Acc. Chem. Res. **1984**, *17*, 311-319

system fixes it in the perpendicular conformation.[32] But the magnitude of the effect demonstrates dramatically that acetal cleavage ordinarily requires lone-pair electrons on the remaining oxygen atom to be antiperiplanar[35] to the bond to the leaving group oxygen, either in the ground state or in some reasonably accessible conformation.

Conclusion

Stereoelectronic effects on the cleavage of acetals and their derivatives (**9**) are thus very similar to those observed for E2 reactions of related systems. The effects are less easily observed than in E2 reactions, because of the several factors which combine to make it difficult to fix oxygen derivatives **9** in unreactive conformations and perhaps also, to some extent, because the two lone pairs on oxygen are less localized than C–H bonding orbitals.[4] But the barrier to the cleavage of a tetrahydropyranyl acetal, or β-glycoside, fixed in the equatorial conformation, is so large that it is certain that observed reactions involving C–O cleavage are finding their way round, rather than over it.

A conformation change of the sort proposed by Phillips and his co-workers for the binding of its substrate by lysozyme is thus an essential part of the cleavage of a β-glycoside. Binding the reacting sugar residue in the ground-state chair conformation would increase the already significant barrier to the conformational change necessary for reaction. We conclude that lysozyme has compelling stereoelectronic reasons for binding its substrate in a non-ground-state conformation.[36]

This work was supported by the Science and Engineering Research Council of Great Britain and done by my excellent co-workers, whose names appear in the references.

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[32] Calculations[33] and some experimental evidence[34] suggest that the energy difference between planar and perpendicular conformations of a simple oxo carbonium ion, $MeOCH_2^+$, is of the order of 20 kcal mol^{-1}. The observed difference in reactivity between **24** and **26** (Ar = 2,4-dinitrophenyl) corresponds to a difference in free energy of activation of 18.4 kcal mol^{-1}.

[33] Farcasiu, D.; Horsley, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 4906.

[34] Lustgarten, R.; Brookhart, M.; Winstein, S. *Tetrahedron Lett.* **1921**, 141.

[35] As pointed out by a reviewer, a lone pair synperiplanar to the bond to the departing group would also allow the development of a planar oxo carbonium ion.

[36] The evidence that lysozyme binds its substrate in a nonground-state conformation is extensive and self-consistent, but not incontrovertible. This work, similarly, shows that binding the ground-state conformation would make the reaction more difficult—not impossible.

Polyhedral Skeletal Electron Pair Approach

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The great interest shown by chemists in materials which have symmetrical polyhedral structures far exceeds that anticipated on utilitarian grounds and seems to reflect a deeper scientific desire to understand and create objects of natural beauty. This interest in polyhedral molecules ranges from transition-metal cluster compounds, with potential as a new generation of homogeneous and heterogeneous catalysts, to boron hydrides and strained hydrocarbons.[1] The fusion of polyhedra to form extended and infinite solids is of interest to chemists investigating structural modifications of elemental boron and the lower valent halides and chalcogenides of the early transition metals—some of which show fascinating superconducting properties.[2] In each of these areas bonding models have been developed to account for their structures and reactivities.[3,4] In this *Account* we outline a scheme, the "Polyhedral Skeletal Electron Pair Approach",[5] which attempts to unify some of these areas. Such a scheme is no replacement for accurate molecular orbital calculations on specific compounds,[4] but it provides a simple way to understand the intriguing structural diversity shown by polynuclear molecules and thereby opens up new areas of chemistry at the interfaces between the various subdisciplines.

Nowhere has the aesthetic pleasure derived from the synthesis of a compound of high symmetry been expressed more flamboyantly than in the recent report of dodecahedrane, $C_{20}H_{20}$ (**1**, Chart I).[6] The synthesis of **1** ("The Mount Everest of Alicyclic Chemistry") was but the final chapter in the planned syntheses of several hydrocarbons based on polyhedra, where all the vertices

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(1) B. F. G. Johnson, "Transition Metal Clusters", John Wiley and Sons, New York, 1980, provides a good general introduction to cluster chemistry.

(2) J. D. Corbett, *Acc. Chem. Res.*, 14, 239 (1981).

(3) K. Wade, *Adv. Inorg. Radiochem.*, 18, 1 (1976); R. Mason and D. M. P. Mingos, *M.T.P. Int. Rev. Sci., Ser. Two*, 11, 121 (1975); J. W. Lauher, *J. Organomet. Chem.*, **213**, 25 (1981); G. Ciani and A. Sironi, *J. Organomet. Chem.*, **197**, 233 (1980); D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* 133 (1974).

(4) P. T. Chesky and M. B. Hall, *Inorg. Chem.*, **20**, 4419 (1981); F. A. Cotton and G. G. Stanley, *Chem. Phys. Lett.*, **58**, 450 (1978); W. C. Trogler and M. C. Manning, *Coord. Chem. Rev.*, **38**, 89 (1981).

(5) The term *polyhedral skeletal electron pair theory* was first introduced in R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, **95**, 3802 (1973), but the basic rules were also developed in R. E. Williams, *Inorg. Chem.*, 10, 210 (1971); K. Wade, *J. Chem. Soc., Chem. Commun.*, 792 (1971); D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972); R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976).

(6) L. A. Paquette, R. J. Ternansky, D. W. Balogh, and G. Kentgen, *J. Am. Chem. Soc.*, **105**, 5446 (1983).

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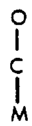
Table I
Contributions to the Polyhedral Electron Count (pec) of Some Commonly Occurring Terminal, Bridging, and Encapsulated Ligands

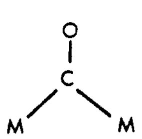
ligand	terminal	bridging doubly	bridging triply	encapsulated
H, CH_3	1	1	1	
CO, CNR	2	2	2	
Cl, Br, I	1	3	5	
SR, OR		3	5	
S, PR		2	4	
C, Si, Ge				4
N, P, As				5
O, S, Se				6
Ru, Os				8
Co, Rh				9
Ni, Pd				10

are three valent. Some representative examples of these three-connected polyhedral molecules are illustrated in **2**–**5**.[7] The bonding in polyhedral C_nH_n molecules can adequately be described in terms of localized two-center two-electron bonds[8] and therefore they are also described as *electron precise* polyhedral molecules. Polyhedra of this type have $3n/2$ edges and n terminal C–H (or C–R) bonds and are characterized by a total of $5n$ electrons.

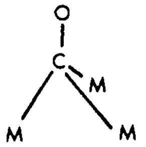
In principle there should be an analogous series of main group molecules with $5n$ electrons, but only the tetrahedral species P_4, As_4, and Si_4^{4-} (**6**) have been structurally characterized.[9] Transition-metal carbonyl clusters analogous to **2**–**5** have been characterized, however, and representative examples are illustrated in **7**–**10**.[10] In contrast to their hydrocarbon analogues these compounds have carbonyl, sulfido, and related ligands bridging two or more metal atoms. The CO ligand behaves as a two-electron donor irrespective of whether it is coordinated in a terminal (**11a**), doubly bridging (**11b**), or triply bridging (**11c**) mode. In contrast a chloro ligand functions as a one-electron terminal ligand (**12a**) and a three-electron doubly bridging (**12b**) and a five-electron triply bridging ligand (**12c**).[11] Some



2 $\bar{e}$ donor
11a

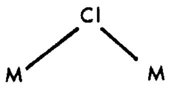


2 $\bar{e}$ donor
11b

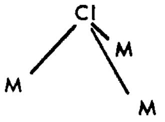


2 $\bar{e}$ donor
11c

1 $\bar{e}$ donor
12a

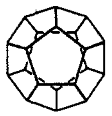


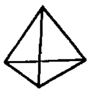
3 $\bar{e}$ donor
12b



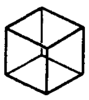
5 $\bar{e}$ donor
12c

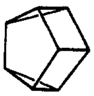
Chart I

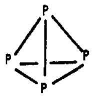

$C_{20}H_{20}$
Dodecahedrane
1


C_4H_4
Tetrahedrane
2

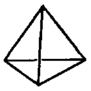

C_6H_6
Prismane
3


C_8H_8
Cubane
4

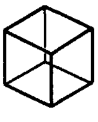

C_8H_8
Cuneane
5

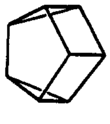


P_4 p.e.c. 20
6


$Rh_4(\mu^2\text{-}CO)_3(CO)_9$
p.e.c. 60 [4Rh(4x9); 3μ^2-CO(3x2); 9CO(18)]
7


$Rh_6C(CO)_{15}{}^{2-}$
p.e.c. 90 [6Rh(6x9); 9μ^2-CO(9x2); 6CO(12)]
8


$Ni_8(\mu^4\text{-}PPh)_6(CO)_8$
p.e.c. 120 [8Ni(8x10); 6μ^4-PPh(6x4); 8CO(16)]
9


$Co_8(\mu\text{-}S)_2(\mu\text{-}NBu^t)_4(NO)_8$
p.e.c. 120
10

transition-metal carbonyl cluster compounds have atoms encapsulated at the center of the polyhedron, e.g., a carbon atom in **8**. For larger clusters the expansion of the central cavity permits the encapsulation of a larger main-group atom, e.g., S or P, when the nuclearity lies in the range 8–11 and even metal atoms, e.g., Rh, when the nuclearity exceeds 11. Molecular orbital calculations have demonstrated that these encapsulated atoms contribute all their valence electrons for bonding.[12] Therefore, it is possible to summarize as in Table I the contributions to the total electron count of bridging and encapsulated atoms.

Utilizing this information, it is possible to evaluate the total number of electrons associated with specific polyhedral molecules (the *polyhedral electron count*, pec). Comparison of the pec's for comparable main-group (**2**–**6**) and transition-metal carbonyl (**7**–**10**) polyhedra indicates an interesting general pattern. The transition-metal polyhedral molecules have a total of $10n$ more electrons than their main-group analogues; i.e., they have polyhedral electron counts of $15n$. This difference in pec's corresponds precisely to the filling of the additional $5n$ d atomic orbitals.

The borane anions $B_nH_n^{2-}$ and related "naked" metal clusters, e.g., Sn_5^{2-}, Ge_9^{2-}, have the deltahedral structures illustrated in **13**–**20** (Chart II). The adoption of

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[7] T. Clark and M. A. McKervey, *Compr. Org. Chem.*, 1, 35 (1979).

[8] J. M. Schulman, C. R. Fischer, P. Solomon, and T. J. Venanzi, *J. Am. Chem. Soc.*, **100**, 2949 (1978).

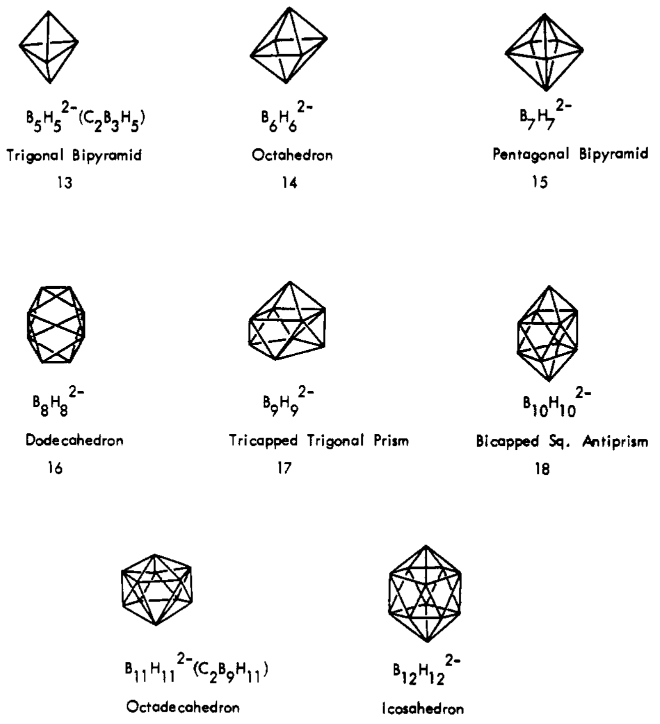
[9] H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, **20**, 33 (1981).

[10] C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969); V. G. Albano, D. Broga, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 651 (1973); L. D. Lower and L. F. Dahl, *J. Am. Chem. Soc.*, **98**, 5046 (1976).

[11] R. E. Benfield and B. F. G. Johnson, *Top. Stereochem.*, **12**, 253 (1981).

[12] D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1163 (1976).

Chart II



$B_5H_5^{2-}$ ($C_2B_3H_5$)
Trigonal Bipyramid
13

$B_6H_6^{2-}$
Octahedron
14

$B_7H_7^{2-}$
Pentagonal Bipyramid
15

$B_8H_8^{2-}$
Dodecahedron
16

$B_9H_9^{2-}$
Tricapped Trigonal Prism
17

$B_{10}H_{10}^{2-}$
Bicapped Sq. Antiprism
18

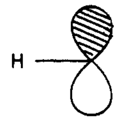
$B_{11}H_{11}^{2-}$ ($C_2B_9H_{11}$)
Octadecahedron
19

$B_{12}H_{12}^{2-}$
Icosahedron
20

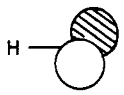
these polyhedra rather than the three-connected polyhedra arises because each B–H fragment has only two electrons available for skeletal bonding. The deltahedral structures maximize the number of nearest-neighbor boron atoms and therefore encourage the most effective delocalization of the boron electron pairs. Molecular orbital calculations on specific deltahedral boranes have established that these molecules are characterized by a total of $2n + 1$ bonding molecular orbitals, i.e., n terminal B–H bonds and $n + 1$ skeletal bonding molecular orbitals.[13–15]

A recent elegant analysis of the bonding in deltahedra by Stone[16] has provided a general analysis of the $4n + 2$ electron rule for such molecules. In essence this approach has demonstrated that the frontier orbitals of the individual B–H units illustrated in **21–23** give a set

21



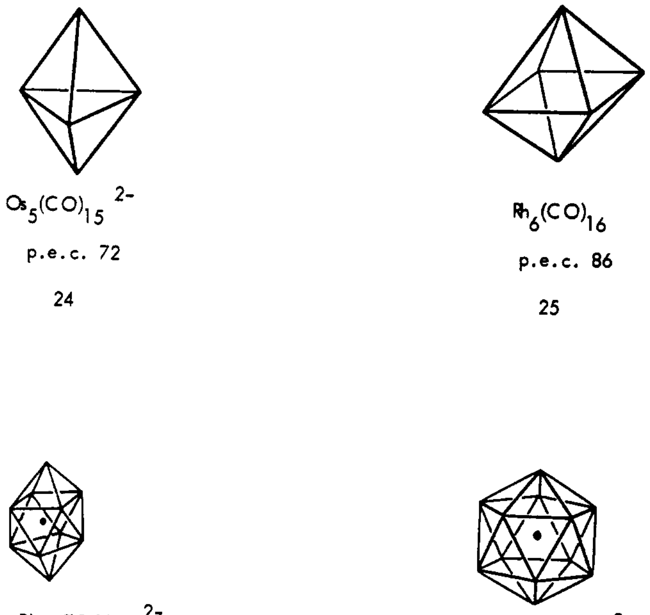
22



23

of radial (**21**) and tangential (**22**,**23**) molecular orbitals. The former generate a single strongly bonding molecular orbital which corresponds to the in-phase combination of all n sp hybrid orbitals of type **21**. The p orbitals (**22**, **23**) perpendicular to the B–H bonds give rise to a set of n bonding and n antibonding molecular orbitals on the surface of the cluster. Therefore in total there are $n + 1$ skeletal molecular orbitals.[17]

Chart III



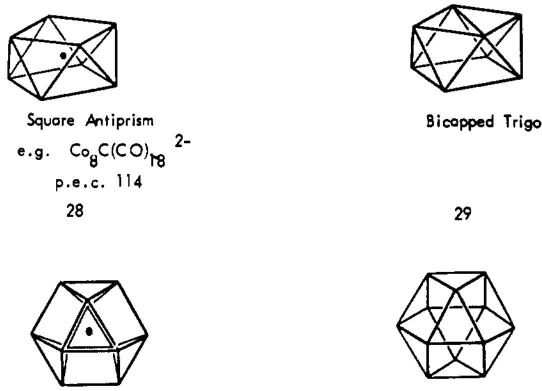
$Os_5(CO)_{15}^{2-}$
p.e.c. 72
24

$Rh_6(CO)_{16}$
p.e.c. 86
25

$Rh_{10}S(CO)_{22}^{2-}$
p.e.c. 142
26

$Rh_{12}Sb(CO)_{27}^{3-}$
p.e.c. 170
27

Chart IV



Square Antiprism
e.g. $Co_8C(CO)_{18}^{2-}$
p.e.c. 114
28

Bicapped Trigonal Prism
29

Twinned Cuboctahedral
e.g. $Rh_{13}(CO)_{24}H_3^{2-}$
p.e.c. 170
30

Cuboctahedron
31

Transition-metal analogues of some of the borane anions have been synthesized and are illustrated in **24-27** (Chart III).[18] It is significant that they are characterized by pec's of $14n + 2$, reinforcing the pattern noted earlier. For some deltahedra additional electrons can be accomodated by a distortion of the structure in a manner which retains the point group. For example, elongated trigonal bipyramidal complexes with pec's of 76, e.g., $[Ni_5(CO)_{12}]^{2-}$, have been characterized in addition to the $14n + 2$ (pec 72) examples cited above. Similarly, the tricapped trigonal prism can accomodate an additional electron pair, cf. Ge_9^{2-} (pec 38) and Bi_9^{5+} (pec 40). The latter showing a longer separation between the trigonal prismatic faces.[19]

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(13) K. Wade, "Electron Deficient Compounds", Nelson, London, 1971.

(14) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. R. Soc. London, Ser. A*, **A224**, 336 (1954).

(15) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

(16) A. J. Stone, *Inorg. Chem.*, **20**, 503 (1981); A. J. Stone, Mol. Phys., **41**, 1339 (1980).

(17) P. Brint, J. P. Cronin, and E. Seward, *J. Chem. Soc., Dalton. Trans.*, 675 (1983) give a more detailed account of radial/tangential mixings.

(18) C. R. Eady, B. F. G. Johnson, J. Lewis, B. E. Reichert, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 271 (1976); E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963); G. Ciani, Faraschelli, A. Sironi, and S. Martinengo, *J. Chem. Soc., Chem. Commun.*, 563 (1981); J. L. Vidal and J. M. Troup, *J. Organomet. Chem.*, **213** 351 (1981).

Table II
Summary of Polyhedral Electron Counts for Main-Group and Transition-Metal Polyhedral Molecules[a]

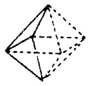
	main-group hydrides		transition-metal carbonyls	
	electrons	examples	electrons	examples
closo deltahedra	$4n + 2$ ($n \geqslant 5$)	$B_nH_n^{2-}$	$14n + 2$	$Os_6(CO)_{18}$
nido deltahedra	$4n + 4$ ($n \geqslant 4$)	B_nH_{n+4}	$14n + 4$	$Ru_5C(CO)_{15}$
arachno deltahedra	$4n + 6$ ($n \geqslant 4$)	B_nH_{n+6}	$14n + 6$	$Fe_4H(CO)_{13}^-$
3-connected polyhedra[b]	$5n$ (n even 4)	C_nH_n, P_4	$15n$	$Rh_4(CO)_{12}$
ring compounds	$6n$ ($n \geqslant 3$)	C_nH_{2n}, S_n	$16n$	$Os_3(CO)_{12}$
isolated vertex atoms held together by bridging groups	$8n$	$Ph_4Al_4N_4Ph_4$	$18n$	$Cu_4I_4(AsMe_3)_4$

[a] The number of skeletal electron pairs (N) in a polyhedral molecule is related to the *polyhedral electron count* (pec) by N = [(pec) − $2n$]/2 for main group and [(pec) − $12n$]/2 for transition-metal clusters. [b] Also described as electron precise polyhedra.

Chart V

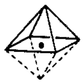

nido-octahedron
B_5H_9
32

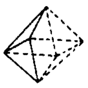

nido-pentagonal bipyramid
B_6H_{10}
33

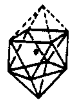

arachno-octahedron
B_4H_{10}
34

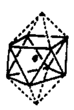

arachno-pentagonal bipyramid
B_5H_{11}
35

Chart VI

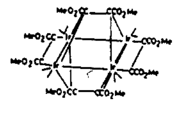

nido-octahedron
e.g. $Ru_5C(CO)_{15}$
36


arachno-octahedron ("butterfly")
e.g. $Fe_4H(CO)_{13}^-$
p.e.c. 62
37


nido-bicapped sq. antiprism
e.g. $Rh_9P(CO)_{21}^{2-}$
38


arachno-bicapped sq. antiprism
e.g. $Ni_8C(CO)_{16}^{2-}$
p.e.c. 118
39


$Os_3(CO)_{12}$
p.e.c. 48
40



$Ir_4(C_2(CO_2Me))_4(CO)_8$
p.e.c. 64
41


C_3H_6
42


C_4H_8
43

There are alternative nondeltahedral structures which also have $2n + 1$ bonding molecular orbitals. For example, the square-antiprismatic (**28**) and bicapped trigonal-prismatic (**29**) (Chart IV) geometries are compatible with pec's of 34 and 114 for main-group and transition-metal polyhedral molecules, respectively.[20] Similarly, the cuboctahedral and twin cuboctahedral geometries (**30** and **31**) represent alternative, yet isoelectronic, geometries for the icosahedron. Examples of these alternative geometries with $14n + 2$ valence electrons have been realized for $[Co_8C(CO)_{18}]^{2-}$ (114 valence electrons—square antiprism) and $[Rh_{13}H_3(CO)_{24}]^{2-}$ (170 valence electrons—twinned cuboctahedral).[21,22] The latter has a rhodium atom encapsulated in the center which donates 9 electrons. More generally it can be demonstrated that four connected polyhedral molecules are also characterized by $2n + 1$ bonding molecular orbitals.

Williams[5] in a very perceptive paper published in 1971 recognized that the boranes B_nH_{n+4} and B_nH_{n+6} had structures derived from the borane deltahedra, $B_nH_n^{2-}$, by the successive loss of one and two vertex atoms. For example, B_5H_9 (**32**) and B_6H_{10} (**33**) (Chart V) have nido skeletal geometries which may be derived from octahedral $B_6H_6^{2-}$ (**14**) and pentagonal $B_7H_7^{2-}$ (**15**) by removing the B–H unit of highest connectivity. Similarly, B_4H_{10} (**34**) and B_5H_{11} (**35**) may be derived from these deltahedra by the loss of two adjacent vertices and are described as arachno fragments. Wade and Rudolph[5] developed this concept and demonstrated that this structural relationship had its origins in the retention of the same number of bonding skeletal molecular orbitals in *closo*-($B_nH_n^{2-}$), *nido*-($B_{n-1}H_{n+3}$), and *arachno*-($B_{n-2}H_{n+4}$) molecules.

There exists an analogous series of nido and arachno transition-metal carbonyl clusters with polyhedral electron counts of $14n + 4$ and $14n + 6$ electrons, respectively. **36**–**39** (Chart VI) provide some specific examples.[23] Currently, such nido and arachno poly-

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(19) P. A. Edwards and J. D. Corbett, *Inorg. Chem.*, **16**, 903 (1977); C. H. E. Belin, J. D. Corbett, and A. Cisar, *J. Am. Chem. Soc.*, **99**, 7163 (1977).

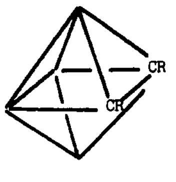
(20) E. L. Muetterties and B. F. Bier, *Bull. Soc. Chim. Belg.*, **84**, 397 (1975).

(21) V. G. Albano, P. Chini, G. Ciani, S. Martinengo, and M. Sansoni, *J. Chem. Soc., Dalton. Trans.*, 463 (1978).

(22) G. Longoni, A. Ceriotti, R. Della Pergolla, M. Manaserro, M. Perego, G. Piro, and M. Sansoni, *Proc. R. Soc. London, Ser. A* **A308**, 47 (1982); G. Ciani, A. Sironi, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 519 (1981).

(23) D. H. Farrar, P. F. Jackson, B. F. G. Johnson, J. Lewis, J. N. Nicholls, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 415 (1981); J. L. Vidal, W. E. Walker, R. L. Pruett, and R. C. Schoening, *Inorg. Chem.*, **18**, 129 (1979); M. Manaserro, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976).

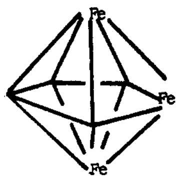
Chart VII



M_4A_2 p.e.c. 66

e.g. $Co_4(CO)_{10}C_2R_2$

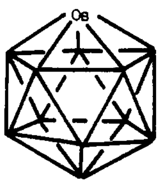
44



M_3A_4 p.e.c. 60

e.g. $Fe_3(CO)_8(C_2Ph_2)_2$

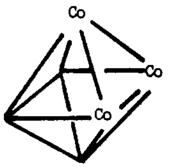
45



MA_{11} p.e.c. 60

e.g. $Os(CO)_3C_2B_9H_{11}$

46



M_3A_3 p.e.c. 56

e.g. $Co_3(C_5H_5)_3B_3H_5$

47

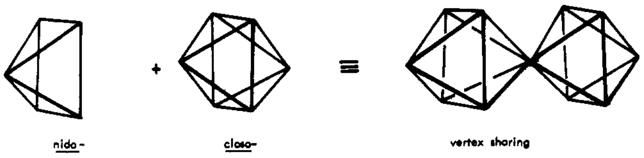
hedra do not represent an important subgroup in metal cluster chemistry.

Table II summarizes the relationships derived thus far for convex polyhedral main-group and transition-metal carbonyl clusters. The same principles can be applied to ring compounds. For example, **40** and **41** represent organometallic analogues of cyclopropane and cyclobutane, **42** and **43**.[24] The relationships developed in the table apply only to metal and ligand combinations which conform to the noble gas rule in mononuclear complexes, and for example are not applicable to halide and sulfide clusters of the earlier transition metals.

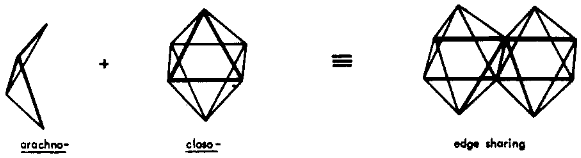
Metalloboranes and Organometallic Polyhedral Molecules

The previous sections have focused attention separately on the electronic requirements of main-group and transition-metal carbonyl polyhedral molecules. The simplicity of the relationships summarized in Table II suggests a ready extrapolation to organometallic compounds and metalloboranes. Since isostructural main group, A_n, and transition metal, M_n, polyhedral molecules are related by pec's of X and $X + 10n$, isostructural mixed species, $A_{n-x}M_x$, are characterized by pec's of $X + 10x$. The following tetrahedral molecules illustrate the incremental nature of this relationship:[25] A_4, tetrahedron, pec 20 (e.g., C_4H_4 tetrahedrane); A_3M, tetrahedron, pec 30 (e.g., $MnB_3H_8(CO)_3$); A_2M_2, tetrahedron, pec 40 (e.g., $Fe_2B_2H_6(CO)_6$; AM_3, tetrahedron, pec 50 (e.g., $Co_3CH(CO)_9$); M_4, tetrahedron, pec 60 (e.g., $Co_4(CO)_{12}$). In this series the main group C–H (or B–H) fragments are successively being replaced by $M(CO)_3$ fragments. The similarlity in bonding capabilities of these fragments has been described by the term *isolobal*[26] and been widely used by theoretical[27] and synthetic chemists.[28] More complex examples of the incremental nature of pec's are illustrated in **44**–**47** (Chart VII).[25]

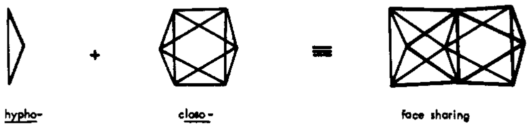
Chart VIII



48



49



50

Condensed Polyhedral Molecules

It has become apparent in recent years that the majority of high-nuclearity transition-metal clusters are derived by the condensation of smaller tetrahedral, octahedral, and trigonal-prismatic fragments. These condensation processes occur by vertex, edge, or face sharing. Fortunately, it has proved possible to derive rules which account for polyhedral electron counts in such condensed polyhedra based on a fragment molecular orbital analysis of the condensation process.[29] The condensed polyhedron is viewed as a complex between two individual polyhedra with one polyhedron acting as a ligand toward the second polyhedron. For example, the vertex-sharing pair of octahedra illustrated in **48** has a nido octahedron (i.e., a square pyramid) acting as a ligand toward the closo octahedron (Chart VIII). **49** and **50** illustrate related edge- and face-bridging situations. Molecular orbital calculations have demonstrated that nido fragments have frontier molecular orbitals of a_1 and e symmetry capable of donating electron density to suitable empty orbitals on the closo fragment. Therefore, the nido fragment can be viewed as a six-electron donor. If the nido fragment has m atoms and the closo fragment n atoms, the pec in the vertex-shared polyhedron with $m + n$ atoms is as follows:

$$[14m + 4] + [14n + 2] - 6 = 14(n + m)$$

If this is reexpressed as a fusion process involving two closo polyhedra with n and p atoms, respectively, where $p = m + 1$, then

$$14(n + m) = [14(m + 1) + 2] + [14n + 2] - 18$$

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(24) M. A. A. F. de C. T. Carrondo and A. C. Skapski, *Acta Crystallogr., Sect. B*, **B34**, 1857 (1978); P. F. Heveldt, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 340 (1978).

(25) Many examples of these types of molecule are to be found in "Metal Interactions with Boron Clusters", R. N. Grimes, Ed., Plenum Press, New York, 1982.

(26) M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, **15**, 1148 (1976).

(27) R. Hoffmann, *Science* (*Washington, D.C.*), **211**, 995 (1981).

(28) F. G. A. Stone, *Acc. Chem. Res.*, **14**, 318 (1981).

(29) D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 706 (1983).

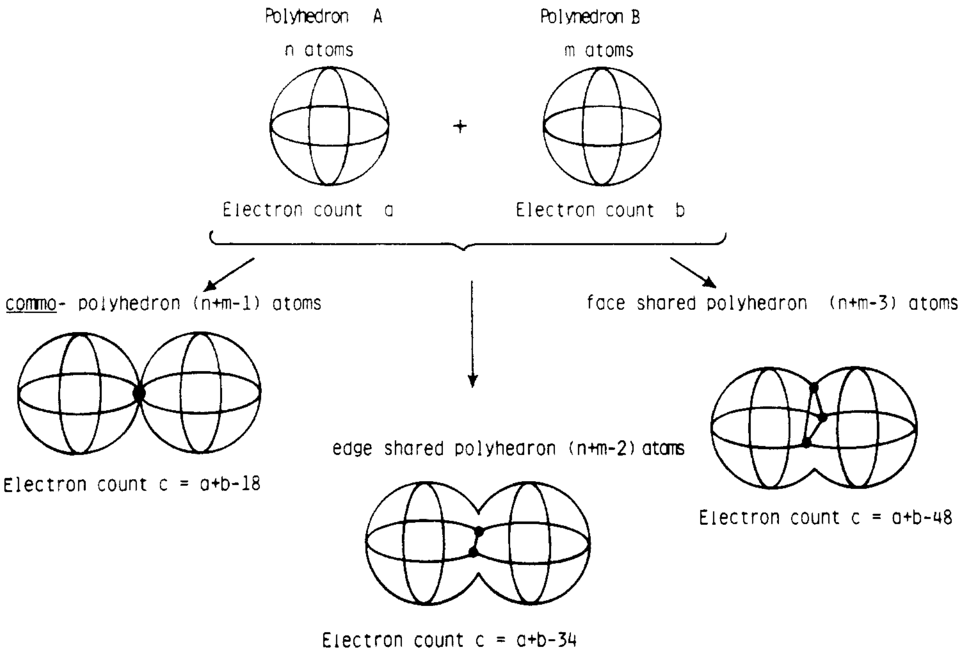

Figure 1. Condensation regimes for polyhedral molecules and their associated electron characteristics.

The electron count for the condensed polyhedron is the sum of those for the separated polyhedra minus the electron count characteristic of the common vertex.

Similarly a pair of edge-sharing deltahedra may be partitioned into a complex between closo and arachno fragments, the latter donating a total of 10 electrons from a_1, e_1, and e_2 frontier molecular orbitals.[30] The following generalization results from this mode of analysis.[29]

The total electron count in a condensed polyhedron is equal to the sum of the electron counts for the parent polyhedra A and B minus the electron count characteristic of the atom, pair of atoms, or face of atoms common to both polyhedra.

This generalization is illustrated in a schematic fashion in Figure 1 for metal carbonyl cluster compounds which adhere to the inert gas formalism, i.e., have the following characteristic electron counts: 18—mononuclear, 34—binuclear, e.g., $Mn_2(CO)_{10}$, and 48—triangular, e.g., $Os_3(CO)_{12}$.

Examples of vertex-sharing condensed polyhedra are illustrated in **51** and **52** (Chart IX). In the former example two identical triangles of metal atoms share a common vertex, whereas in the latter example an open triangle (characterized by a pec of 50) and a butterfly cluster with a pec of 62 condense through the two wing-tip vertices to give the "arrow-head" cluster (**52**), i.e., 50 + 62 - (2 × 18) = 76. $Ru_5C(CO)_{16}$ and $Ru_5H_2C(CO)_{15}$ provide examples of such clusters.[31]

There are numerous examples of condensed polyhedral clusters with shared edges and some examples are illustrated in **53–56**. In each instance the pec has been derived by adding the pec's of the polyhedra prior to condensation and subtracting the electron count characteristic of the shared edge, i.e., 34. The condensation process involving triangular clusters has the same result as edge bridging and of course can be repeated successively to build up a two-dimensional close-packed array of metal atoms. The addition of each metal atom is associated with an increment of 14 in the total electron count, and therefore it becomes a simple matter to derive the pec's for raft clusters such as **55**.[32] A more interesting example of edge sharing is provided by **56**, which results from the condensation of a pair of octahedra through a common edge. An example of such a cluster, viz., $[Ru_{10}C_2(CO)_{24}]^{2-}$, has recently been structurally characterized by Shapley, Churchill, and their co-workers.[33]

The condensation of a tetrahedron to a second polyhedron through a triangular face, e.g., **57**, has the net effect of capping. The condensation rule suggests an increment of 12 electrons in the pec for capping, i.e., 60 for the tetrahedron minus 48 for the common triangular face. Some illustrative examples of this capping principle are as follows:[34] tetrahedron, pec 60 (e.g., $Rh_4(CO)_{12}$); capped tetrahedron, pec 72 (e.g., $Os_5(CO)_{15}{}^{2-}$; bicapped tetrahedron, pec 84 (e.g., $Os_6(CO)_{18}$); tricapped tetrahedron, pec 96 (e.g., $Ru_4(CO)_{12}H(AuPPh_3)_3$). Octahedron, pec 86 (e.g., $Rh_6(CO)_{16}$); capped octahedron, pec 98 (e.g., $Rh_7(CO)_{16}{}^{3-}$); bicapped octahedron, pec 110 (e.g., $Re_8C(CO)_{24}{}^{2-}$); tetracapped octahedron, pec 134 (e.g., $Os_{10}C(CO)_{24}{}^{2-}$). Trigonal prism, pec 90 (e.g., $Rh_6C(CO)_{15}{}^{2-}$); bicapped trigonal prism, pec 114 (e.g., $Rh_6C(CO)_{15}(CuNCCH_3)_2$).

The structures of some of these polyhedra are illustrated in **58–60**. More complex examples of this condensation process are illustrated in **61** and **62** (Chart X).[35]

The condensation of polyhedra through square faces is not such a common aggregation process, but some examples are illustrated in **63–66** (Chart XI). When one of the polyhedral components has been derived

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(30) A. J. Stone and M. J. Alderton, *Inorg. Chem.*, **21**, 2297 (1982); D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 602 (1977).

(31) J. Lewis and B. F. G. Johnson, *Adv. Inorg. Radiochem.*, **24**, 225 (1981).

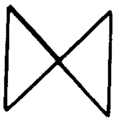
(32) J. Lewis and B. F. G. Johnson, *Proc. R. Soc. London, Ser. A*, **A308**, 5 (1982).

(33) C-M. T. Hayward, J. R. Shapley, M. R. Churchill, C. Bueno, and A. L. Rheingold, *J. Am. Chem. Soc.* **104**, 7347 (1982).

(34) See ref 31 and 32 and M. I. Bruce and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1141 (1982).

(35) J. S. Bradley, R. L. Pruett, G. B. Ausell, M. E. Leonowicz, and M. A. Modrich, *Organometallics*, 1, 74 (1982); L. F. Dahl, unpublished results.

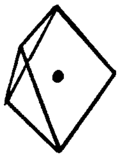
Chart IX



p.e.c. 78

e.g. $Os_5(CO)_{19}$

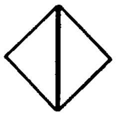
51



p.e.c. 76

e.g. $Ru_5C(CO)_{16}$

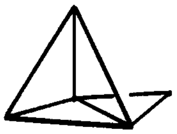
52



p.e.c. 62

e.g. $Re_4(CO)_{16}{}^{2-}$

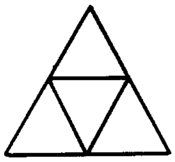
53



p.e.c. 74

e.g. $Os_5H_2(CO)_{16}$

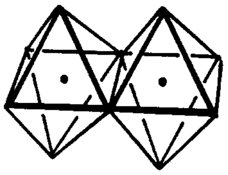
54



p.e.c. 90

e.g. $Os_6(CO)_{21}$

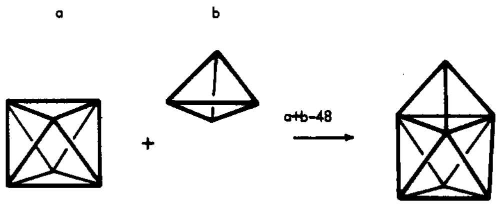
55



p.e.c. 138

e.g. $Ru_{10}C_2(CO)_{24}{}^{2-}$

56



p.e.c. 98

capped octahedron

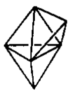
57

from a deltahedron, then the pec for the condensed polyhedron is obtained by subtracting 62 for the common square face. It follows that capping a square face results in an increment in the pec of 12, and some illustrative examples are as follows:[36] square antiprism, pec 118 (e.g., $Ni_8C(CO)_{16}{}^{2-}$); capped square antiprism, pec 130 (e.g., $Rh_9P(CO)_{21}{}^{2-}$); bicapped square antiprism, pec 142 (e.g., $Rh_{10}S(CO)_{22}{}^{2-}$).

For the condensation of three-connected polyhedra through square faces the appropriate pec is obtained by subtracting 64 for the common face, i.e., corresponding to a localized description of the bonding in the common face. $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ derived from two trigonal prisms sharing a common square face provides an example (pec = 116 = 2 × 90 − 64).

It is also possible to condense a pair of polyhedra through a pair of adjacent triangular faces, e.g., 67. The

Chart X

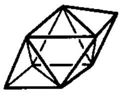


Bicapped Tetrahedron

p.e.c. 84

e.g. $Os_6(CO)_{18}$

58

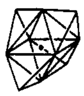


Bicapped Octahedron

p.e.c. 110

e.g. $Os_8(CO)_{22}{}^{2-}$

59

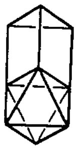


Tetracapped Octahedron

p.e.c. 134

e.g. $Os_{10}C(CO)_{24}{}^{2-}$

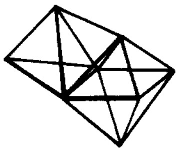
60



p.e.c. 128

e.g. $Ni_9(CO)_{18}{}^{2-}$

61

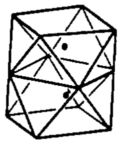


p.e.c. 110

e.g. $Ru_6C(CO)_{16}\{Cu(NCCH_3)\}_2$

62

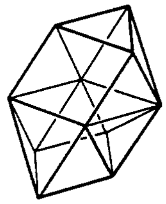
Chart XI



p.e.c. 166

e.g. $Rh_{12}C_2(CO)_{24}{}^{2-}$

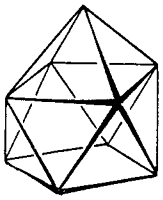
63



p.e.c. 154

e.g. $Co_{11}C_2(CO)_{22}{}^{3-}$

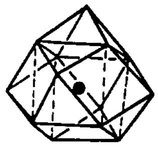
64



p.e.c. 130

Capped Square Antiprism

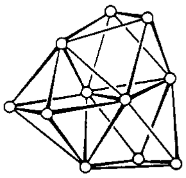
65



p.e.c. 180

Pentacapped Cube

66



p.e.c. 148

e.g. $Rh_{11}(CO)_{23}{}^{3-}$

67

pec is equal to the sum of the pec's of the component polyhedra minus that characteristic for the common butterfly, i.e., 62.[37]

As a result of the condensation principle given above it is possible to derive the pec's of high nuclearity but

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[36] See ref 22 and 23.

[37] A. Fumagalli, S. Martinengo, G. Ciani, and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 453 (1983).

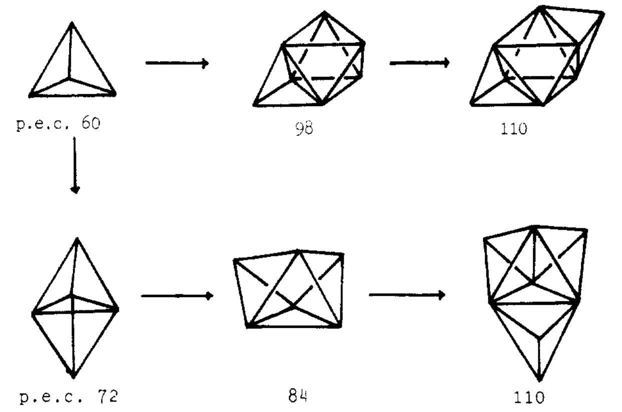


Figure 2. Examples of the use of the condensation rules to build up clusters and evaluate their polyhedral electron counts.

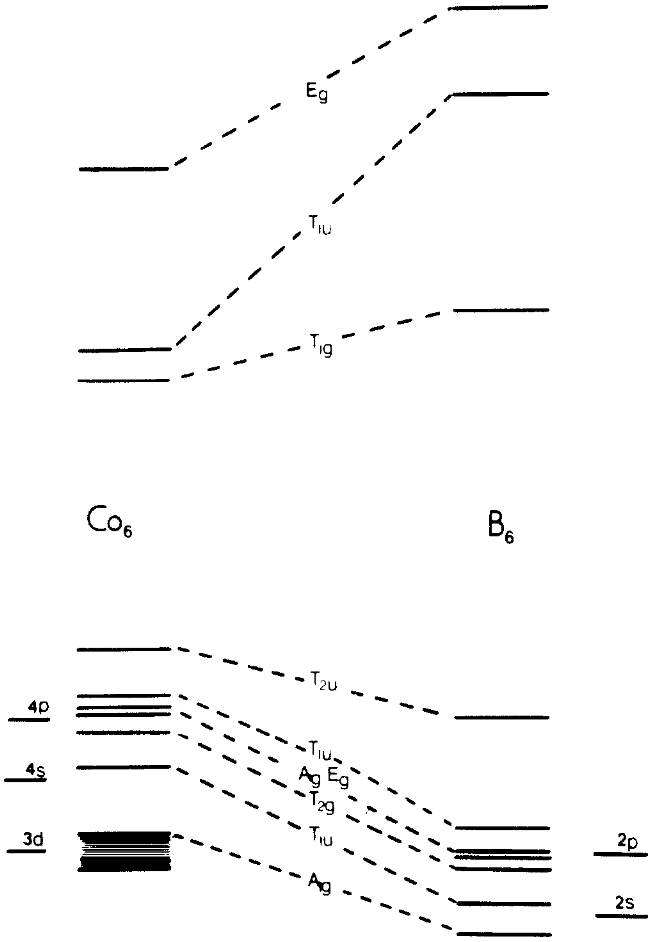
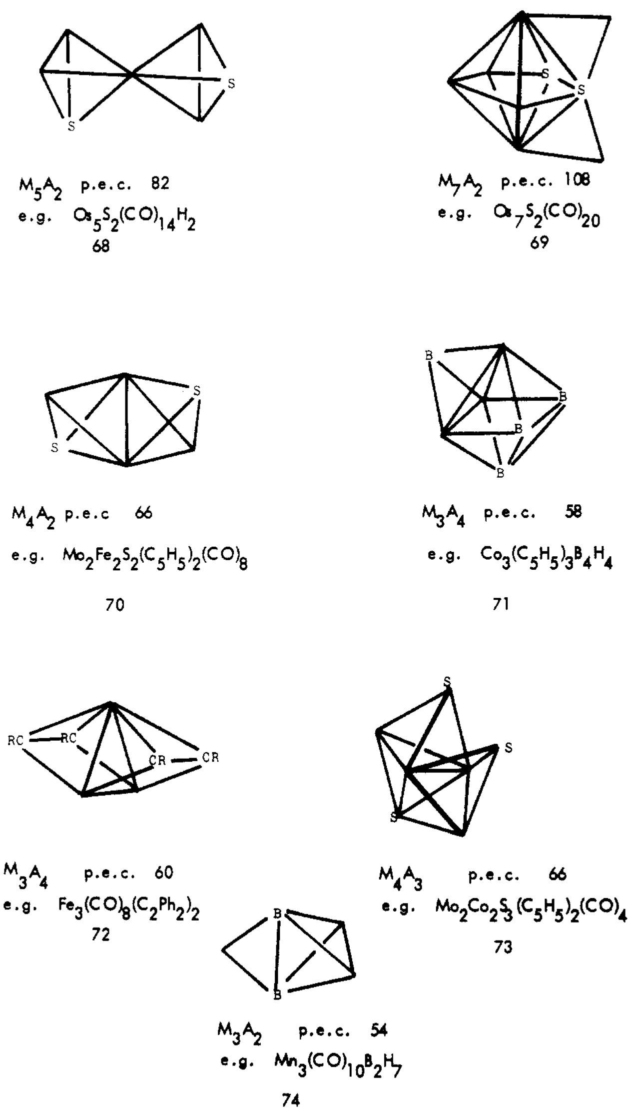


Figure 3. Molecular orbitals for naked octahedral of boron and cobalt derived from extended Hückel molecular orbital calculations.

low symmetry clusters, in an *aufbau* fashion. Figure 2 illustrates how the condensation rules can be used sequentially to build up alternative geometries for eight atom clusters with pec's of 110.[38,39] It can also be readily adapted for use with organometallic and metalloborane structures derived by fusion processes. Some illustrative examples are given in **68**–**74** (Chart XII).[40]

Chart XII



π-Acceptor vs. π-Donor Ligands

Figure 3 compares the calculated spectra of molecular orbital energies for "bare" octahedral cobalt and boron clusters. Both clusters have similar molecular orbitals originating from the s and p valence orbitals. The cobalt cluster has, in addition, a narrow band of molecular orbitals derived from the d valence orbitals—the narrow width reflecting the small d–d overlap integrals. The 10*n* relationship between borane and metal carbonyl clusters orginates from the complete utilization of this band of molecular orbitals by the σ-, π-, and π^*-levels of the bridging carbonyl ligands. Therefore, the two classes of compound share in common a set of antibonding skeletal molecular orbitals with identical symmetry characteristics and similar radial characteristics, T_{2u}, T_{1g}, T_{1u}, and E_g in the figure.

Therefore the π-acceptor qualities of the supplementary ligands are essential to the development of analogies between main-group and transition-metal carbonyl polyhedral molecules. If the carbonyl ligands

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are replaced by π-donor ligands such as sulfide and chloride, then those orbitals in the d band which match the symmetry characteristics of the π-donor orbitals of the sulfide or halide ligands are destabilized and give rise to a set of antibonding skeletal molecular orbitals which now have a predominance of metal d orbital character. It is the bonding capabilities of the metal d orbitals which now influence the polyhedral electron counts in such molecules. The utilization of 4 metal d orbitals in localized metal–metal bonds is a common characteristic of such molecules and leads to a polyhedral of electron count of $14n$ if the 18-electron rule is adhered to in this class of molecule.[41] Examples of π-donor clusters which approximate closely to this generalization are as follows.[42] octahedral, pec 84 (e.g., $Mo_6Cl_8L_6^{4+}$); square pyramidal, pec 69 (calcd 70) (e.g., Mo_5Cl_{13}); butterfly, pec 55 (:calcd 56) (e.g., $Mo_4I_{11}^{2-}$); triangular, pec 42 (e.g., $Re_3Cl_{12}^{3-}$). Clusters with π-donor ligands can also adopt bonding regimes which involve the four metal d orbitals in three-center bonding interactions on the triangular faces of deltahedra. For example, $Ta_6Cl_{12}L_6^{2+}$ has a pec of 76, consistent with the formation of eight three-center bonds on the faces of the octahedron. Detailed descriptions of the bonding in these clusters are given in ref 41. These clusters form condensed, and at times infinite, chain molecules, by utilizing lone pairs on the bridging groups. Incomplete filling of the band structures resulting from the cluster molecular orbitals gives these materials their interesting conduction properties.[43]

Clusters Which Do Not Conform to the 18-Electron Rule

For the heavier transition metals, e.g., Pt and Au, it is more common for the metals to form complexes with either 16 or 14 valence electrons. This behavior is reflected in the electronic requirements of clusters derived from these metals. Molecular orbital calculations on platinum clusters[44] have established the following characteristic electron counts:

dimer, pec 30; triangle, pec 44 (42 if ligands are not π-acids); tetrahedron, pec 56. Figure 4 illustrates the manner in which the condensation principle can be used in conjunction with these characteristic electron counts to account for the structures of some high-nuclearity platinum clusters. The bonding in gold clusters is based on the 14-electron rule and has been discussed in detail elsewhere.[45]

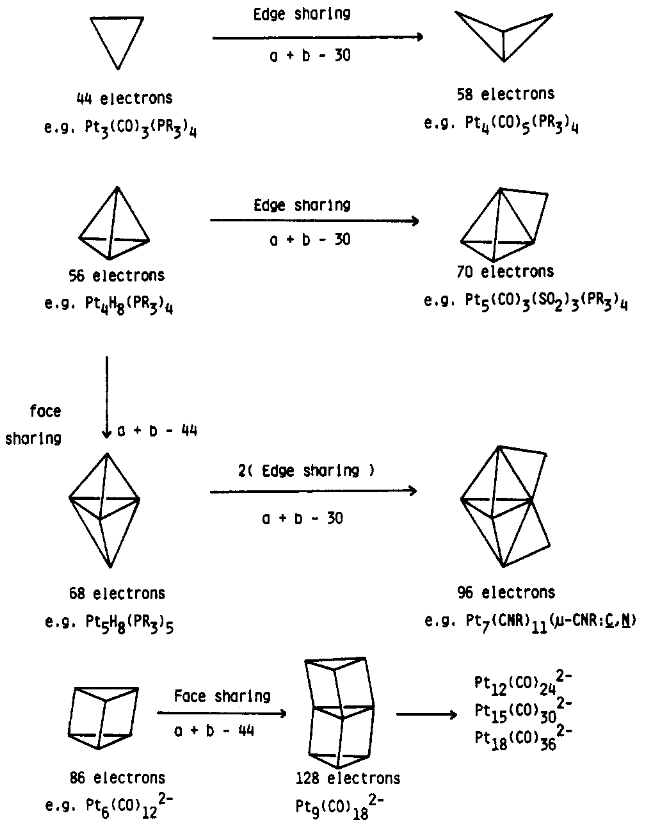

Figure 4. Some condensation processes in platinum clusters.

Concluding Remarks

This *Account* has demonstrated that some very simple principles govern the structures of main-group and transition-metal polyhedral molecules. Spherical polyhedral molecules can in general be described in terms of the general formulae given in Table II. Condensed polyhedral molecules can be accounted for by using the condensation principle. For complexes which do not conform to the 18-electron rule small modifications are required, but they can be incorporated within the general scheme. Although much of the emphasis in cluster chemistry during the last 10 years has been directed toward their structures, it is hoped that the emergence of generalizations such as those developed in this *Account* will lead in the future to a more detailed examination of their chemistries.

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