Table V. Selected Metal–Carbon and C–C Bond Distances (Å) in Group 3 Cyclopentadienyl–Metal Derivatives

	metal-bridging carbon distances		other M–C	C–C distances in the C_5 rings					
compd	ring A	ring A′	distances	C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_1	av
$Al(\mu\text{-}C_5H_5)Me_2$	2.203 (2)	2.248 (2)	1.959 (2) 1.947 (2)	1.397 (3)	1.402 (3)	1.430 (3)	1.355 (3)	1.418 (3)	1.400
$Ga(\mu\text{-}C_5H_5)Me_2$[b]	2.215 (2)	2.314 (2)	1.972 (2) 1.962 (1)	1.415 (2)	1.415 (2)	1.415 (2)	1.365 (2)	1.426 (3)	1.407
$In(\mu\text{-}C_5H_5)(C_5H_5)_2$[c]	2.374 (7)	2.466 (8)		1.395 (13)	1.381 (13)	1.443 (13)	1.358 (15)	1.412 (14)	1.398
ring B			2.243 (9)	1.405 (14)	1.344 (14)	1.412 (13)	1.340 (13)	1.426 (13)	1.385
ring C			2.237 (9)	1.425 (14)	1.370 (14)	1.411 (15)	1.337 (16)	1.430 (14)	1.395
$Al(C_5H_5)Me_2$[d]	Al–C(1) = Al–C(2) = 2.21 (2)			1.422 (2)					
$AlCl(C_5Me_5)(Me)$[e]				1.43 (1)	1.39 (1)	1.37 (11)	1.38 (1)	1.44 (1)	
$Mg(C_5H_5)_2$[f]	2.304 (8) av			1.39 (2) av, range 1.35 (2)–1.41 (2)					
$Na(C_5H_5)\cdot TMEDA$[g]	2.283 (7)–2.324 (7)			1.381 av, range 1.366–1.402 (18)					

[a] This work. [b] Reference 11. [c] Reference 12; rings B and C are σ bonded to the In atom. [d] Reference 19; monomer, gas phase $Al(C_5H_5)(CH_3)_2$; all C–C distances assumed to be equivalent in the cyclopentadienyl ring. [e] Reference 20. [f] Reference 21. [g] Reference 22.

the magnesium[21] and sodium[22] cyclopentadienides cited in Table V.

These differences have been assumed to be averaged or nonexistent for the monomeric aluminum in the gas phase, with subsequent molecular orbital calculations[23] providing support for an η^2-C_5H_5–metal interaction. The present work, as noted above, supports a more localized interaction for the compound in the solid state.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $[Al(\mu\text{-}C_5H_5)(CH_3)_2]_n$, 79255-65-5.

Supplementary Material Available: Listings of observed and calculated structure amplitudes (×10) (6 pages). Ordering information is given on any current masthead page.

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Correspondence

Closo Clusters with Unusual Electron Numbers: Molecular Orbital Considerations and Localized Bonding Schemes

Sir:

Most known closo borane clusters with *n* skeletal atoms, like the anions $B_nH_n^{2-}$ (n = 6–12) and carboranes $C_2B_{n-2}H_n$ (n = 5–12) are held together by (n + 1) skeletal bond pairs.[1-6] However, there is an increasing number of closo systems now known, including neutral boron halides such as B_8Cl_8[7] and B_9Cl_9,[8] the cationic bismuth cluster Bi_9^{5+},[9] and the interesting pair of metallaboranes $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$[10] and $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$,[11] which are diamagnetic species with closed electronic shells even though they contain either *n* or (*n* + 2) skeletal bond pairs, for which capped closo or nido structures, respectively, might have appeared more appropriate. The existence of these apparent anomalies has been variously attributed either to the compatibility of individual structures with particularly apt localized bond schemes or to the effect of substituents, particularly to π back-bonding from halogen substituents.[12,13] Here we draw attention to some commonly overlooked molecular orbital considerations that allow one to establish which closo structures may be compatible with *n* or (*n* + 2) bond pairs. We also point out that, although localized bond schemes have certain advantages (some of which we illustrate) in describing the bonding in clusters of known structure, they cannot be regarded as explanations of these structures, since equally plausible localized bond networks can be devised for the whole range of hypothetical closo *n*-atom clusters (*n* = 6–12) with *n* or (*n* + 2) bond pairs, most of which, on the basis of molecular orbital (MO) considerations, are not expected to exist.

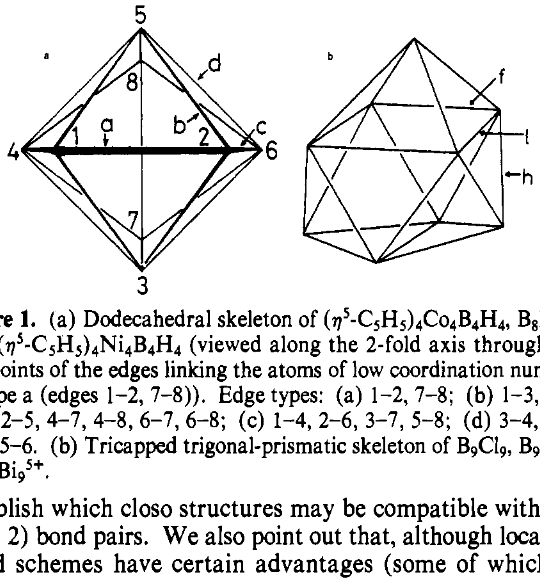

Figure 1. (a) Dodecahedral skeleton of $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, $B_8H_8^{2-}$, and $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ (viewed along the 2-fold axis through the midpoints of the edges linking the atoms of low coordination number, of type a (edges 1–2, 7–8)). Edge types: (a) 1–2, 7–8; (b) 1–3, 1–5, 2–3, 2–5, 4–7, 4–8, 6–7, 6–8; (c) 1–4, 2–6, 3–7, 5–8; (d) 3–4, 3–6, 4–5, 5–6. (b) Tricapped trigonal-prismatic skeleton of B_9Cl_9, $B_9H_9^{2-}$, and Bi_9^{5+}.

MO Considerations. It is convenient to consider first why the 8-vertex D_{2d} dodecahedron and the 9-vertex D_{3h} tricapped trigonal prism (Figure 1) can accommodate *n*, (*n* + 1), or (*n* + 2) skeletal bond pairs, as represented by B_8Cl_8[7] (eight pairs), $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$[10] (eight pairs), $B_8H_8^{2-}$[14] (nine pairs),

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Table I. HOMO's and LUMO's of Closo Borane Anions $B_nH_n^{2-}$

n	5[a]	6	7	8	9	10	11[b]	12
symmetry group	D_{3h}	O_h	D_{5h}	D_{2d}	D_{3h}	D_{4d}	C_{2v}	I_h
LUMO	e′	t_{2u}	e_2''	a_2	a_2'	e_3		g_g
HOMO	e″	t_{2g}	e_2'	b_2	a_2''	e_1		g_u
ref	17	18	17	15	14	17		18

[a] $B_5H_5^{2-}$ is as yet unknown. [b] Though the HOMO and LUMO of $B_{11}H_{11}^{2-}$ have not been identified, both are expected to be singly degenerate.

$(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$[11] (ten pairs), B_9Cl_9[8] (nine pairs), $B_9H_9^{2-}$[15] (ten pairs), and Bi_9^{5+}[9] (eleven pairs). We suggest that this can be traced to the nondegeneracy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of $B_8H_8^{2-}$ and $B_9H_9^{2-}$. For example, the HOMO of $B_8H_8^{2-}$ has b_2 symmetry, while the LUMO has a_2 symmetry.[16] Whether these MO's are both empty, as in the case of the hypothetical B_8H_8 or a derivative thereof such as B_8Cl_8[7] or $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$,[10] or both filled as in the case of a derivative of the hypothetical anion $B_8H_8^{4-}$ such as $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$,[11] the result is a closed-shell electronic configuration with no unpaired electrons. (N.B. We are assuming that the ordering of the skeletal MO's of $B_8H_8^{2-}$ applies also to the skeletal MO's of B_8Cl_8, $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, and $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$, an assumption we believe to be justified in view of (a) the high symmetry of the metallaboranes and (b) the isolobal relationship[17] among BH, $Co(\eta^5\text{-}C_5H_5)$, and $Ni(\eta^5\text{-}C_5H_5)$ groups, as sources of two, two, and three skeletal electrons respectively.) However, in each case the resulting configuration generates rather weaker skeletal bonding than when all the bonding MO's and no antibonding MO's are occupied. For example, the chloroborane B_8Cl_8[7] (eight bond pairs) has an average boron–boron bond length of 181 pm, whereas the anion $B_8H_8^{2-}$[14] (nine pairs) has an average boron–boron bond length of 178 pm. Moreover, the polyhedral edge-bonding or -antibonding characteristics of the b_2 HOMO of $B_8H_8^{2-}$ (bonding with respect to edges of types a, c, and d; antibonding with respect to edges of type b, Figure 1(a)) are neatly reflected in the individual edge lengths of B_8Cl_8, which are as follows (figures for $B_8H_8^{2-}$ in parentheses): a, 168 (158) pm; b, 175 (178) pm; c, 178 (174) pm; d, 200 (193) pm.

The tricapped trigonal-prismatic $B_9H_9^{2-}$ likewise has nondegenerate frontier orbitals. The HOMO has a_2' symmetry, and the LUMO has a_2'' symmetry.[15] Closed-shell electronic configurations are obtained with nine, ten, or eleven skeletal bond pairs, as exemplified by B_9Cl_9,[8] $B_9H_9^{2-}$,[15] and Bi_9^{5+},[9] respectively. The skeletal bonding is strongest when there are nine skeletal pairs (compare $B_9H_9^{2-}$, average B–B bond length 176 pm,[15] with B_9Cl_9, average B–B bond length 181 pm[8]), and the edge-bonding characteristics of the a_2' HOMO (bonding with respect to edges of types h and l, antibonding with respect to edges of type f, Figure 1(b)) are reflected in the individual edge lengths for B_9Cl_9 (figures for $B_9H_9^{2-}$ in parentheses): h, 175 (171) pm; l, 208 (181) pm; f, 180 (188) pm.

In contrast to the 8- and 9-vertex polyhedra, the symmetries of most of the other closo borane polyhedra are such as to cause the HOMO's and LUMO's of the anions $B_nH_n^{2-}$ to be degenerate[18,19] (see Table I). Adding two electrons to most closo boranes, or removing two electrons from them, without changing their shapes would thus generate paramagnetic species prone to Jahn–Teller distortion.[2,20] For example, two-electron oxidation or reduction of $B_6H_6^{2-}$ would generate paramagnetic species that would be expected to distort to achieve spin-paired closed-shell electronic configurations. Similar distortions, of the types that have led to the familiar rules correlating shapes with electron numbers, are expected if electrons are added to or removed from other *n*-vertex closo clusters, where $n = 5, 6, 7, 10$, or 12.

The energy sequence of the MO's of the C_{2v} octadecahedral anion $B_{11}H_{11}^{2-}$ has not, to our knowledge, been reported. However, in view of the symmetry, all the MO's must be of the types a_1, a_2, b_1, or b_2 and so any degeneracies must be accidental. Both HOMO and LUMO are expected to be nondegenerate,[21] and the closo geometry of $B_{11}H_{11}^{2-}$ may therefore also prove to be compatible with 11 or 13 bond pairs. A nido icosahedral-fragment shape has, however, been observed for the 11-atom, 13-bond-pair clusters isolated to date.

It should be stressed that these considerations of the degeneracies of HOMO's and LUMO's do not indicate which shapes will be the most stable for particular clusters but merely show which shapes are compatible with a range of electron numbers and which are not. In order to explain why $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$[10] and $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$[11] have D_{2d} dodecahedral structures, it would be necessary to show that other shapes such as a capped pentagonal bipyramid for the former or a bicapped trigonal prism for the latter are less stable alternatives (as they evidently are). That a bicapped trigonal-prismatic structure is possible for an 8-atom cluster held together by 10 skeletal bond pairs is indicated by the nido structure of B_8H_{12}.[22] Theoretical studies[15,18,19,23,24] of the alternative geometries possible for closo clusters like $B_8H_8^{2-}$ have shown that in certain cases there is little energy difference between various possible geometries, and whether an 8-atom, 10-bond-pair cluster adopts an expanded closo structure like that of $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$[11] or a nido structure like that of B_8H_{12}[22] probably depends crucially on the bonding requirements of the ligands, especially the "extra" four hydrogen atoms of B_8H_{12}. Bridging hydrogen atoms in borane clusters are exceedingly rare in closo systems and are normally associated with boron atoms of relatively low coordination number in nido or arachno systems.[25] The D_{2d} dodecahedron offers but two moderately suitable sites for bridging hydrogen atoms, the two edges of type a (Figure 1), so it may provide a possible structure for an anion $B_8H_{10}^{2-}$, though not for the neutral borane B_8H_{12}, the nido structure of which clearly makes better use of the available skeletal electrons. Another species with a structure of particular interest is the tetracarbaborane $H_4C_4B_4H_4$, the NMR spectra[26,27] of derivatives of which appear to rule out a structure analogous to that of $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$.

The positions of the metal atoms in $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ and $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ are worth noting. They occupy sites 3, 4, 5, and 6 in the former and 1, 2, 7, and 8 in the latter. The preference of $(\eta^5\text{-}C_5H_5)Ni$ for the site of lowest coordination number reveals another similarity between this group and its isolobal analogue, CH.[17] Both function as sources of three skeletal electrons (contrast BH or $(\eta^5\text{-}C_5H_5)Co$ units, which act as sources of two skeletal electrons) and therefore tend to occupy those sites that, in a homonuclear closo cluster, would

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Table II. Values of t (the Number of 3-Center Skeletal Bonds, $(n - c)$) and y (the Number of 2-Center Skeletal Bonds, $3c/2$) for Species $B_nH_n^{c-}$ and Isoelectronic Analogues

	n	5	6	7	8	9	10	11	12
B_nH_n ($y = 0$)	t	5	6	7	8	9	10	11	12
$B_nH_n^{2-}$ ($y = 3$)	t	3	4	5	6	7	8	9	10
$B_nH_n^{4-}$ ($y = 6$)	t	1	2	3	4	5	6	7	8

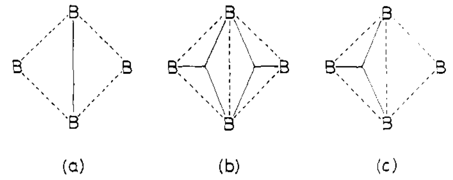

Figure 2. Bond arrangements by which a particular polyhedral edge may be bonded: (a) one 2-center bond; (b) two 3-center bonds; (c) one 3-center bond.

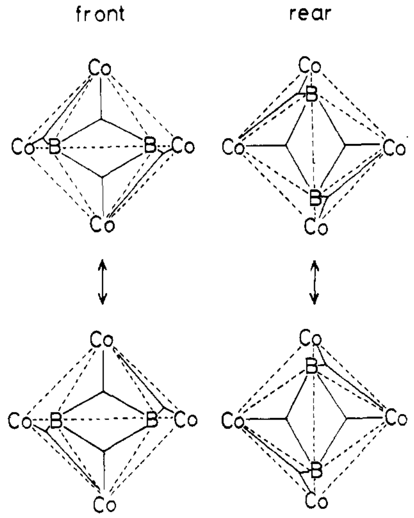

Figure 3. Localized bond arrangements for $(C_5H_5)_4Co_4B_4H_4$. (In this and the following figures, separate views of the front and rear halves of the polyhedral skeleton are shown for the sake of clarity. Broken lines represent edges not occupied by 2-center bonds.)

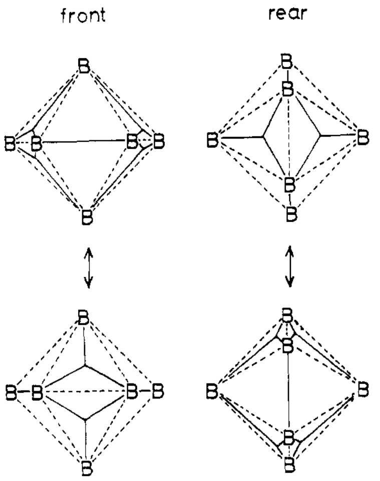

Figure 4. Localized bond arrangements for $B_8H_8^{2-}$.

have the highest skeletal electron density, i.e., the sites of lowest coordination number. The positions occupied by the metal atoms in $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ show that the unit $(\eta^5\text{-}C_5H_5)Co$ may be slightly less electronegative than its isolobal analogue, BH.

Localized Bond Treatments. We turn now to a consideration of the value of localized bond treatments for closo clusters with n atoms and n, $(n + 1)$, or $(n + 2)$ skeletal bond pairs and show (a) how the numbers of 2- and 3-center bonds can be deduced directly by using Lipscomb's *styx* numbers and equations of balance,[18,28] (b) how these bonds may be allocated to the polyhedral edges and faces, (c) how such bond networks can provide useful insight into the bonding in known structures, and (d) how plausible bond networks can, however, be devised for improbable species.

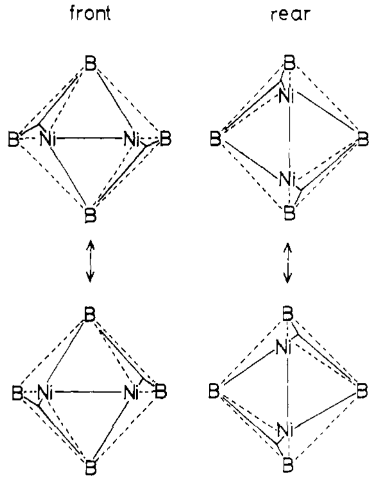

Figure 5. Localized bond arrangements for $(C_5H_5)_4Ni_4B_4H_4$.

Lipscomb has shown how the bonding in borane clusters can usefully be described in terms of s BHB bonds, t BBB bonds, y BB bonds, and x extra BH bonds in addition to the one exo BH bond each boron atom normally forms.[18] For species $B_nH_n^{c-}$, the equations of balance reduce to the unique solutions $s = x = 0$, $t = n - c$, and $y = 3c/2$ (Table II).[29] Thus for $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, formally analogous to the hypothetical B_8H_8, the eight skeletal pairs need to be allocated to eight 3-center skeletal bonds ($t = 8$). The nickel analogue $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$, with four more electrons, requires six 2-center and four 3-center bonds to describe its skeletal bonding.

The numbers of 2- and 3-center bonds required by Lipscomb's *styx* rules to describe the skeletal bonding in clusters $B_nH_n^{c-}$ (n = 5–12; c = 0, 2, or 4) are given in Table II. Note that, when $c = 0$, the bonding consists exclusively of 3-center bonds; when $c = 2$, three 2-center and $(n - 2)$ 3-center bonds are needed; and when $c = 4$, six 2-center and $(n - 4)$ 3-center bonds are required.

These 2- and 3-center bonds can be allocated in a satisfactory manner to the polyhedral edges and faces by ensuring that each skeletal atom participates in three skeletal bonds, which link that atom directly to each of its neighbors. Thus each polyhedral edge must be bonded in one of the three following ways (Figure 2): (a) by a 2-center bond; (b) by a 3-center bond in each of the two faces sharing that edge; or (c) by a 3-center bond in only one of the two faces sharing that edge. These correspond to edge bond orders of 1, $^2/_3$, and $^1/_3$, respectively. Resonance between various canonical forms can lead to intermediate bond orders.

Bond networks for $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ (or B_8Cl_8), for $B_8H_8^{2-}$, and for $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ that are compatible with these conditions are shown in Figures 3–5. The approximate edge bond orders that they imply are given in Table III, which also lists the relevant edge lengths. Qualitatively, the localized bond schemes provide a satisfactory fit to the structural data, in that bond orders increase as B–B bond lengths decrease. Moreover, whereas the bonds of type a (Figure 1, linking the atoms of low coordination number) are invariably those of highest bond order and those of type d (linking the atoms of high coordination number) are invariably those of lowest bond order, the bonds of intermediate types b and c suffer a reversal

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Table III. Edge Bond Orders in D_{2d} Polyhedral Clusters Implied by Localized 2- and 2-Center Bond Schemes

edge type[a]	skel coord nos. of linked atoms	edge bond orders ($\bar{n}$)[b] and lengths (l, pm)				
		B_8Cl_8		$B_8H_8^{2-}$		$B_8H_8^{4-}$
		$\bar{n}$	l	$\bar{n}$	l	$\bar{n}$
a	4–4	$^2/_3$	168	$^5/_6$	158	1
b	4–5	$^1/_2$	175	$^1/_3$	178	$^5/_6$
c	4–5	$^1/_3$	178	$^5/_6$	174	$^1/_3$
d	5–5	$^1/_3$	200	$^1/_3$	193	$^1/_3$

[a] See Figure 1. [b] Deduced by giving equal weight to each of the contributing canonical forms.

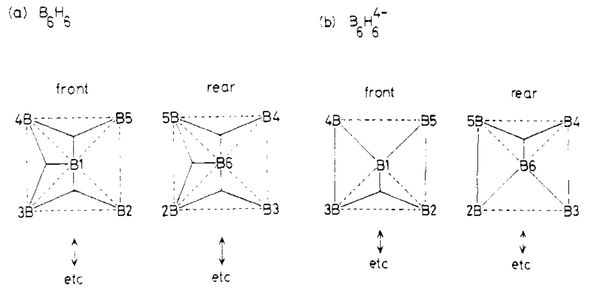

Figure 6. Localized bond arrangements for hypothetical octahedral species B_6H_6 and $B_6H_6^{4-}$.

of their relative bond orders on going from B_8Cl_8 to $B_8H_8^{2-}$, a reversal matched by their relative lengths. This localized bond treatment thus provides an alternative rationale to the MO treatment outlined above, in which the differences in bond lengths between B_8Cl_8 and $B_8H_8^{2-}$ were seen to correlate directly with the edge-bonding or -antibonding character of the HOMO of $B_8H_8^{2-}$.

Similar arguments to the above can be used to allocate nine 3-center bonds to the skeleton of B_9Cl_9, or three 2-center and seven 3-center bonds to the skeleton of $B_9H_9^{2-}$, allowing the differences between these tricapped trigonal-prismatic structures to be rationalized. These arguments will be elaborated in a systematic study of the complete range of known closo systems, to be published elsewhere.

A corollary of the condition that each vertex atom should be involved in three skeletal bonds is that, as the skeletal coordination number of an atom increases, so must the number of 3-center bonds it forms. This implies that the atoms of high coordination number will be more positively charged and those of low coordination number will be more negatively charged than the average, since the electron density on an atom will decrease as the proportion of 3-center bonds it forms increases. This correlation between electron density and coordination number in closo species is a familiar feature of borane-type clusters that also emerges from MO treatments.

One disadvantage of localized bond schemes is the progressive increase in edge bond order they imply for sequences $B_nH_n < B_nH_n^{2-} < B_nH_n^{4-}$ and the n, $(n + 1)$, and $(n + 2)$ electron pairs available respectively are all given a bonding role, whereas the MO argument outlined above suggests the bond order peak will be reached for the species $B_nH_n^{2-}$, since the extra two skeletal electrons in species $B_nH_n^{4-}$ (or their isoelectronic analogues) would have to be accommodated in antibonding MO's.

A more serious disadvantage is illustrated in Figure 6, which shows the apparently plausible bond arrangements that can be drawn for hypothetical octahedral clusters of formulas B_6H_6 and $B_6H_6^{4-}$, which would have six and eight electron pairs, respectively, available for skeletal bonding. Resonance between canonical forms such as these would provide apparently satisfactory bonding descriptions of these species, neither of which, however, would be expected to have regular octahedral structures (see Table I). These localized bond schemes, and the similar plausible localized bond networks that can be drawn for other hypothetical deltahedral clusters B_nH_n or $B_nH_n^{4-}$ (or isoelectronic analogues), cannot therefore be taken as reliable indicators of which structures may exist. (In many cases, localized bond schemes of known closo anions $B_nH_n^{2-}$ appear less plausible than those that can be drawn for hypothetical species B_nH_n or $B_nH_n^{4-}$.)

One further unsatisfactory feature of localized bond schemes is worthy of comment. This is that closo → nido reductive cage opening is predicted to occur as the number of skeletal bond pairs is increased from $(n + 2)$ to $(n + 3)$, whereas such changes normally occur when the number of skeletal bond pairs increases from $(n + 1)$ to $(n + 2)$. This follows from a consideration of hypothetical species $B_nH_n^{6-}$, for which the equations of balance require nine 2-center and $(n - 6)$ 3-center skeletal bonds. Since a 2-center bond can account for the bonding of only one polyhedral edge, while a 3-center bond can account for the bonding of at most the three edges surrounding the face it occupies, these skeletal bonds can account for the bonding of a maximum of $9 + 3(n - 6)$, i.e., $3(n - 3)$ polyhedral edges. The bonding capacity of these bond networks is thus insufficient to account for all of the $3(n - 2)$ polyhedral edges of a closo n-vertex polyhedron. The implication is that closo geometries are inappropriate for clusters $B_nH_n^{6-}$ or isoelectronic species. Adding a pair of electrons to a species $B_nH_n^{4-}$ would be expected to lead to reductive cluster opening of the closo → nido type that actually normally accompanies the conversion of $B_nH_n^{2-}$ into $B_nH_n^{4-}$.

Conclusion. The arguments elaborated above illustrate that the degeneracies of the HOMO and LUMO of closo, n-atom, $(n + 1)$-bond-pair clusters provide a better guide to the possible shapes of related clusters with two more or two fewer electrons than do localized bond schemes. These latter do, however, have value in deducing the electron distribution and approximate bond orders in clusters of known structure.

Acknowledgment. We thank Professors T. P. Fehlner and R. B. King for helpful suggestions and the SRC for financial support. We dedicate this paper to the memory of Professor R. W. Rudolph, some of whose ideas it develops.

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Received April 17, 1981

Steric Effects in Metal Cluster Compounds

Sir:

The qualitative discussion of the role of steric effects in influencing the stereochemistries, stabilities, and catalytic properties of mononuclear transition-metal complexes, particularly of tertiary phosphines, has been greatly assisted by the cone-angle concept introduced by Tolman.[1] The current interest in the chemical properties of transition-metal cluster compounds raises similar problems regarding the relative importance of steric and electronic effects. Some progress has been made toward understanding the electronic factors responsible for the adoption of particular metal polyhedral geometries,[2] but the discussion of steric effects has been limited by the absence of a simple procedure for assessing the relative

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[1] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
[2] Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1974**, 133; **1976**, 1163.