

Polyhedral Skeletal Electron Pair Approach. A Generalised Principle for Condensed Polyhedra

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A general procedure for evaluating the number of cluster valence molecular orbitals in molecules with condensed polyhedral geometries has been derived from molecular orbital calculations and shown to be widely applicable.

The *polyhedral skeletal electron pair approach* which interrelates the number of valence electrons in isostructural main group and transition metal carbonyl polyhedral molecules is now widely used,¹ and the electronic factors responsible for its success are reasonably well understood.² However, the rapid development of metal cluster chemistry which has occurred in recent years has revealed a degree of complexity and variety in the polyhedra adopted by the metal atoms unparalleled in main group chemistry. Thus, although boranes

adopt either spherical deltahedra or fragments derived from them, metal carbonyl clusters adopt only a limited number of polyhedra of this type and the observed structures are often better described in terms of condensed polyhedra based on octahedral, tetrahedral, trigonal prismatic, and triangular fragments.³ To a limited extent this deficiency has been overcome by using the *capping principle* in conjunction with the established bonding requirements for the parent symmetrical polyhedra,⁴ but this principle is not sufficiently flexible to

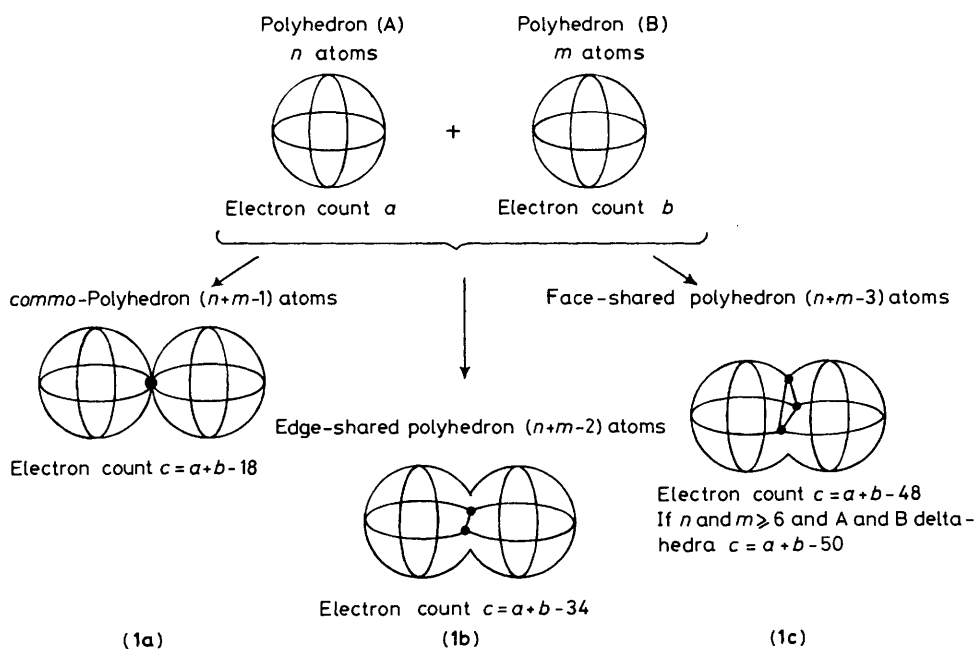


Figure 1. Condensation regimes for polyhedral molecules and their associated electron characteristics.

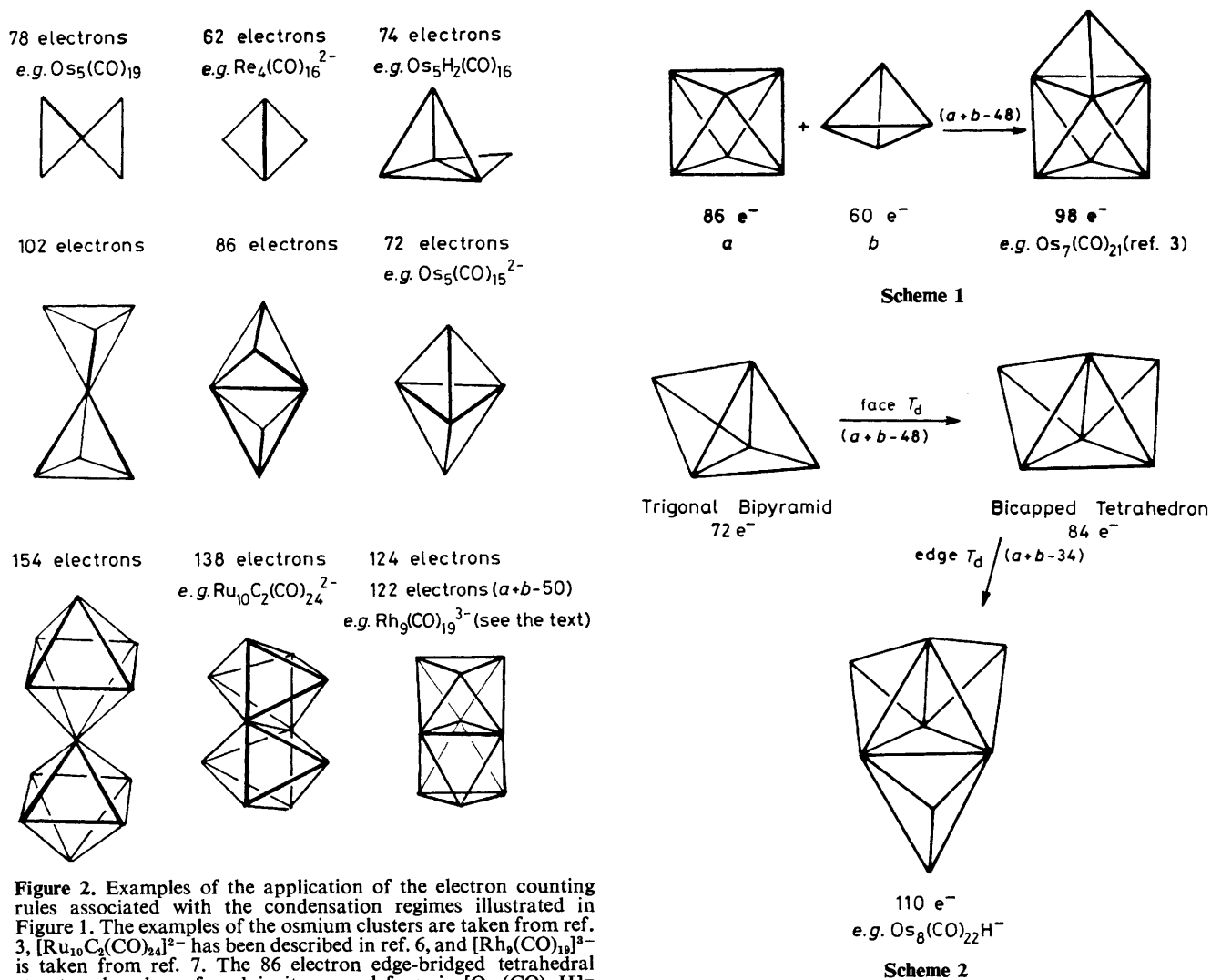


Figure 2. Examples of the application of the electron counting rules associated with the condensation regimes illustrated in Figure 1. The examples of the osmium clusters are taken from ref. 3, $[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$ has been described in ref. 6, and $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ is taken from ref. 7. The 86 electron edge-bridged tetrahedral structure has been found in its capped form in $[\text{Os}_8(\text{CO})_{22}\text{H}]^-$ (see the text).

permit the evaluation of the bonding requirements of a large proportion of known polyhedral compounds. As a result of an extensive theoretical investigation of the factors governing the number and type of bonding molecular orbitals generated when two polyhedra condense⁵ a widely applicable yet simple generalisation has emerged for predicting the number of cluster valence molecular orbitals in condensed clusters and is the subject of this communication.

Three fundamental condensation regimes which lead to cluster aggregation have been identified and are illustrated in Figure 1 (1a–c). In the first the parent polyhedra (A) and (B) are joined through a common vertex, whereas in the second and third regimes the polyhedra are condensed through either a common edge or face. The conclusions summarised below are not limited to cases where (A) and (B) are identical polyhedra and are applicable equally to electron precise and deltahedral clusters. The results of the calculations can be summarised in an economical generalisation as follows.

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

For metal carbonyl clusters certain electron counts are characteristic,¹ viz. mononuclear 18; dinuclear 34; triangular 48 [50 when (A) and (B) are deltahedra with m and $n \geq 6$]; electron precise polyhedra $15n$, e.g. tetrahedral 60; deltahedra $14n + 2$, e.g. octahedron 86.

On the basis of these characteristic electron counts the preferred electron counts for condensed polyhedra derived from triangular, tetrahedral, and octahedral clusters are illustrated in Figure 2. It is noteworthy that the generalisation is equally applicable to condensation processes involving different component polyhedra (A) and (B) as the example shown in Scheme 1 illustrates. From this example and those illustrated in Figure 2 it will be appreciated that the previously described *capping principle* is but a specific example of the condensation generalisation.

Besides providing a very simple procedure for rationalising the structures of the cluster compounds illustrated in Figure 2, the generalisation also makes some specific predictions regarding the preferred electron counts in vertex-shared tetrahedral and octahedral clusters. Although metallic clusters of this type have not been synthesised to date, the *isolobal* analogy can be used to illustrate the general principle. For example $[\text{Re}(\text{CO})_3(\text{C}_2\text{B}_9\text{H}_{11})]^-$ (icosahedral, 60 valence electrons) and $[\text{Ni}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ (*commo*-icosahedral, 102 valence electrons) bear the correct relationship for a pair of polyhedra sharing a common vertex.¹

The *aufbau* type of approach indicated by the condensation processes illustrated in Figures 1 and 2 can be used to build up a picture of the bonding requirements of low symmetry and complex polyhedral molecules by the successive use of the fundamental generalisation as the example shown in Scheme 2 demonstrates.

The S.E.R.C. is thanked for financial support and Mr. D. G. Evans is thanked for assistance with the molecular orbital calculations and many useful discussions.

Received, 15th March 1983; Com. 337

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