Molecular-orbital Calculations on Transition-metal Cluster Compounds containing Six Metal Atoms

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Extended-Hückel calculations on model M_6H_6 (M = Co or Ir) cluster compounds with octahedral, bicapped-tetrahedral, and trigonal-prismatic geometries are reported. The theoretical basis of the polyhedral skeletal electron-pair theory is discussed and the important role played by terminal and bridging ligands in such clusters is emphasised. The capping principle which has been used to rationalise the geometries of metal cluster compounds such as $[Os_6(CO)_{18}]$ and $[Os_7(CO)_{21}]$ is shown to have a quite general quantum-mechanical basis.

In recent years the geometries of metal carbonyl cluster compounds have been rationalised and predicted by a set of simple rules which may be described collectively as *the polyhedral* skeletal electron-pair theory.[1-3] These rules originated from a perceptive analogy between isostructural borane and transition-metal cluster compounds [4] and have been subsequently extended to describe carbametallaborane,[5] metal π-complexes,[6] capped metal cluster compounds,[7,8] and electron-precise and -rich polyatomic aggregates.[7] Molecular-orbital (m.o.) calculations on an octahedral cobalt cluster indicated that this analogy has its basis in the similar *s*- and *p*-orbital-overlap integrals in this and the isostructural borane anion $[B_6H_6]^{2-}$.[9] The electronic factors responsible for the breakdown of the polyhedral skeletal electron-pair approach when applied to gold cluster compounds, *e.g.* $[Au_6(PPh_3)_6]^{3+}$, $[Au_9(PPh_3)_8]^{3+}$, and $[Au_{11}I_3(PPh_3)_7]$, have also been analysed.[10]

An octahedron of metal atoms is the most common structural unit for clusters containing six metal atoms and such carbonyl cluster compounds have been characterised for most of the platinum metals. The elegant

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[1] K. Wade, *Chem. in Britain*, 1975, 177.

[2] K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

[3] R. Mason and D. M. P. Mingos, *M.T.P. Internat. Rev. Sci., Phys. Chem. Ser. II*, 1975, 121.

[4] K. Wade, *Chem. Comm.*, 1971, 792.

[5] C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J.C.S. Chem. Comm.*, 1973, 543.

[6] K. Wade, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 559.

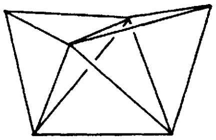
[7] D. M. P. Mingos, *Nature Phys. Sci.*, 1972, **236**, 99.

[8] K. M. Thomas, R. Mason, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, 1973, **95**, 3802.

[9] D. M. P. Mingos, *J.C.S. Dalton*, 1974, 133.

[10] D. M. P. Mingos, *J.C.S. Dalton*, 1976, 1163.

experimental work of Lewis,[11] Chini,[12] and their co-workers has also resulted in the characterisation of two six-atom clusters which do not have this polyhedral geometry. The carbido-compound $[Rh_6C(CO)_{15}]^{2-}$, which has 90 valence electrons, has a trigonal prism of rhodium atoms and a carbon atom situated at the origin of the polyhedron. The compound $[Os_6(CO)_{18}]$, which has 84 valence electrons, has the bicapped-tetrahedral arrangement of metal atoms shown in (1).[8] The geometries of these compounds have been rationalised qualitatively on the basis of the polyhedral skeletal electron-pair approach by Thomas *et al.*[8] In order to obtain a more detailed picture of this bonding in these and related molecules, we have completed m.o. calculations on model hydrido-cluster compounds M_6H_6 (M = Co or Ir) with the three polyhedral geometries discussed above. The calculations were also undertaken to examine the reliability of analogies based on borane m.o. pictures, and the role played by terminal and bridging ligands.


(1)

The bicapped tetrahedral cluster $[Os_6(CO)_{18}]$ is the simplest member of what appears to be an extensive series of capped polyhedral cluster compounds of the later transition elements. The geometries of these molecules have been rationalised on the basis of a capping principle which was first introduced by Mingos.[7] This principle states that a capped polyhedral cluster has the same number of bonding skeletal m.o.s. as the parent uncapped polyhedron. The quantum-mechanical basis of this principle has not been discussed previously.

CALCULATIONS

All the calculations were made using the extended-Hückel method.[13,14] The basis-set orbitals for the transition metals consisted of 3*d*, 4*s*, and 4*p* (for cobalt) and 5*d*, 6*s*, and 6*p* orbitals (for iridium). The *s* and *p* orbitals were described by single Slater-type orbitals, and the *d*-orbital wavefunctions were taken as contracted linear combinations of two Slater-type wavefunctions. The orbital exponents were those of Richardson *et al.*[15] and Basch and Gray.[16] The parameters for the extended-Hückel calculations are summarised below: [13-15,17,18,*]

Orbital	Slater exponent	H_{ii}/eV	Ref.
H 1*s*	1.30	−13.60	14
B 2*s*	1.30	−15.20	13
2*p*	1.30	−8.50	13
Ir 6*s*	2.50	−11.36	16, 17
6*p*	2.20	−4.50	16, 17
Co 4*s*	1.70	−7.31	15, 18
4*p*	1.05	−3.84	15, 18

Metal *d* wavefunctions

Orbital	H_{ii}/eV	ξ_1	C_1	ξ_2	C_2	Ref.
Ir 5d	−12.17	5.796	0.669 8	2.557	0.586 0	16
Co 3d	−9.42	5.550	0.551 1	1.900	0.646 1	15

The metal polyhedra were idealised and the following bond lengths (Å) were assumed:

B–B	1.690	B–H	1.200
Co–Co	2.500	Co–H	1.600
Ir–Ir	2.800	Ir–H	1.600

The calculations were made on the computer at this College using the ICON 8 programs developed by Hoffmann and his co-workers. The perturbation-theory analysis of the capping problem relies heavily on the formalism of Fujimoto and Hoffmann[19] and the frontier m.o. program developed by them.

RESULTS AND DISCUSSION

Figure 1 illustrates the results of extended-Hückel m.o. calculations on model Co_6H_6 clusters with octahedral, trigonal-prismatic, and bicapped-tetrahedral geometries. Analogous results were found for the related iridium clusters. Each of the m.o. diagrams has the following essential features: (*a*) a set of low-lying stable m.o.s which may be described as terminal hydrogen–metal bonding; (*b*) a narrow band of m.o.s centred about the 3*d* atomic level and with predominantly *d*-orbital character; (*c*) some higher-lying levels with predominantly 4*s*- and 4*p*-orbital character and which are bonding between the metal atoms.

The features (*b*) and (*c*) are a direct consequence of the radial characteristics of the cobalt valence orbitals (as shown in Figure 2). The cobalt 3*d* orbitals are very contracted [see Figure 2(*a*)] and give very poor overlaps for typical metal–metal distances of 2.500 Å. This feature is a characteristic of the later transition elements and arises primarily from inefficient screening effects as the atomic number increases across the transition series. The poor 3*d*–3*d* overlaps therefore give rise to a narrow spectrum of m.o. energies and the 3*d* band shown in Figure 1. The cobalt 4*s* and 4*p* orbitals are far more diffuse and their radial characteristics [see Figure 2(*b*) and (*c*)] give rise to very reasonable overlap integrals (0.2—0.5) for a cobalt–cobalt bond length of 2.500 Å. These valence orbitals therefore generate a wide spectrum of m.o. energies in these six-atom clusters. The more stable m.o.s of this type are shown in Figure 1. In this paper these will be described as *s*–*p* skeletal m.o.s.

Cobalt–cobalt and boron–boron *s*- and *p*-overlap integrals are comparable for analogous polyhedral molecules and therefore give rise to similar m.o. splitting

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[*] 1 eV = 96.5 kJ mol^{-1}.

[11] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1975, 2606.

[12] V. G. Albano, P. Chini, S. Martinengo, D. J. A. McCaffery, D. Strumulo, and B. T. Heaton, *J. Amer. Chem. Soc.*, 1974, **96**, 8106.

[13] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

[14] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179, 3489; **37**, 2872.

[15] J. W. Richardson, W. C. Nieuwport, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

[16] H. Basch and H. B. Gray, *Theor. Chim. Acta*, 1966, **4**, 367.

[17] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1967, **6**, 376.

[18] C. J. Ballhausen and H. B. Gray, 'Molecular Orbital Theory,' Benjamin, New York, 1964.

[19] H. Fujimoto and R. Hoffmann, *J. Phys. Chem.*, 1974, **78**, 1167; R. Hoffmann, H. Fujimoto, J. R. Swerson, and C.-C. Wan, *J. Amer. Chem. Soc.*, 1973, **95**, 7644.

patterns. Indeed the individual overlap integrals are sufficiently similar that the calculated energies for the bonding m.o.s of the isopolyhedral boranes B_6H_6 shown in Figure 3 follow the same order as the cobalt s–p skeletal m.o.s shown in Figure 1. As previously pointed out, it is this similarity which forms a theoretical basis for the polyhedral skeletal electron-pair approach.[9] Although there is a one-to-one correspondence for the bonding m.o.s for these two series of polyhedral molecules, we have noticed some significant differences in the relative orders of the antibonding skeletal m.o.s. This observation could result in different excited-state properties and reactivities for the main-group and transition-metal polyhedral compounds but is unlikely to significantly influence the ground-state properties of these molecules.

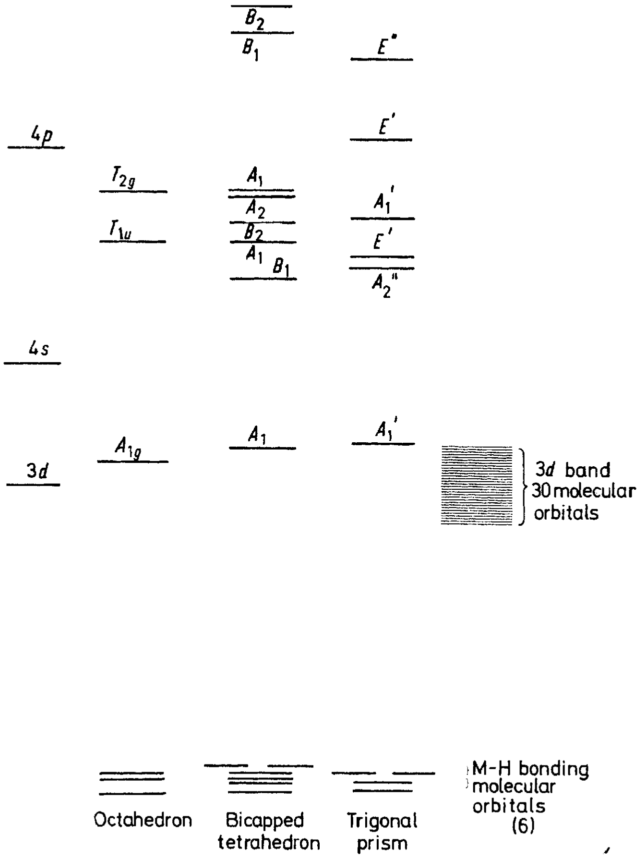


FIGURE 1 Low-lying molecular orbitals for Co_6H_6 based on octahedral, bicapped-tetrahedral, and trigonal-prismatic polyhedral geometries

For the borane polyhedra the following m.o. occupations will give rise to stable closed-shell electronic configurations:

Octahedron	. . . $(A_{1g})^2(T_{1u})^6(T_{2g})^6$
Bicapped tetrahedron	. . . $(A_1)^2(B_1)^2(A_1)^2(B_1)^2(A_2)^2(A_1)^2$
Trigonal prism	. . . $(A_1')^2(A_2'')^2(E')^4(A_1')^2(E')^4(E'')^4$

These correspond to seven, six, and nine skeletal electron pairs respectively. Filling the corresponding energy levels in the cobalt cluster compounds would result in the following hypothetical ions:

Octahedron	$[Co_6H_6]^{24-}$	86 valence electrons
Bicapped tetrahedron	$[Co_6H_6]^{22-}$	84 valence electrons
Trigonal prism	$[Co_6H_6]^{28-}$	90 valence electrons

Although the total charges on these cobalt anions make such simple hydrides totally unrealistic synthetic possibilities, it is significant that the total number of valence electrons in each case corresponds to those found in the carbonyl cluster compounds which have been isolated; *e.g.* $[Rh_6(CO)_{16}]$ octahedral (86 valence electrons), $[Os_6(CO)_{18}]$ bicapped tetrahedral (84 valence electrons), and $[Rh_6C(CO)_{15}]^{2-}$ trigonal prism (90 valence electrons).

The large number of carbonyl ligands in these cluster compounds play an additional role besides providing the necessary valence electrons, however. They effectively lower the energy of the s–p skeletal m.o.s of the cluster. In the simple hydrido-cluster Co_6H_6 these m.o.s have a high proportion of metal $4p$-orbital character and therefore lie at relatively high energies above the $3d$ band (see Figure 1 for example). The bridging ligands stabilise these m.o.s by providing linear combinations of atomic orbitals which can overlap effectively with them. This effect is illustrated in Figure 4 for the hypothetical Co_6H_{15} cluster which has six terminal metal–hydrogen bonds and hydrogen bridges on each of the edges of the trigonal-prismatic metal cluster. The 1s wavefunctions of the bridging hydrido-ligands give rise to the symmetry-adapted linear combinations $2A_1'$, A_2'', $2E'$, and E'' which have precisely the correct symmetry characteristics to interact with the nine s–p skeletal m.o.s of the Co_6H_6 cluster. The extended-Hückel calculations indicate a strong interaction between these two sets of m.o.s and this results in the nine stable bridging hydrogen–metal m.o.s shown at the bottom of Figure 4. These m.o.s.

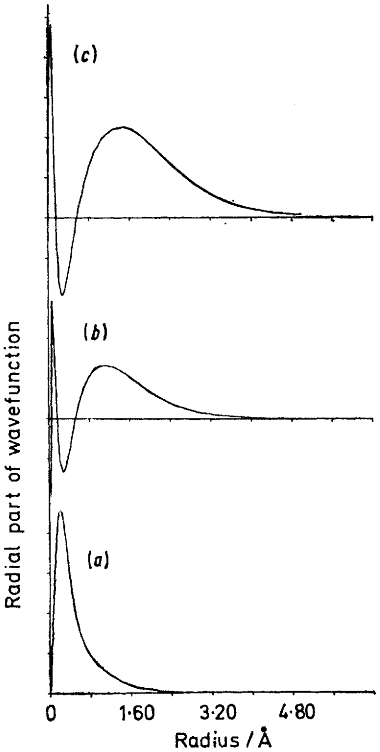


FIGURE 2 Radial parts of the wavefunctions for cobalt $3d$ (a), $4s$ (b), and $4p$ (c) orbitals. The plots were calculated on the basis of the multiple zeta-type Slater wavefunctions of Richardson *et al.*[15]

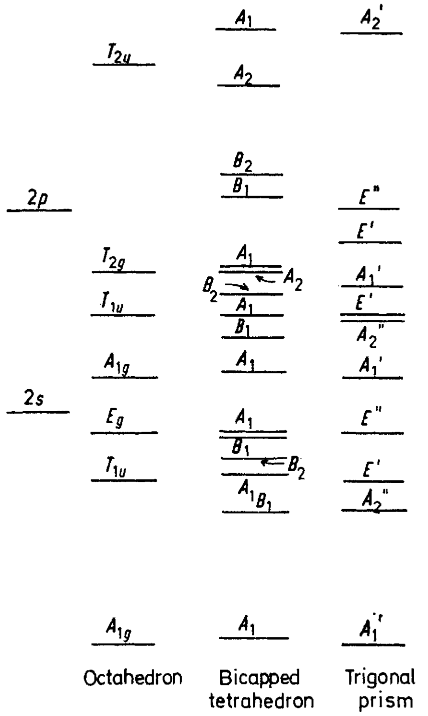


FIGURE 3 B–H and bonding skeletal molecular orbitals of B_6H_6 with octahedral, bicapped-tetrahedral, and trigonal-prismatic polyhedral geometries

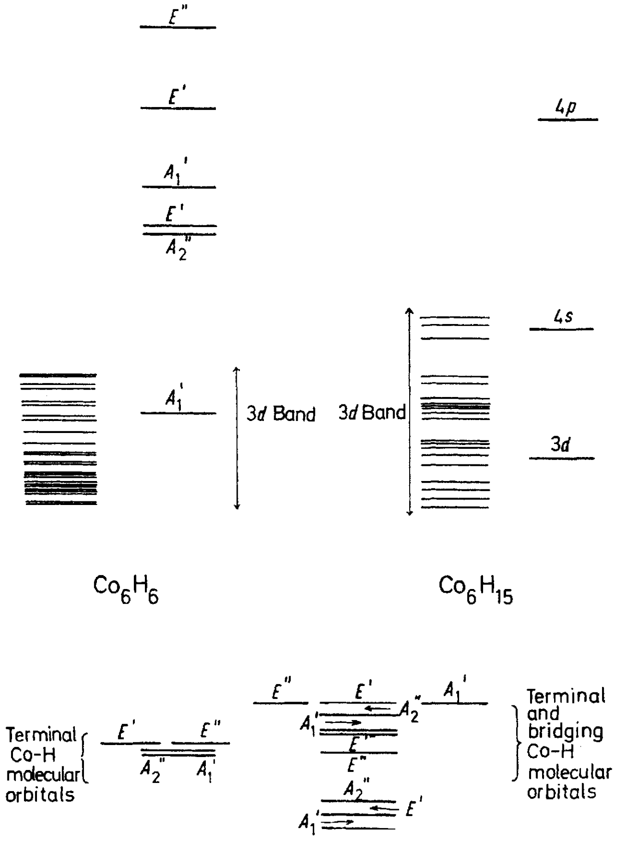
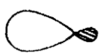


FIGURE 4 Illustration of the interaction between the bridging hydrido-ligands and the metal skeletal molecular orbitals in Co_6H_{15}. The calculations were based on a trigonal-prismatic metal polyhedral geometry

have predominantly hydrogen 1*s* character and are only weakly metal–metal bonding. For Co_6H_{15} a closed-shell stable electronic configuration will be associated with an occupation of the stable bonding Co–H m.o.s and the 3*d* band (*i.e.* 90 valence electrons). The hydrogen 1*s* orbitals overlap effectively with the 3*d* cobalt orbitals as well as the 4*s* and 4*p* orbitals and have the effect of increasing the width of the 3*d* band. Replacement of the hydrido-ligands by carbonyls should lead to essentially the same bonding picture, but some stabilisation of the 3*d* band levels is anticipated as a result of back-donation effects.

Terminally bonded carbonyl ligands also provide a stabilising influence on the skeletal m.o.s but employ a different mechanism. The Co–H fragment is characterised by the frontier m.o.s shown in (2)—(4); (2) is an out-pointing *s*–*p* hybrid, and (3) and (4) are a degenerate pair of $4p_\pi$ orbitals. The detailed analysis of metal tricarbonyl fragments by Elian and Hoffmann [20] demonstrated that replacement of the hydrido-ligand by three carbonyl ligands gives a set of similar frontier orbitals which have more *d*-orbital character and may be represented schematically by (5)—(7).* This rehybridisation permits the utilisation of the more stable valence *d* orbitals but at the same time introduces sufficient *p*- and *s*-orbital character to give effective metal–metal overlaps. A similar analysis of the effect of terminal carbonyl ligands was presented by Korol'kov and Meissner [22] for the tetrahedral cluster $[Ir_4(CO)_{12}]$.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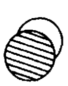
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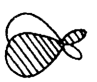
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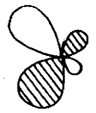
(7)

Capping Principle.—The original qualitative analysis of the bonding in $[Os_6(CO)_{18}]$ depended on the assumption that the bicapped tetrahedron has the same number of bonding skeletal m.o.s as the parent uncapped tetrahedral cluster, *i.e.* six.[8] The calculations reported in this paper and illustrated in Figures 1 and 3 have confirmed the correctness of this assumption. This capping principle, which was first recognised from an analysis of published m.o. data on borane polyhedra, is quite general and has been useful for rationalising the structures of a wide range of metal cluster compounds of the later transition elements.[11] This principle has a very simple quantum-mechanical basis which will be described below.

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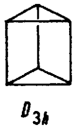
* The term isolobal has been suggested to indicate this similarity (see refs. 20 and 21 for a fuller discussion of this term).

[20] M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

[21] M. Elian, M. M.-L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148.

[22] D. V. Korol'kov and H. Meissner, *Z. phys. Chem.* (*Leipzig*), 1973, **253**, 25.

When an M–H [or an isolobal $M(CO)_3$ fragment] caps a symmetric polyhedron it causes a lowering of the symmetry of the molecule. The point group of the capped polyhedron is characterised by a new principal axis which passes through the capping atom and the centroid of the polyhedron [see (8) and (9) for example]. The interaction between the capping atom and the parent polyhedron can be simply analysed using perturbation-theory arguments if the frontier m.o.s of the two interacting fragments are re-defined with respect to this new symmetry axis. The frontier orbitals of the M–H fragment shown in (2)—(4) will transform according to the A_1 and E irreducible representations of the new point group if $n \geqslant 3$ for the principal rotation axis C_n and as A, $B(x)$, and $B(y)$ if $n \leqslant 2$. The frontier m.o.s of the parent polyhedron are the bonding and antibonding skeletal m.o.s.



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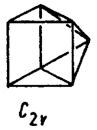
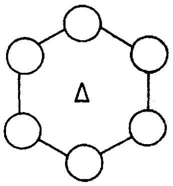
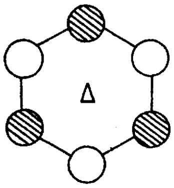


(9)

The interfragment interaction will be governed by the following basic considerations derived from perturbation theory.[23-25] First only orbitals with the same symmetry will interact, and secondly the strongest interactions will originate from those m.o.s which overlap effectively and are separated by a small energy difference. Where there is a choice between m.o.s with the same symmetry and orbital compositions, pseudo-symmetry considerations will generally predominate, *i.e.* those frontier orbitals with the same pseudo-symmetry give larger interfragment overlap integrals and therefore interact more strongly. This point may be illustrated by the schematic representations (10) and (11) for a polyhedral face with three-fold symmetry. Clearly the frontier orbital of the capping group which is nodeless overlaps more effectively with (10) which is also nodeless than the noded skeletal m.o. (11). Similarly the frontier orbitals (3) and (4) will interact most strongly with those skeletal m.o.s which have similar energies and a single nodal plane coincident with the principal symmetry axis. Skeletal m.o.s with these pseudo-symmetry restrictions must in general be bonding and therefore the simplified interaction diagram in Figure 5 can be suggested for the capping process.



(10)



(11)

The pseudo-symmetry properties of the interacting orbitals are indicated in parentheses after the symmetry labels. The strong interactions between the frontier orbitals of the capping atom and lower-lying skeletal m.o.s will result in the destabilisation of the former as shown in the Figure. It follows that the capped and parent polyhedrons have the same number of bonding skeletal m.o.s.

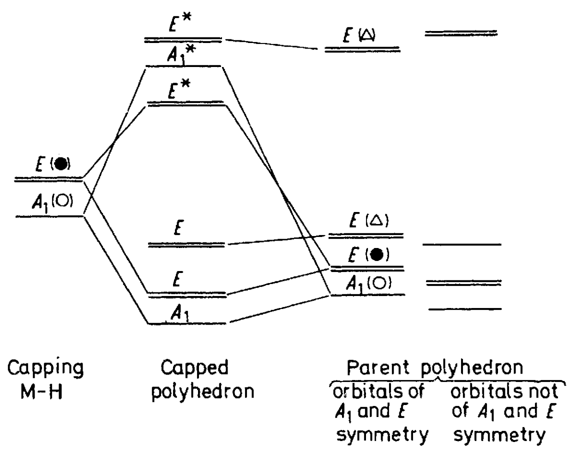


FIGURE 5 Schematic representation of the primary interactions between the frontier molecular orbitals of a capping group M–H and a symmetric polyhedron M_nH_n. The pseudo-symmetry characteristics of the molecular orbitals are represented by: (○), no nodal plane; (●), single nodal plane; and △, two nodal planes

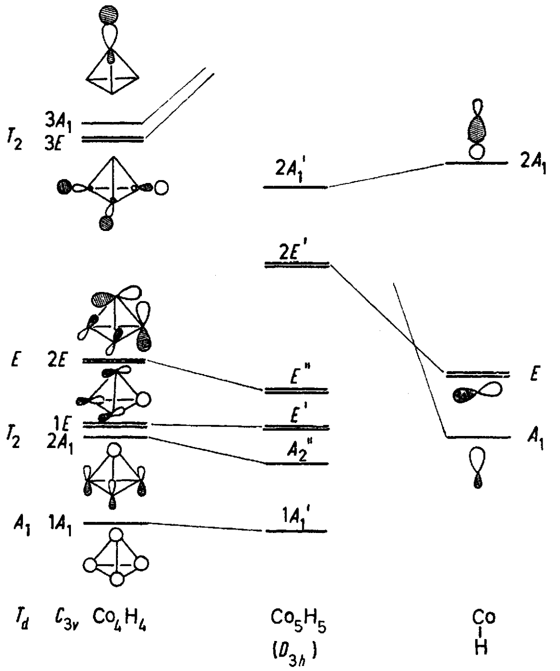


FIGURE 6 Interaction diagram for the capping process Co_4H_4 (tetrahedron) + Co–H $\longrightarrow$ Co_5H_5 (trigonal bipyramid). Only one component of the E molecular orbitals has been illustrated

This general quantum-mechanical argument is supported by extended-Hückel calculations on the capped-

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[23] L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, 1974, **96**, 1370.

[24] W. L. Jørgenson and L. Salem, 'The Organic Chemist's Book of Orbitals,' Academic Press, New York, 1973.

[25] R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1.

tetrahedral (trigonal bipyramid) and tetrahedral clusters Co_5H_5 and Co_4H_4 (see Figure 6). The Co_4H_4 cluster m.o.s have been defined with respect to the three-fold axis in order to clarify the analysis of the capping process. The $1E$ and $2E$ m.o.s of $[Co_4H_4]$ have the same pseudo-symmetry but the latter interacts more strongly because the energy match and overlap with the capping atom's E set is more favourable. Similar considerations apply to the $1A_1$ and $2A_1$ m.o.s.

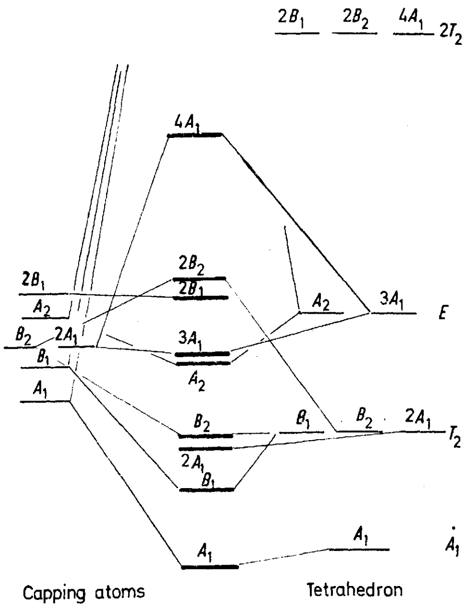
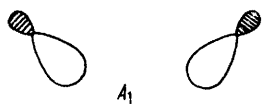
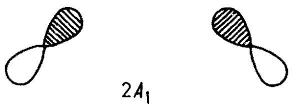


FIGURE 7 Orbital interactions between the two capping CoH fragments and the tetrahedral Co_4H_4 cluster in Co_6H_6

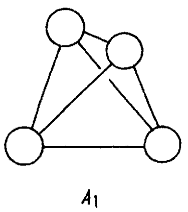
In the bicapped tetrahedron the frontier m.o.s of the two capping M–H fragments generate symmetry-adapted linear combinations belonging to the following irreducible representations of the C_{2v} point group: $A_1 + B_1$ [sp hybrids (2)]; $A_1 + B_1 + B_2 + A_2$ [p_π orbitals (3) and (4)]. These orbitals interact with the skeletal m.o.s of the parent polyhedron in the manner shown in Figure 7. The composition of the resulting m.o.s can be readily understood from the perturbation-theory arguments outlined above. The symmetric A_1 combinations of the capping-atom frontier orbitals (12) and (13) interact primarily with the skeletal m.o.s (14) and (15) which have the same pseudo-symmetry. The calculated inter-fragment overlap integrals shown below indicate the origins of these preferences and the importance of the pseudo-symmetry argument.


A_1

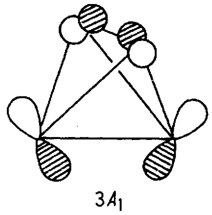
(12)


$2A_1$

(13)


A_1

(14)


$3A_1$

(15)

	(12)	(13)
(14)	0.6771	0.1734
(15)	0.0665	0.6271

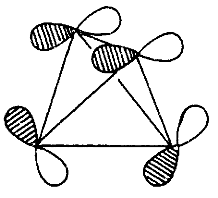
[The $2A_1$ skeletal m.o. has the same pseudo-symmetry as A_1 and therefore also interacts primarily with (12).] The two orbitals of B_1 symmetry (16) and (17) both overlap effectively with the skeletal m.o.s shown schematically in (18) and (19) respectively. Orbitals (16) and (18) have similar energies and therefore a strong interaction results, but (19) is one component of a high-energy antibonding T_2 skeletal m.o. of the parent tetrahedron and its interaction with (17) is rather small as a consequence. The combination (17) is somewhat antibonding in its own right and therefore becomes the major contributor to the low-lying antibonding m.o. of B_1 symmetry in the bicapped cluster ($2B_1$ in Figure 7).


B_1

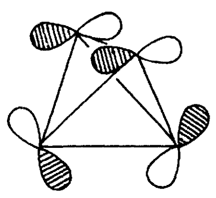
(16)


$2B_1$

(17)

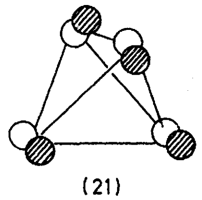

B_1

(18)


$2B_1$

(19)

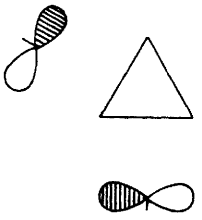

(20)


(21)

The A_2 frontier-orbital combination of the capping atoms finds a good match with an orbital of like symmetry derived from the E m.o.s of the parent tetrahedron. The B_2 orbital combination (20) interacts poorly with the bonding skeletal m.o. of the same symmetry (21) (also for reasons of pseudo-symmetry) and generates a low-lying antibonding m.o., $2B_2$, in the bicapped polyhedron. In summary, all the orbital combinations presented by the capping atoms give rise to antibonding skeletal m.o.s and therefore the capped polyhedron is characterised by the same number of bonding m.o.s as the parent polyhedron.

For a larger number of capping atoms some linear combinations are generated which have the correct energy, symmetry, and pseudo-symmetry requirements to interact strongly with the antibonding m.o.s of the parent polyhedron. Such interactions will give rise to additional bonding m.o.s and the capped and parent polyhedra will no longer have the same number of bonding skeletal m.o.s. An interesting example of this effect is provided by the tricapped trigonal prism which belongs to the same point group as the parent uncapped trigonal prism (D_{3h}). The frontier orbitals of the three capping M–H fragments generate the following irreducible representations: $A_1' + E'$ (*sp* hybrids); A_2'', E', A_2', and E'' (p_π orbitals). All these linear combinations except A_2' have the correct symmetry and pseudo-symmetry characteristics to interact effectively with the corresponding bonding skeletal m.o.s of the parent trigonal prism and therefore do not give rise to any additional m.o.s. The A_2' linear combination shown in (22) is ideally suited to interact with a low-lying A_2' antibonding skeletal m.o. of the parent polyhedron. This gives rise to the additional bonding skeletal m.o. of A_2' symmetry for the tricapped trigonal prism (see Figure 8). This analysis accounts simply for the observation that prismane, C_6H_6, has nine skeletal electron pairs, but the borane anion $[B_9H_9]^{2-}$ which has tricapped trigonal-prismatic geometry has ten skeletal electron pairs.[26,27] On this basis one can confidently predict that the $[Os_9(CO)_{27}]^{2-}$ and $[Ir_6(CO)_{18}]$ clusters will have tricapped trigonal-prismatic and trigonal-prismatic geometries, respectively.

The capping principle described above is clearly related and at times the obverse of the *debor* principle used to describe *nido*- and *arachno*-borane networks. These open polyhedral networks are generated when one or two vertices are removed from the deltahedra which are characteristic of the $[B_nH_n]^{2-}$ anions. The electronic basis of the *debor* principle was first recognised by Williams[28] and has proved to be an important generalisation in carbaborane and carbametallaborane chemistry.[29] Briefly this principle states that *arachno* and *nido* structures have the same number of bonding skeletal m.o.s as the parent *closo*-$[B_nH_n]^{2-}$ anion although they have one and two vertices fewer respectively. The relation between the *debor* and capping principles can be appreciated if the *nido* structure is described as 'capped-*arachno*' and the *closo* polyhedron as 'capped *nido*'. Clearly the interaction between the capping atom and the *arachno* (or *nido*) open network will be governed by similar symmetry and pseudo-symmetry considerations as those discussed above.



(22)

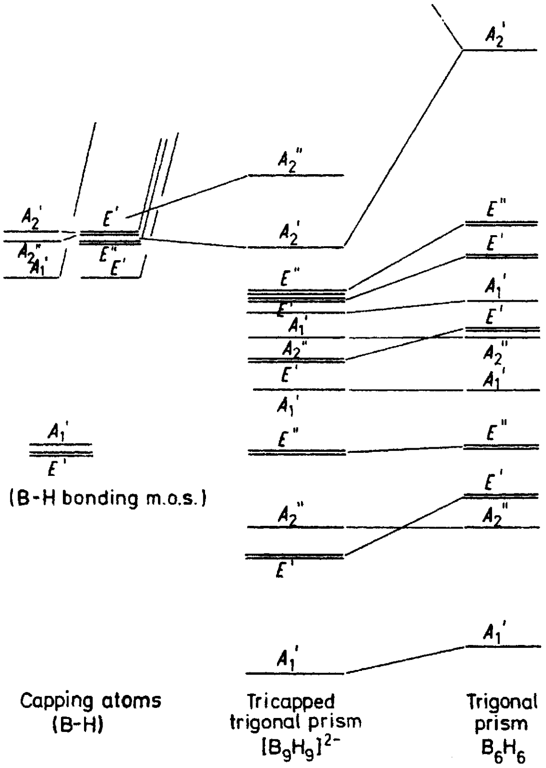


FIGURE 8 Interrelation between the bonding molecular orbitals of B_6H_6 (trigonal prism) and $[B_9H_9]^{2-}$ (tricapped trigonal prism)

In a subsequent paper the relation between these principles will be discussed in more detail and attention will be focused on the connectivity of the capping (or departing) atom. Rudolph and Pretzer[30] have given an alternative and complimentary theoretical account of the *debor* principle in terms of the polyhedral deformations introduced by the addition of electrons to *closo*-borane deltahedra.

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