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THE STOICHIOMETRIES OF HIGH-NUCLEARITY TRANSITION METAL CARBONYL CLUSTER COMPOUNDS

I. COMPACT CLOSE-PACKED CLUSTERS

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Summary

Extended Hückel MO calculations have been applied to a large number of compact close-packed bare clusters of rhodium in order to establish their bonding abilities. The results show that the number of cluster valence molecular orbitals (CVMOs) can be expressed in the form $6N + X$, with N equal to the number of metals and X a variable depending upon the cluster geometry. The value of X (which ranges from 6 to 11) is very often equal to 7. We suggest that any compact close-packed cluster compound should have $6N + 7$ CVMOs or a number very close to this, and this is the case for the few known actual examples.

Introduction

The number of known high-nuclearity carbonyl cluster compounds of the transition metals increases from day to day [1,2]. The largest cluster is a compact cubic Pt_{38} species synthesized by Chini and co-workers [3]. These compounds serve as models for small metallic crystallites covered by ligands and can play an important role in the study of metal surfaces involved in catalytic processes. (See ref. 2 and references therein.)

Various approaches have been suggested to rationalize the relationship between the geometry of the metal atoms and the bonding ability of cluster compounds. The application of the noble gas rule to these species gives good results with very small metallic aggregates, but fails with octahedral and larger clusters, usually predicting a smaller number of valence electrons. In recent years a set of empirical rules, known as the polyhedral-skeletal electron-pair theory, has been developed by Wade and Mingos [4,5], based on the analogy

between isostructural boranes and transition metal clusters. It has been used successfully to predict the stoichiometry of some species but large metal clusters assume usually compact geometries which are quite different from the borane deltahedra. Some semiempirical LCAO-MO calculations have also been performed for particular cases by Mingos [6–8], who first pointed out the fundamental role of the *s-p* metal orbitals in these systems, as a justification of the borane analogy. More recently Lauher has shown that the bonding abilities of transition metal cluster compounds can be estimated on the basis of extended Hückel MO calculations (EHMO) on the isolated clusters, and the method has been successfully applied to a number of known species [9].

These encouraging results led us to consider the possibility that calculations for a large number of cases might reveal some kind of rule to relate the geometry and stoichiometry of cluster compounds. In particular the small number of real examples limits the prospect of finding such an empirical rule.

In this study we have restricted our investigation to compact close-packed clusters, and we report the results of EHMO calculations on about 100 such cases, which have enabled us to suggest a relationship for assigning probable stoichiometries to this class of cluster compounds.

EHMO calculations on high-nuclearity rhodium clusters

Lauher [9] has shown that a reliable method of estimating the bonding abilities of transition metal cluster compounds (at least for small clusters) involves the use of EHMO calculations on the bare clusters as a guide. On the basis of energy the MOs can be divided into two sets: a lower set of cluster valence MOs (CVMOs) and a high-lying set of antibonding orbitals (HLAOs) which are too high in energy to be occupied by electrons or to serve as acceptors for ligands. The empirical upper limit for the CVMOs was set by Lauher at the *p* level of the isolated metal atoms. The CVMOs, whose number depends upon the cluster geometry, are suitable for containing metal electrons and/or to interact with the ligand orbitals; they can therefore give a reliable indication of the stoichiometry of the cluster compound. The method has given correct results for some known cases [9].

These results have prompted us to apply the procedure to a series of bare clusters, but before doing this we tested the method on almost all the known high-nuclearity cluster species of rhodium (with $N > 7$) in order to ascertain its reliability in cases of low symmetry and with higher nuclearity. Moreover we needed to obtain more information about the empirical choice of the upper limit for the CVMOs which was mentioned above.

The species investigated are shown in Fig. 1 and the results are summarized in Table 1. We performed the calculations on these clusters using experimental geometries (as determined by X-ray analysis) along with the parameters given in the Appendix. As previously observed in this type of calculation, we found in all cases a low-lying *d* band of $5N$ MOs (N = number of metal atoms). These are followed, with partial mixing, by a set of $N + X$ orbitals of *s-p* character up to about the *p* level of the isolated metals. In some cases, as II and IV, there is good separation between the highest CVMO (HCVMO) and the lowest HLAO (LHLAO) and the calculations give the correct numbers of CVMOs. In case V

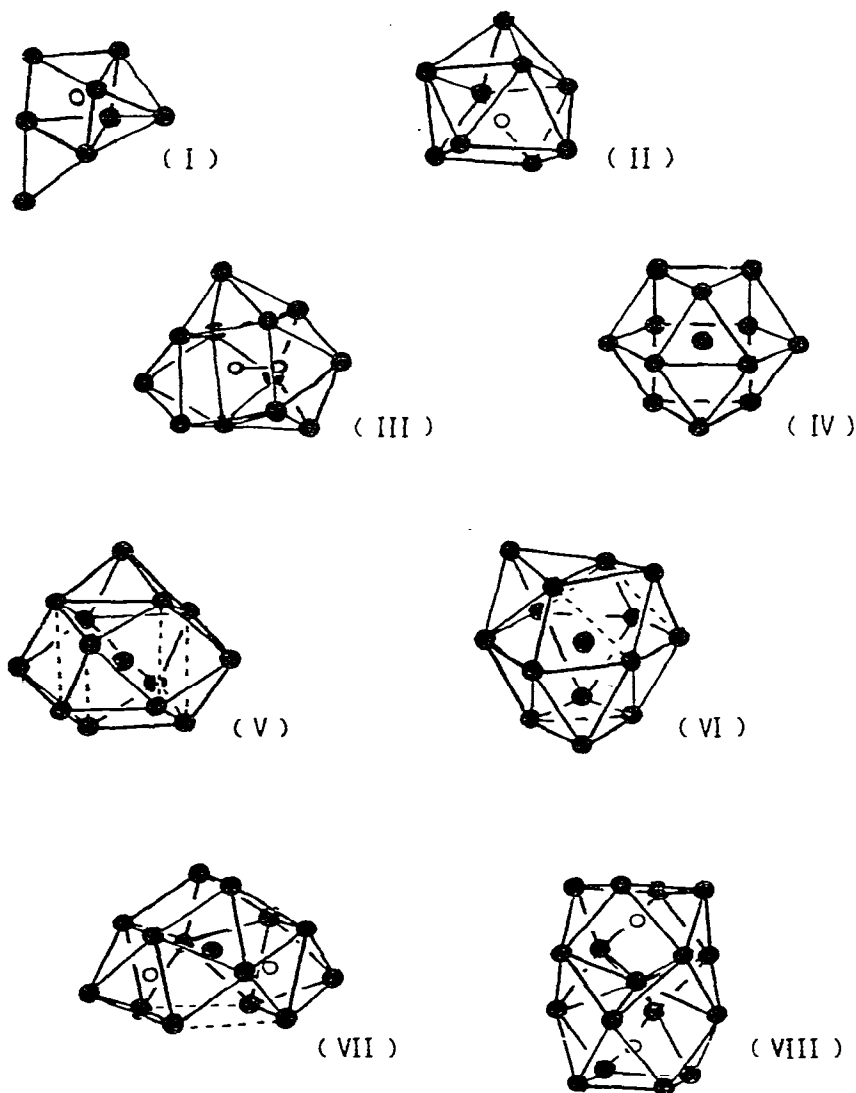


Figure 1. The metal atom clusters of the compounds listed in Table 1. The positions of interstitial C, P and S atoms are shown.

the HCVMO/LHLAO separation is smaller but the result is still correct. The other cases are more ambiguous (I and III) or give incorrect results (VI, VII and VIII). We observe that: a) the results for cases I and III suggest that the HCVMO level must not be chosen at too high an energy with respect to the p level of the isolated metal, and b) with increasing nuclearity the calculations lead often to a rather confused situation with a nearly continuous band of levels, weakly-bonding, non-bonding or weakly-antibonding, in the vicinity of the pure p level, and this can result in an incorrect count of the CVMOs. Neverthe-

TABLE 1
STRUCTURALLY CHARACTERIZED HIGH-NUCLEARITY RHODIUM CLUSTER COMPOUNDS

No.	Species	Ref.	Number of Valence Electrons	Number of Valence MOs	Energies of the Frontier MOs in eV (<i>p</i> level = -4.57eV)
I	Rh ₈ C(CO) ₁₉	10	114	57 (6 <i>N</i> + 9)	-3.62 -4.14 57 -4.39 -4.57 -4.62
II	[Rh ₉ P(CO) ₂₁] ²⁻	11	130	65 (6 <i>N</i> + 11)	-2.64 65 -4.46 -4.47
III	Rh ₁₂ (C ₂)(CO) ₂₅	12	164	82 (6 <i>N</i> + 10)	-3.91 -4.24 82 -4.52 -4.59 -4.63
IV	[Rh ₁₃ H _{5-n} (CO) ₂₄] ⁿ⁻	13	170	85 (6 <i>N</i> + 7)	-3.96 -3.99 85 -4.93 -4.93
V	[Rh ₁₄ (CO) ₂₅] ⁴⁻	14	180	90 (6 <i>N</i> + 6)	-4.28 -4.45 90 -4.98(deg.) -5.08
VI	[Rh ₁₅ (CO) ₂₇] ³⁻	14	192	96 (6 <i>N</i> + 6)	-4.19 -4.40 97 -4.71 -4.93
VII	[Rh ₁₅ (C) ₂ (CO) ₂₈] ⁻	15	200	100 (6 <i>N</i> + 10)	-4.27 -4.28 98 -4.50 -4.79 -4.81
VIII	[Rh ₁₇ (S) ₂ (CO) ₃₂] ³⁻	16	232	116 (6 <i>N</i> + 14)	-4.29 -4.37 114 -4.37 -4.61 -4.76

^a The number on the left, in each case, indicates the sequence number of the MO on the corresponding line.

less we consider the method a good way to get at least approximate information on the stoichiometries of cluster compounds.

Compact close-packed clusters

We performed the EHMO calculations on a number of three-dimensional * bare rhodium clusters taken from a compact close-packed lattice (cubic, hexa-

* A few two-dimensional cases were also considered. In these cases the HCVMO level must generally be chosen to be well above the energy of the *p* level of isolated metals in order to agree with the number of CVMOs of the available examples (triangle, butterfly, square).

gonal or mixed; Rh–Rh 2.69 Å) with the aim of establishing possible criteria for predicting their stoichiometries. Although few examples are known at present such arrangements can be expected to be more frequently encountered in the high-nuclearity cluster species which will be synthesized in the future.

The results are reported in Table 2, which shows the cases with a number of metal atoms (N) ranging from 6 to 15*; calculations on some other examples in the same range of nuclearity but with low symmetry or with a HCVMO/LHLAO separation (D) of <ca. 0.30 eV have been omitted, even though the results were often in line with the general pattern discussed below. Some of the reported cases were also previously considered by Lauher [9,17].

Analysis of the results leads to the following comments: a) In all cases there is a set of $6N + X$ CVMOs, which contains $5N$ orbitals of dominant d character, N orbitals of large s character and X s - p or p orbitals. The number X depends upon the cluster geometry but we have observed that for this class of clusters it is often equal to 7 or close to this value. b) The HCVMO/LHLAO separation usually becomes smaller as the number of metal atoms is increased, and so for large clusters it is difficult to determine the number of CVMOs reliably by direct calculation. c) On combining two pieces of compact layers there are various possibilities but the number of CVMOs for the resulting clusters is usually the same or nearly so (see, for instance, 6-1, 6-2 and 6-3, and many other cases).

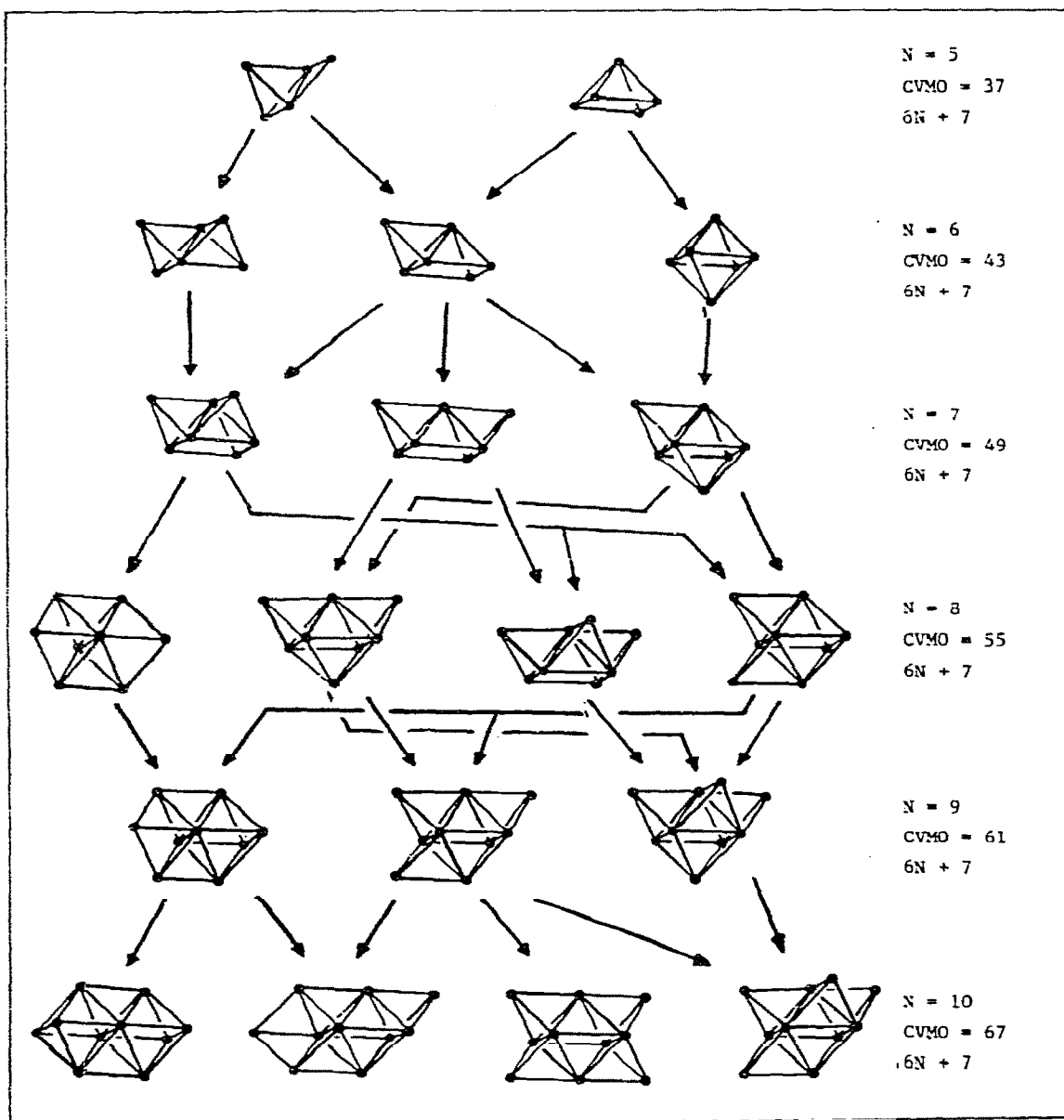
The most interesting result is that specified under (a) above. The polyhedral-skeletal electron-pair theory of borane polyhedra [4,5] extended to transition metal clusters requires $7N + X$ CVMOs ($X = 1$ for closo-, 2 for nido-, 3 for arachno-species) [1]. We have found instead $6N + X$ CVMOs, with X about constant. Our result leads, with a very large number, N , of metal atoms, to a maximum contribution of 6 MOs per metal atom, as it is the case in bulk metals. The near constancy of X originates in the fact that on adding atoms to a cluster each formally contributes 6 more CVMOs to the total number. This is illustrated in Scheme 1, and can be considered as a generalization of Mingos' capping principle [8], which states that capping atoms usually leave the number of the polyhedral-skeletal MOs of a particular cluster unchanged.

The values of X found in our examples (see Table 2) range from 6 to 11. However the more frequent value is 7, which was found in more than 50% of cases, followed by 8, in ca. 25% of cases. A value of 6 was found only in one doubtful case (15-1), but it applies to two small compact clusters, the tetrahedron (30 CVMOs) and the trigonal bipyramid (36 CVMOs). A value of 11 was found only in 14-14.

A similar trend was found also for larger compact clusters (see Table 3), but with increasing nuclearity the results of direct calculations are increasingly difficult to interpret.

* The choice of the HCVMO level was sometimes doubtful because of the presence of two comparable energy gaps in the vicinity of the p level of the isolated metals (E_p). Since in the more reliable cases, showing a good HCVMO/LHLAO separation, the HCVMO level was never found to lie more than ca. 0.30 eV above E_p and the LHLAO level was always significantly above E_p , we have used these indications as "self-consistent" criteria in the ambiguous cases (indicated by an asterisk in Tab. 2). For instance, in some multicapped octahedra there are two possible choices but one of them has a LHLAO level very close to E_p and was therefore rejected.





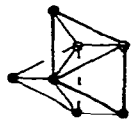
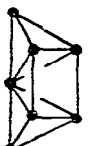
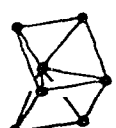
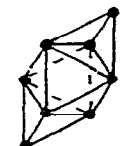
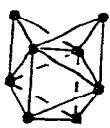
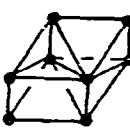
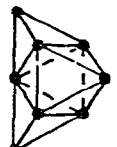
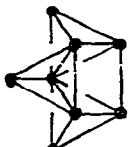
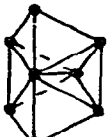

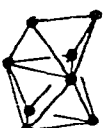

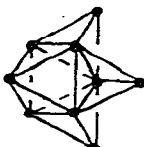
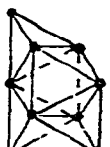
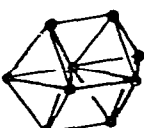
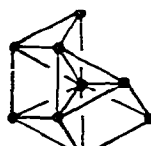
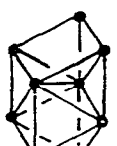
SCHEME 1



We have been unable to find a precise relationship between the X values and the cluster geometries. However, some useful information can be derived from our calculations. We describe as "closed" those cluster species which show X values equal to or possibly lower than 7, and as "open" those with $X > 7$. The following features are relevant: i) clusters obtained by superimposition of fully-triangulated pieces of compact layers (containing at least one triangle), in such a way that all atoms are at least triconnected, are usually either "closed" spe-

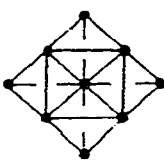
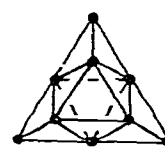
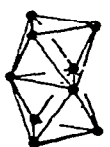
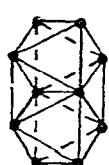

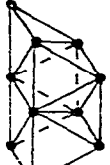









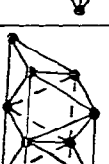


TABLE 2

EXAMPLES OF COMPACT CLOSE-PACKED CLUSTERS WITH A NUMBER OF METAL ATOMS (N) FROM 6 TO 15^a

 <p>6-1 O_h CVMO = 43 $6N + 7$ NG = 42 $D = 2.23$</p>	 <p>6-2 C_s CVMO = 43 $6N + 7$ NG = 43 $D = 1.10$</p>	 <p>6-3 D_{2h} CVMO = 43 $6N + 7$ NG = 43 $D = 1.49$</p>
 <p>7-1 C_{3v} CVMO = 49 $6N + 7$ NG = 48 $D = 1.19$</p>	 <p>7-2 C_s CVMO = 49 $6N + 7$ NG = 49 $D = 1.11$</p>	 <p>7-3 C_{2v} CVMO = 49 $6N + 7$ NG = 49 $D = 0.55$</p>
 <p>7-4 C_{2v} CVMO = 50 $6N + 8$ NG = 50 $D = 0.92$</p>	 <p>8-1 D_{3d} CVMO = 55 $6N + 7$ NG = 54 $D = 0.94$</p>	 <p>8-2 C_{2v} CVMO = 55 $6N + 7$ NG = 54 $D = 0.94$</p>
 <p>8-3 C_{2h} CVMO = 55 $6N + 7$ NG = 55 $D = 0.60$</p>	 <p>8-4 C_{2v} CVMO = 55 $6N + 7$ NG = 54 $D = 0.75$</p>	 <p>8-5 C_s CVMO = 55 $6N + 7$ NG = 55 $D = 0.77$</p>
 <p>8-6 C_{2v} CVMO = 55 $6N + 7$ NG = 55 $D = 0.73$</p>	 <p>8-7 C_s CVMO = 55 $6N + 7$ NG = 55 $D = 0.66$</p>	 <p>8-8 C_s CVMO = 56 $6N + 8$ NG = 55 $D = 1.14$</p>
 <p>8-9 C_{2v} CVMO = 56 $6N + 8$ NG = 56 $D = 0.42$</p>	 <p>9-1 C_s CVMO = 61 $6N + 7$ NG = 60 $D = 0.59$</p>	 <p>9-2 C_s CVMO = 61 $6N + 7$ NG = 60 $D = 0.75$</p>
 <p>9-3 C_{2v} CVMO = 61 $6N + 7$ NG = 60 $D = 0.90$</p>	 <p>9-4 C_1 CVMO = 61 $6N + 7$ NG = 61 $D = 0.58$</p>	 <p>9-5 C_s CVMO = 61 $6N + 7$ NG = 60 $D = 0.50$</p>

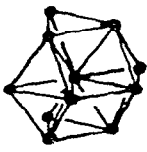
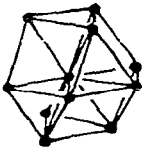
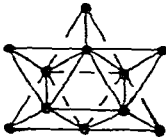
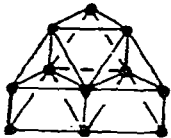
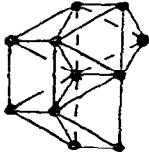

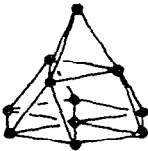
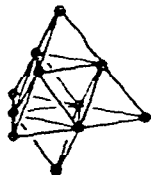
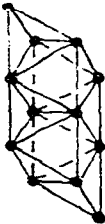
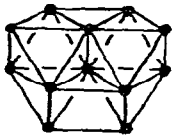
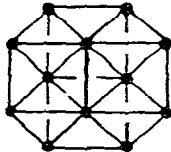
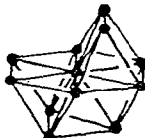
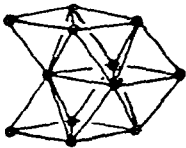
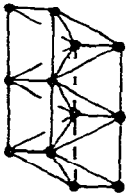
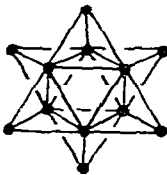
cies or "open" species with a number of CVMOs equal to $6N + 8$. Higher values of X are rare, and seem to be typical of one-directional chain structures as 12-13 and 14-10. ii) Certain capping systems cause specific increments in the X values

TABLE 2 (continued)

 <p>9-6 C_{4v} CVMO = 61 $6N + 7$ NG = 61 D = 0.64</p>	 <p>9-7 C_{3v} CVMO = 62 $6N + 8$ NG = 60 D = 0.66</p>	 <p>9-8 D_{3h} CVMO = 62 $6N + 8$ NG = 60 D = 1.34</p>
 <p>10-1 D_{2h} CVMO = 67 $6N + 7$ NG = 65 D = 0.37</p>	 <p>10-2 D_{2h} CVMO = 67 $6N + 7$ NG = 66 D = 0.40</p>	 <p>10-3 C_1 CVMO = 67 $6N + 7$ NG = 66 D = 0.51</p>
 <p>10-4 C_2 CVMO = 67 $6N + 7$ NG = 66 D = 0.51</p>	 <p>10-5 C_{4v} CVMO = 67 $6N + 7$ NG = 66 D = 0.54</p>	 <p>10-6 C_{3v} CVMO = 67 $6N + 7$ NG = 66 D = 0.79</p>
 <p>10-7 C_{2v} CVMO = 67 $6N + 7$ NG = 65 D = 0.55</p>	 <p>10-8 C_s CVMO = 67 $6N + 7$ NG = 65 D = 0.77</p>	 <p>10-9 C_s CVMO = 68 $6N + 8$ NG = 67 D = 0.36</p>
 <p>10-10 C_s CVMO = 68 $6N + 8$ NG = 66 D = 0.53</p>	 <p>10-11 C_{3v} CVMO = 68 $6N + 8$ NG = 66 D = 0.60</p>	 <p>10-12 T_d CVMO = 70 $6N + 10$ NG = 66 D = 2.63</p>
 <p>11-1 C_s CVMO = 73 $6N + 7$ NG = 71 D = 0.39</p>	 <p>11-2 C_s CVMO = 73 $6N + 7$ NG = 71 D = 0.58</p>	 <p>11-3 C_{2v} CVMO = 73 $6N + 7$ NG = 70 D = 0.62</p>

of the parent clusters (opening) as already observed by Mingos [8], who explained the effect in terms of interaction between the symmetry of the frontier orbitals of the original cluster and that of the orbitals of the capping atoms. This seems to be the case, for instance, for the tricapped octahedron 9-7, the

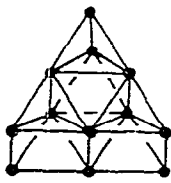
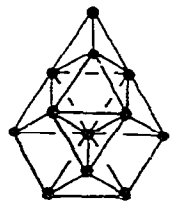
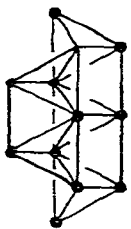
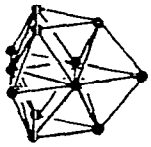
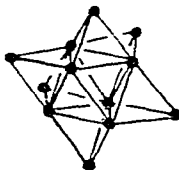
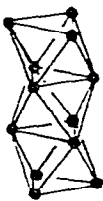
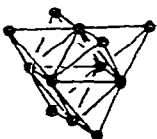
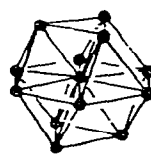
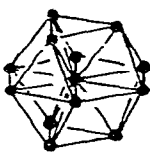
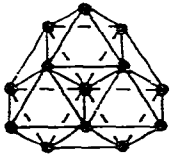
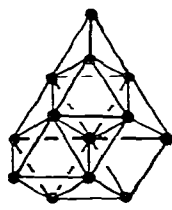
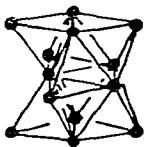
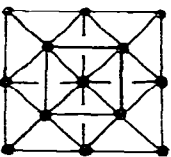
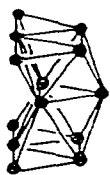
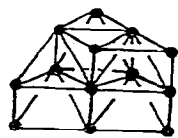
TABLE 2 (continued)

 <p>11-4 C_{2v} CVMO = 73 6N + 7 NG = 72 D = 0.71</p>	 <p>11-5 C_s CVMO = 73 6N + 7 NG = 72 D = 0.78</p>	 <p>11-6 C_s CVMO = 74* 6N + 8 NG = 72 D = 0.31</p>
 <p>11-7 C_s CVMO = 74 6N + 8 NG = 72 D = 0.41</p>	 <p>11-8 C₁ CVMO = 74 6N + 8 NG = 72 D = 0.37</p>	 <p>11-9 D_{3h} CVMO = 74 6N + 8 NG = 72 D = 0.35</p>
 <p>11-10 C_{3v} CVMO = 75 6N + 9 NG = 72 D = 0.78</p>	 <p>11-11 C_{3v} CVMO = 76 6N + 10 NG = 72 D = 1.10</p>	 <p>12-1 C_{2h} CVMO = 79 6N + 7 NG = 77 D = 0.43</p>
 <p>12-2 C_s CVMO = 79 6N + 7 NG = 76 D = 0.46</p>	 <p>12-3 D_{2d} CVMO = 79 6N + 7 NG = 78 D = 0.52</p>	 <p>12-4 C_{2v} CVMO = 79 6N + 7 NG = 77 D = 0.82</p>
 <p>12-5 C_{2v} CVMO = 79 6N + 7 NG = 77 D = 0.64</p>	 <p>12-6 C_{2h} CVMO = 80 6N + 8 NG = 79 D = 0.39</p>	 <p>12-7 D_{3d} CVMO = 80* 6N + 8 NG = 78 D = 0.42</p>

tetracapped octahedron 10-12 *, and the bicapped cube-octahedra 15-11 and 15-12. iii) Application of the noble gas rule ($NG = 9N - n_{\text{metal-metal bonds}}$) to

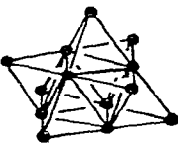
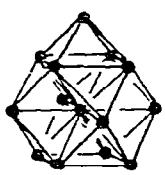
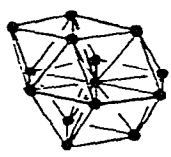
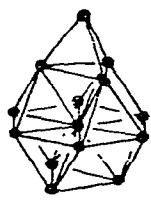
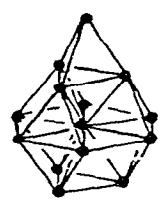
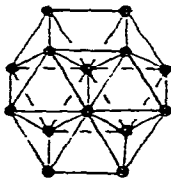
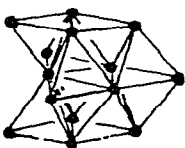
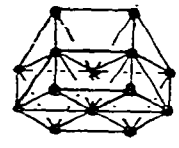
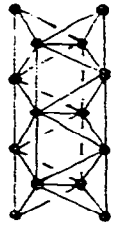
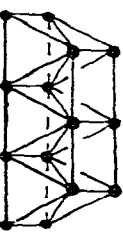
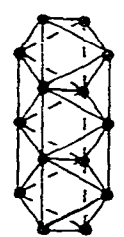
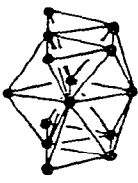
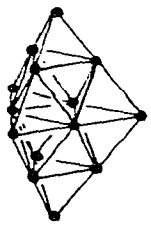
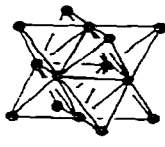
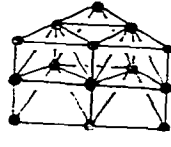
* But see note added in proof (p. 248).

TABLE 2 (continued)

 <p>12-8 C_s CVM0 = 80 $6N + 8$ NG = 78 $D = 0.30$</p>	 <p>12-9 C_s CVM0 = 80 $6N + 8$ NG = 77 $D = 0.50$</p>	 <p>12-10 C_s CVM0 = 80 $6N + 8$ NG = 79 $D = 0.38$</p>
 <p>12-11 D_{3h} CVM0 = 80 $6N + 8$ NG = 75 $D = 0.68$</p>	 <p>12-12 C_{2v} CVM0 = 81^a $6N + 9$ NG = 78 $D = 0.49$</p>	 <p>12-13 D_{3d} CVM0 = 81 $6N + 9$ NG = 78 $D = 0.80$</p>
 <p>12-14 C_{2v} CVM0 = 82 $6N + 10$ NG = 78 $D = 0.64$</p>	 <p>13-1 O_h CVM0 = 85 $6N + 7$ NG = 81 $D = 1.28$</p>	 <p>13-2 D_{3h} CVM0 = 85 $6N + 7$ NG = 81 $D = 1.19$</p>
 <p>13-3 C_{3v} CVM0 = 85 $6N + 7$ NG = 81 $D = 0.35$</p>	 <p>13-4 C_1 CVM0 = 85 $6N + 7$ NG = 82 $D = 0.37$</p>	 <p>13-5 C_{2v} CVM0 = 85 $6N + 7$ NG = 82 $D = 0.41$</p>
 <p>13-6 C_{4v} CVM0 = 87 $6N + 9$ NG = 85 $D = 0.49$</p>	 <p>13-7 C_{2v} CVM0 = 87 $6N + 9$ NG = 84 $D = 0.52$</p>	 <p>13-8 C_s CVM0 = 88 $6N + 10$ NG = 86 $D = 0.35$</p>

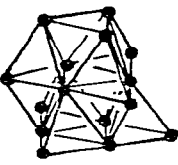
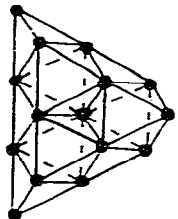
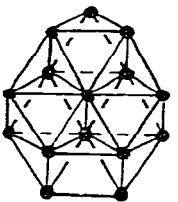
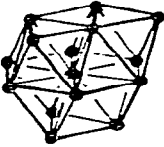
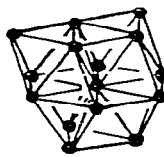
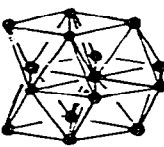
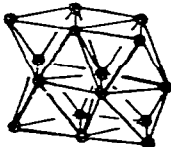
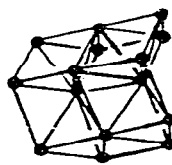
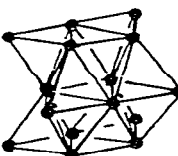
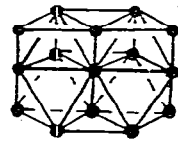
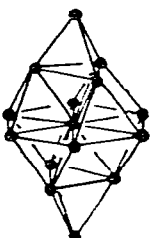
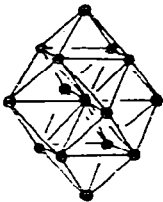
this type of cluster results in many cases in a lower number of CVMOs than that indicated by EHMO calculations (and also, when known, than that present in the actual species). The number of computed CVMOs was never found to be $< NG$; this implies that, on sampling clusters from a compact lattice, arrange-

TABLE 2 (continued)

 <p>13-9 C_{3v} CVMO = 88* $6N + 10$ NG = 84 D = 0.34</p>	 <p>14-1 C_{4v} CVMO = 91 $6N + 7$ NG = 86 D = 0.81</p>	 <p>14-2 C_s CVMO = 91 $6N + 7$ NG = 86 D = 0.83</p>
 <p>14-3 C_{3v} CVMO = 91 $6N + 7$ NG = 87 D = 0.83</p>	 <p>14-4 C_{3v} CVMO = 91 $6N + 7$ NG = 87 D = 0.79</p>	 <p>14-5 C_{2h} CVMO = 91 $6N + 7$ NG = 87 D = 0.59</p>
 <p>14-6 C_{2v} CVMO = 92* $6N + 8$ NG = 87 D = 0.36</p>	 <p>14-7 C_{2v} CVMO = 92 $6N + 8$ NG = 87 D = 0.34</p>	 <p>14-8 D_{2h} CVMO = 92 $6N + 8$ NG = 89 D = 0.53</p>
 <p>14-9 C_s CVMO = 92* $6N + 8$ NG = 91 D = 0.43</p>	 <p>14-10 D_{2h} CVMO = 93* $6N + 9$ NG = 88 D = 0.37</p>	 <p>14-11 C_{2v} CVMO = 93 $6N + 9$ NG = 89 D = 0.35</p>
 <p>14-12 D_{3h} CVMO = 94 $6N + 10$ NG = 87 D = 0.71</p>	 <p>14-13 O_h CVMO = 94* $6N + 10$ NG = 90 D = 0.37</p>	 <p>14-14 C_{4v} CVMO = 95 $6N + 11$ NG = 90 D = 0.79</p>

ments can be selected with a particularly low number of metal-metal bonds with respect to the number of metal atoms which cannot be "closed" since NG would be $>6N + 7$. This is illustrated by the following examples (see also 7.4 and 8-9):

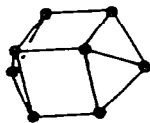
TABLE 2 (continued)

 <p>15-1 C_{3v} CVMO = 96* 6N + 6 NG = 93 D = 0.54</p>	 <p>15-2 C_s CVMO = 97* 6N + 7 NG = 93 D = 0.35</p>	 <p>15-3 C_s CVMO = 97 6N + 7 NG = 92 D = 0.41</p>
 <p>15-4 C_{2v} CVMO = 97 6N + 7 NG = 91 D = 0.62</p>	 <p>15-5 C_s CVMO = 97 6N + 7 NG = 91 D = 0.75</p>	 <p>15-6 C_{2v} CVMO = 97 6N + 7 NG = 91 D = 0.74</p>
 <p>15-7 C_{2v} CVMO = 97 6N + 7 NG = 92 D = 0.46</p>	 <p>15-8 C_{2v} CVMO = 97 6N + 7 NG = 96 D = 0.33</p>	 <p>15-9 C_{2v} CVMO = 98 6N + 8 NG = 94 D = 0.46</p>
 <p>15-10 C_s CVMO = 98 6N + 8 NG = 94 D = 0.36</p>	 <p>15-11 C_{3v} CVMO = 99 6N + 9 NG = 93 D = 0.94</p>	 <p>15-12 D_{4h} CVMO = 99 6N + 9 NG = 91 D = 0.68</p>

For each case we report the cluster symmetry, the number of cluster valence MOs (CVMO), with an asterisk in uncertain assignments, the number of MOs from the noble gas rule (NG) and the HCVMO/LHLAO separation (D) in eV.



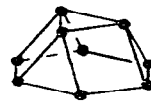
CVMO = 51 (6N + 9)
NG = 51



CVMO = 59 (6N + 11)
NG = 59



CVMO = 65 (6N + 11)
NG = 65



CVMO = 66 (6N + 12)
NG = 66

We have given some comments on "closed" and "open" species. What we think to be most important, however, is that the X value, though with some oscillations, remains substantially constant with increasing nuclearity in compact close-packed species, since an increase in X in certain arrangements (opening process) can be followed with further addition of metal atoms by a decrease (closing process) and so on. This is shown, for example, in Scheme 2.

Known examples

Few examples are known of clusters showing undistorted arrangements of compact close-packed metals. Besides a number of octahedral clusters with 43 CVMOs ($6N + 7$) there is a monocapped square pyramid, $\text{Os}_6\text{H}_2(\text{CO})_{18}$ [18], also with 43 CVMOs, various monocapped octahedra, such as $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ [19], $\text{Os}_7(\text{CO})_{21}$ [20] and $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$ [21], all with 49 CVMOs ($6N + 7$), and a bicapped octahedron, $[\text{Os}_8(\text{CO})_{22}]^{2-}$ [22], with 55 CVMOs ($6N + 7$). Moreover, a recently characterized mixed-metal species $[\text{Fe}_6\text{Pd}_6(\text{CO})_{24}\text{H}]^{3-}$ [23] contains an octahedral Pd_6 cluster hexacapped by iron atoms as in case 12-7 and possesses 80 CVMOs ($6N + 8$). The "twinned" cube-octahedron present in the anions $[\text{Rh}_{13}\text{H}_{5-n}(\text{CO})_{24}]^{n-}$ ($n = 2, 3, 4$) [13] is another good example, with 85 CVMOs ($6N + 7$). The recent structural investigations of novel high-nuclearity species such as $[\text{Rh}_{22}(\text{CO})_{37}]^{4-}$ [24] (with a cluster like that of case 22-2 of Table 3), $[\text{Pt}_{26}(\text{CO})_{32}]^{2-}$ [3] (with a hcp cluster) and $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ [3] (with a ccp cluster) provide important new examples which are substantially in agreement with our suggestions.

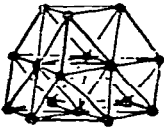
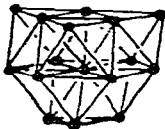
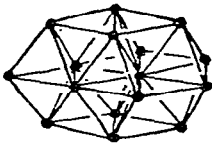
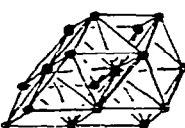
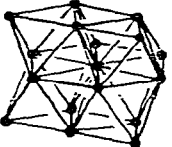
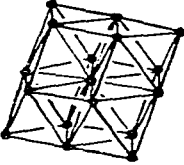
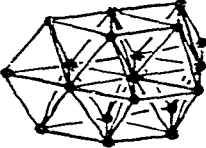
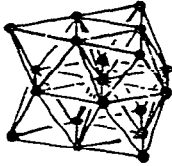
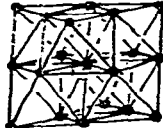
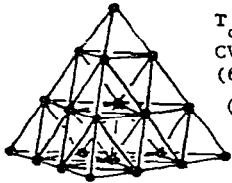
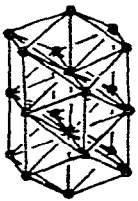
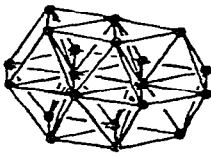
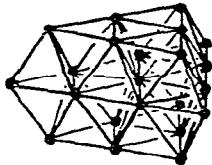
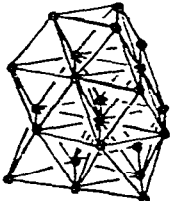
We also note that when distortions are present in a metal atom pattern, the X -value is different from that in the undistorted case. Thus the distorted octahedron of the paramagnetic $[\text{Co}_6\text{C}(\text{CO})_{14}]^-$ anion [25] requires 44 CVMOs (instead of 43), and the distorted monocapped octahedron of the $[\text{Rh}_7\text{I}(\text{CO})_{16}]^{2-}$ anion [26] requires 50 CVMOs (instead of 49). An interesting case is that of the D_{3h} cluster of the anions $[\text{Ni}_{12}\text{H}_{4-n}(\text{CO})_{21}]^{n-}$ ($n = 2, 3, 4$) [27] (see case 12-11); the real cluster is elongated in the direction of the three-fold axis so that the inter-layer bonds are significantly longer than the basal ones. This distortion causes an increase in the number of CVMOs (83 vs 80) and the computed correlation diagram shows that with an increase in the ratio of axial to equatorial distances a set of 3 or even 5 orbitals becomes available for bonding. A final example is the structure of the anion $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ [14], which contains a cluster derived from the monocapped cube-octahedron 14-1 with a tetragonal compression towards a bcc arrangement. This leads to a decrease of the number of CVMOs from 91 to 90.

In conclusion, a transition metal cluster compound possesses $6N + X$ CVMOs. Each family of clusters shows a preference for a particular value of X , which is related to its compactness. Thus, for Group VIII organometallic clusters a value of X of 7 can be associated with compact close-packed species, while a value of 6 is typical of clusters formed by condensed face-sharing tetrahedra and of clusters taken from a bcc lattice. Higher values of X (9 or more) are characteristic of compounds containing trigonal prisms and square antiprisms, as often found in species with interstitial C, N, P and S atoms (see Table 1). These non-compact species will be discussed in another paper*.

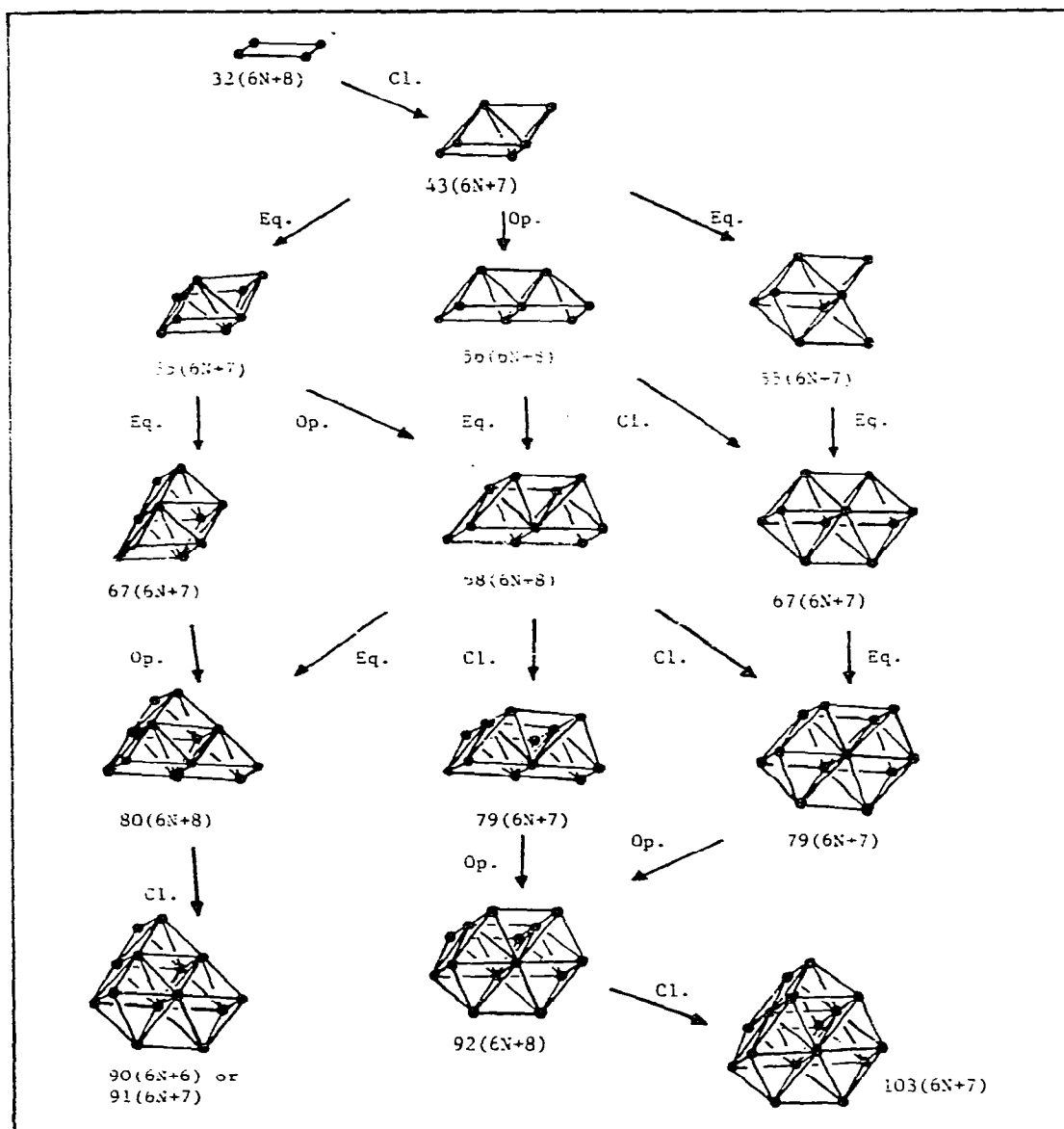
* See note added in proof (p. 248).

TABLE 3

SOME EXAMPLES OF CLUSTERS WITH NUCLEARITY BETWEEN 16 AND 22

 <p>16-1 T_d CVMO = 103 (6N+7)</p>	 <p>16-2 C_{3v} CVMO = 103 (6N+7)</p>	 <p>16-3 C_{2v} CVMO = 103 (6N+7)</p>
 <p>17-1 C_s CVMO = 109 (6N+7)</p>	 <p>17-2 C_{2v} CVMO = 109 (6N+7) or 110 (6N+8)</p>	 <p>17-3 D_{4h} CVMO = 112 (6N+10)</p>
 <p>19-1 C_{2v} CVMO = 121 (6N+7) or 122 (6N+8)</p>	 <p>19-2 D_{3h} CVMO = 122 (6N+8)</p>	 <p>19-3 O_h CVMO = 124 (6N+10) (Ref. 17)</p>
 <p>20-1 T_d CVMO = 127 (6N+7) (Ref. 17)</p>	 <p>20-2 D_{2h} CVMO = 128 (6N+8) (Ref. 17)</p>	 <p>20-3 C_{2v} CVMO = 128 (6N+8)</p>
 <p>22-1 D_{3h} CVMO = 140 (6N+8)</p>		 <p>22-2 C_{3v} CVMO = 140 (6N+8)</p>

SCHEME 2



^aEach step indicates the insertion of a couple of bonded metals.

^bEq.=equal X; Op.=opening process; Cl.=closing process (see text).

Appendix

The calculations were based on Hoffmann's extended Hückel method [28] using a local programme written by Dr. A. Gavezzotti. The K value in the H_{ij} formula was 1.75. All the parameters for rhodium, chosen as the representative element of Group VIII metals, were those previously used by Hoffmann (see ref. 29 and refs. therein) and very similar to those used by Lauher [9]. They were as follows: the $5s$ and $5p$ orbitals were described by single Slater-type

orbitals with exponents 2.135 and 2.10, respectively, and the $4d$ -wavefunctions were taken as linear combinations of two Slater-type orbitals ($C_1 = 0.5807$, $\zeta_1 = 4.29$; $C_2 = 0.5685$, $\zeta_2 = 1.97$). The H_{ii} values were -8.09 , -4.57 and -12.5 eV for $5s$, $5p$ and $4d$ orbitals, respectively. The Rh—Rh distance in compact close-packed cases was assumed equal to 2.69 \AA , as in the bulk metal. Use of slightly different metal—metal distances, such as those found in real clusters, gives analogous results.

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Note added in Proof.

The recently characterized anion $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ [P.F. Jackson, B.F.G. Johnson, J. Lewis, M. McPartlin and W.J.H. Nelson, *J. Chem. Soc. Chem. Commun.*, (1980) 224] contains a cluster like that of case 10-12 and possesses 67 CVMOs in contrast with the direct calculation (70 CVMOs) but in accord with our suggestion of a probable number of $6N + 7$ CVMOs for a compact close-packed cluster.