mirror-plane geometry has *shorter* As(1)···As(2) and Ni(2)···Ni(3) distances of 3.932 (7) and 4.732 (8) Å, respectively, than the other 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.

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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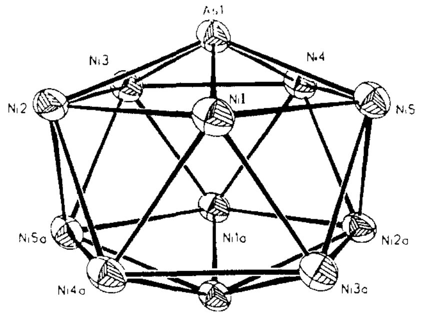

Figure 2. Noncentered icosahedral $Ni_{10}As_2$ core in the $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$ dianion (2) of crystallographic C_i-$\bar{1}$ site symmetry. This idealized D_{5d}-$\overline{10}2m$ core is considerably flattened along its pseudo-five-fold axis (As···As distance of 3.689 (3) Å vs. centrosymmetrically related Ni···Ni distances of range 4.957 (2)–5.043 (2) Å). The five independent Ni–Ni distances (range, 2.621 (2)–2.731 (2) Å; mean, 2.686 Å) within the two symmetry-equivalent As-capped Ni_5 pentagons are 0.20 Å *longer* than the five independent interpentagonal Ni–Ni distances (range, 2.417 (2)–2.522 (2) Å; mean, 2.490 Å). The five independent Ni–As distances vary from 2.405 (2) to 2.450 (2) Å (mean, 2.428 Å). A terminal carbonyl ligand is attached to each of the ten nickel atoms; of the other eight carbonyl ligands, six are doubly bridging and two may be considered as triply bridging.

The syntheses of **1** and **2** were accomplished as part of an extension of our exploratory studies of the reactions of the polynuclear nickel carbonyl dianions[14] with dihalophosphines PRX_2 (R = Ph, *t*-Bu, Me; X = Cl, Br) which have yielded a wide variety of intriguing large nickel carbonyl phosphinidene clusters.[13,15] The preparation of **1** resulted from the addition of 1 equiv (0.61 g, 1.7 mmol) of $AsPhCl_2$ to a room-temperature solution of $[NMe_4]_2^+[Ni_6(CO)_{12}]^{2-}$ (1.53 g, 1.83 mmol) in 50 mL of dry THF. The solution quickly changed from a dark red to a black color. After the mixture was stirred for 8 h under N_2, the solvent was removed under vacuum. Extraction of the residue with toluene gave a small amount of red-brown solution; attempts to crystallize this fraction have been unsuccessful. Extraction of the remaining residue with THF gave a black powder from which crystals were obtained by a layering of cyclohexane on a THF solution. An infrared spectrum of **1** in THF exhibited a strong terminal band at 1995 cm^{-1} and a broad bridging carbonyl band centered approximately at 1805 cm^{-1}. The synthesis and isolation of **2** from $[NMe_4]_2^+[Ni_6(CO)_{12}]^{2-}$ and $AsMeBr_2$ were carried out in a similar manner. An infrared spectrum of **2** in THF showed carbonyl bands at 2005 (s) and 1840 (m) cm^{-1}. Both **1** and **2** were obtained in ~40% yield.

X-ray structural determinations[16–18] of the tetramethylammonium salts of **1** and **2** revealed the existence of Ni–As frameworks which approximate *noncentered* icosahedral architectures (Figures 1 and 2). In **2** the two trans pentagonal faces of a pentagonal antiprism of 10 nickel atoms are capped by two methylarsinidene ligands thereby giving rise to the centrosymmetric closo-1,12-disubstituted icosahedral $Ni_{10}As_2$ isomer; in **1** the icosahedral Ni_9As_3 arrangement corresponds to the closo-1,2,12-trisubstituted isomer.

Application of the Wade–Mingos skeletal electron-pair model[19] shows that **1** and **2** are electronically equivalent with the regular icosahedral $[B_{12}H_{12}]^{2-}$ dianion in possessing 13 skeletal electron pairs.[20] This electronic equivalence of **1** and **2** is a consequence of the formal replacement of a four-electron-donating arsinidene fragment in **1** with a four-electron-donating $Ni(CO)_3$ fragment in **2**. Further substitution of the two arsinidenes in **2** with two isolobal $Ni(CO)_3$ fragments leads to the electronically equivalent, hypothetical $[Ni_{12}(CO)_{24}]^{2-}$ dianion whose valence electron count of 170 is consistent not only with the Wade–Mingos rules[19] but also with both the Lauher model[21] and the Teo topological electron-counting model[22] for an icosahedral geometry. The fact that the electronically analogous $[Pt_{12}(CO)_{24}]^{2-}$ dianion, whose overall configuration consists of an essentially trigonal prismatic metal stacking of four $Pt_3(CO)_3(\mu_2\text{-}CO)_3$ layers, does *not* adopt an icosahedral metal arrangement (even though it has the appropriate 170 valence electrons) is presumed to be due to steric repulsions of the overcrowded 24 carbonyl ligands rendering an icosahedral metal geometry unstable relative to its observed geometry. From steric considerations, we conclude that it is unlikely that an icosahedral $[Ni_{12}(CO)_{24}]^{2-}$ dianion can be isolated.

Current work in our laboratories is directed at (1) exploring the reactivities of **1** and **2** including protonation reactions and (2) carrying out further reactions of the nickel carbonyl anions with PRX_2, $AsRX_2$, and $SbRX_2$ reagents. In fact, these latter studies have recently led to the formation of noncentered icosahedral nickel–phosphorus and nickel–antimony clusters; details of these investigations will be presented elsewhere.[23]

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Supplementary Material Available: Tables listing the atomic parameters and appropriate distances and bond angles for both $[NMe_4]_2^+[Ni_9(AsPh)_3(CO)_{15}]^{2-}\cdot 2THF$ and $[NMe_4]_2^+[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$ (13 pages). Ordering information is given on any current masthead page.

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(16) $[NMe_4]_2^+[Ni_9(AsPh)_3(CO)_{15}]^{2-}\cdot 2THF$ (fw = 1697.1): Monoclinic; Cc (C_s^4 No. 9); a = 22.556 (7) Å, b = 14.871 (4) Å, c = 19.028 (2) Å, β = 98.99 (2)°, V = 6304 Å^3; ρ_{obsd} = 1.81 g/cm^3 (flotation method) vs. ρ_{calcd} = 1.79 g/cm^3 for Z = 4. The crystal structure (with the independent unit consisting of two monocations and one dianion) was determined from direct methods (MULTAN[17]) followed by successive Fourier syntheses. Anisotropic least-squares refinement converged at $R_1(F)$ = 6.9% and $R_2(F)$ = 5.9% for 2323 independent reflections (with $I \geq 2.5\sigma(I)$) obtained at room temperature via a Syntex (Nicolet) P$\bar{1}$ diffractometer with Mo Kα radiation.

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(20) By analogy to the *closo*-$[B_{12}H_{12}]^{2-}$ dianion in which two electrons are assigned to each terminal B–H bond leaving 13 electron pairs for skeletal bonding, each Ni or As atom is considered to contribute three valence orbitals for skeletal cluster bonding; on the basis of each Ni(CO) fragment contributing zero electrons and the arsinidine and other carbonyl ligands each providing four and two electrons, respectively, the resulting electron count for skeletal bonding in both **1** and **2** is also 13 electron pairs.

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