Influence of Interstitial Atoms in Transition-metal Carbonyl Clusters *

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The interactions between interstitial atoms (i.a.s) and cluster orbitals have been classified using qualitative perturbation theory arguments. The number of cluster valence orbitals contributed by the i.a. is shown to depend on the energy, shape and contraction of the i.a. and cage orbitals. Stereochemical effects of the i.a.s on transition-metal carbonyl clusters are discussed on the basis of molecular mechanics and extended Hückel computations. In general, a strong influence of the interstitial atoms on the ligand stereogeometry is expected. However, the energy and the shape of the cluster orbitals depend on the details of the ligand stereochemistry and the exact relationships between the inner interstitial atom, the cluster stoichiometry, and the outer ligand geometry need to be determined for each individual case. Interstitial atoms can affect both the cluster electronic requirements and the ligand stereochemistry and cannot merely be considered as *innocent* 'internal ligands'.

The properties of medium-size metal carbonyl clusters are often rationalized by partitioning the cluster into a few different entities: a metal cage, a ligand envelope and, if present, an interstitial atom (i.a.). These entities, even in the presence of strong reciprocal interactions, are commonly assumed to have independent natures. In other words, the following implicit assumptions are commonly found in the literature: (*i*) the required number of cluster valence electrons (c.v.e.s) reflects only the shape of the metal cage and it is not affected by the ligand number and stereochemistry; (*ii*) the shape of the ligand envelope is mainly dictated by the need of a rational filling of the volume around the metal cage; (*iii*) the interstitial atom is an 'internal ligand' not affecting the required number of c.v.e.s (two clusters with a similar metal cage have to be isoelectronic, whether or not the cage contains an i.a.); (*iv*) the interstitial atom size is of key structural importance in defining the metallic cluster shape but the ligand envelope is unaffected by the presence of an i.a.

There are many exceptions to the relationship between cluster shape and electron book-keeping, but nevertheless it rationalizes an amazing amount of data.[1,2] On the contrary, the identification of the number of c.v.e.s of empty and filled cavities relies mainly on data concerning interstitial main-group elements (Table 1); experimental results for interstitial transition-metal atoms are somewhat sparse, since there are only few data about large cavities which, when an i.a. is lacking, are unstable and normally relax to a more compact shape. The only clusters structurally characterized so far in both forms (containing either an empty cage or an interstitial transition element) have icosahedral or cuboctahedral shape and contradict the isoelectronicity principle (Table 1). Moreover, when clusters of valence-electron-poor metals with π-donor ligands are considered, 'closed-shell' d-filled metal clusters are found to have four valence electrons more than the corresponding empty or p-filled ones.[8]

Molecular orbital (MO) computations can in principle afford information about the missing large empty cavities. Empty anticuboctahedral clusters, for instance, are still lacking but, on the basis of extended Hückel (EH)[9] computations on the model compounds Rh_nH_{36} (n = 12 or 13),[10] have been proposed to be isoelectronic to the well known family of filled anticuboctahedral rhodium clusters $[Rh_{12}(\mu_{12}\text{-}Rh)(CO)_{24}H_{5-n}]^{n-}$ (n = 1–5).[5] The interstitial Rh atom, in such a case, should behave as a *genuine* internal ligand.

We have recently rationalized, on the basis of EH computations, the electron book-keeping in $[Ni_{10}Sb_2(\mu_{12}\text{-}Ni)(CO)_{18}\{Ni(CO)_3\}_2]^{n-}$ (n = 2–4)[11] and $[Ag_{12}(\mu_{12}\text{-}Ag)\{Fe(CO)_4\}_8]^{4-}$,[7] where the interstitial transition-metal atoms show all their distinctive differences from interstitial main-group elements. The aim of this paper is to generalize these results using a perturbational approach.

Results and Discussion

Influence on Cluster Electron Requirements.—Within the perturbation theory the amount of interaction between two fragments, *i.e.* the i.a. and the cluster (empty cage plus ligand envelope), depends on the relative energy and overlap of the interacting orbitals.[12] Depicted in Fig. 1 are the conceivable diagrams describing the interaction between one i.a. orbital and its cluster counterparts on varying their relative energy. The multitude of cluster orbitals has been idealized by selecting just two of them, one each from the two boxes of valence and empty orbitals. Even if the interactions are not limited to these orbitals, and metal–i.a. bonding cannot be rationalized using a localized bonding scheme, the idealized diagrams are equally informative when electron book-keeping alone is concerned.

The interaction diagrams in Fig. 1 have been labelled according to the relative energy of the i.a./cage orbitals. In particular **A**, **B** and **C** refer to i.a. orbitals with energy less than, similar to, and larger than the HOMO–LUMO gap of the cage (HOMO = highest occupied, LUMO = lowest unoccupied molecular orbital), respectively, and the subscripts correspond to the number of cluster valence (c.v.) orbitals contributed per i.a. orbital in the specific interaction. All the orbitals of the filled cluster are omitted in Fig. 1 except those resulting from the (idealized) interaction of the three selected orbitals, two from the cage and one from the i.a. These three MOs (at low, intermediate and high energy, respectively) are represented in Fig. 1 as black (filled by two electrons) or white (empty) boxes. When the intermediate MO has similar or lower energy than

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* *Supplementary data available* (No. SUP 56909, 6 pp.): calculated geometrical parameters for $[Rh_6(CO)_{14}]$ stereoisomers **I**–**III** obtained by molecular mechanics computations. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: eV ≈ 1.6 × 10^{-19} J, kcal ≈ 4.184 kJ.

Table 1 Classification of cluster geometries and comparison of predicted *vs.* observed c.v.e. number[a]

Cage geometry (c.v.e.s)	Empty (c.v.e.s)	p-Filled (c.v.e.s)	d-Filled (c.v.e.s)
Octahedron (86)	$[Rh_6(CO)_{16}]$ (86)	$[Ru_6(\mu_6\text{-}C)(CO)_{17}]$ (86)	—
Trigonal prism (90)	$[Re(CO)_{18}(\mu_4\text{-}PMe)_3]$ (90)	$[Rh_6(\mu_6\text{-}C)(CO)_{15}]^{2-}$ (90)	—
Square antiprism (118)	—	$[Co_8(\mu_8\text{-}C)(CO)_{18}]^{2-}$ (114)	—
	$[Bi_8]^{2+}$ (118) [48]	$[Ni_8(\mu_8\text{-}C)(CO)_{16}]^{2-}$ (118)	—
Cube (120)	$[Ni_8(\mu_4\text{-}PPh)_6(CO)_8]$ (120)	—	—
Capped square antiprism (130)	$[Sn_9]^{4-}$ (130) [40]	$[Rh_9(\mu_9\text{-}P)(CO)_{21}]^{2-}$ (130)	—
Bicapped square antiprism (142)	—	$[Rh_{10}(\mu_{10}\text{-}S)(CO)_{22}]^{2-}$ (142)	—
Pentagonal antiprism (146)	—	$[Ni_{10}(\mu_{10}\text{-}Ge)(CO)_{20}]^{2-\,b}$ (156) [146]	—
Icosahedron (170)	$[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$ (170) [150]	$[Ni_{12}(\mu_{12}\text{-}Sn)(CO)_{22}]^{2-\,b}$ (180) [170]	$[Ni_{10}Bi_2(\mu_{12}\text{-}Ni)(CO)_{18}]^{n-}$ (n = 2–4)[c] (178–180) [158–160]
Anticuboctahedron (170)	—	—	$[Rh_{12}(\mu_{12}\text{-}Rh)(CO)_{24}H_{5-n}]^{n-,\,d}$ (170)
Cuboctahedron (170)	$[Cu_{12}S_8]^{4-\,e}$ (168)	—	$[Ag_{12}(\mu_{12}\text{-}Ag)\{Fe(CO)_4\}_8]^{4-,\,f}$ (179)
Rhombododecahedron (198)	—	—	$[Rh_{14}(\mu_{14}\text{-}Rh)(CO)_{30}]^{3-}$ (198)

[a] The table has been compiled from ref. 1, which contains the references to the original literature. The absence of an entry means that there are no known examples. In parentheses below the polyhedron type is the number of c.v.e.s expected on the basis of polyhedral skeletal electron pair approach (PSEP) theory.[1] In parentheses below the formulae are the number of observed c.v.e.s obtained on adding 10 d electrons for each main-group element (if present). In square brackets are the number of observed c.v.e.s assuming the absence of a d-electron contribution from the main-group element(s). Note, however, interstitial- and cage-main-group elements have (currently) a different status in electron book-keeping, the 'missing d' electrons being considered only for the latter. [b] Ref. 3. [c] Ref. 4. [d] Ref. 5. [e] Ref. 6. [f] Ref. 7.

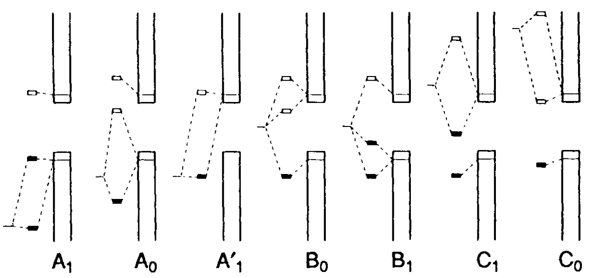

Fig. 1 Molecular orbital diagrams for one interstitial atom orbital interacting with its cluster counterparts on varying their relative energy. On each diagram the two large boxes indicate (*i*) the valence- and (*ii*) the empty-cluster orbitals separated by the HOMO–LUMO gap. The interaction with the cluster has been idealized by selecting two orbitals, one from each of the two boxes. Clearly the interactions are not limited to these orbitals, nevertheless, when only the electron book-keeping is concerned, the idealized diagrams are equally informative. The interaction diagrams have been labelled according to the relative energy of the i.a./cage orbitals. In particular **A**, **B** and **C** refer to i.a. orbitals with energy less than, similar to, and larger than the HOMO–LUMO gap of the cage, respectively, and the subscripts correspond to the number of c.v. orbitals contributed per i.a. orbital. All the orbitals of the filled cluster are omitted except those resulting from the (idealized) interaction of the three selected orbitals, two from the cage and one from the i.a. These three MOs (at low, intermediate and high energy, respectively) are represented in the figure as black (filled by two electrons) or white (empty) boxes. When the intermediate MO has similar or lower energy than the HOMO of the empty cage it will contain two electrons and the filled cluster will have an extra c.v. orbital

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On raising the i.a. orbital energy the following cases can be foreseen.

(*i*) Low energy and contracted i.a. orbitals (d orbitals of the late-transition elements, 'valence' d orbitals of the heaviest main-group elements) will interact marginally with the cluster orbitals and hence afford $\mathbf{A}_1$-type interactions.

(*ii*) Well shaped and suitable energy i.a. orbitals (s or p orbitals of the main-group elements, d orbitals of the early-transition elements) are normally involved in $\mathbf{A}_0$-type interactions or, if they do not match (the symmetry of) any valence cluster orbitals, in $\mathbf{A}_1'$-type interactions; in the latter case the extra c.v. orbital derives almost exclusively from the unchanged i.a. orbital which, being lower in energy than the cage HOMO, must be filled.

(*iii*) i.a. orbitals with energy within the HOMO–LUMO gap of the empty cluster give rise to $\mathbf{B}_0$- or $\mathbf{B}_1$-type interactions depending on their better overlap with the valence or virtual orbitals, respectively.

(*iv*) Medium and high energy i.a. orbitals (s or p orbitals of the transition elements) will be involved in $\mathbf{C}_1$- or $\mathbf{C}_0$-type interactions.

Interaction diagrams like those depicted in Fig. 1 are rather trivial and have been discussed before.[2,13,14] Nevertheless, little attention (if any) has been devoted to $\mathbf{A}_1$, $\mathbf{B}_1$ and $\mathbf{C}_1$ interaction types and most of the generalization, focusing on $\mathbf{A}_0$,[15] $\mathbf{B}_0$ and/or $\mathbf{C}_0$ interactions,[16] leads to the conclusion that i.a.s are 'innocent internal ligands' which do not perturb the cluster electron requirements. A notable exception has been the bonding analysis of transition-metal centred zirconium (and rare-earth metal) halide clusters, all sharing the common $M_6(\mu\text{-}X)_{12}X_6$ local ligand stereogeometry, where two i.a. d orbitals of e_g symmetry (involved in two $\mathbf{A}_1'$-type interactions) have been clearly recognized to contribute two extra c.v. orbitals.[8]

Relative orbital energy is the only apparent variable in Fig. 1. Nevertheless, knowing that ⟨i.a.-d|cage⟩ overlap integrals are normally smaller (by a factor of two, or more) than the corresponding ⟨i.a.-s|cage⟩ and ⟨i.a.-p|cage⟩ overlap integrals it may be assumed that d orbitals interact less effectively than the s and p orbitals, leading to a smaller spread of levels in the diagrams. This implies, for instance, that the transition between

Table 2 Relative energies of stereoisomers **I**, **II** and **III** for $[M_6(CO)_{14}]$, $[Rh_6(CO)_{14}]^{4-}$ and $[Rh_6(\mu_6\text{-}C)(CO)_{14}]$[a]

Stereoisomer	MM[b] $[M_6(CO)_{14}]$	EH[c] $[Rh_6(CO)_{14}]^{4-}$	EH[c] $[Rh_6(\mu_6\text{-}C)(CO)_{14}]$
I	2.5	0.0	77.8
II	0.0	40.3	25.7
III	2.6	20.1	0.0

[a] All the energies (kcal mol^{-1}) are relative to the most stable stereoisomer. [b] Steric energies computed using molecular mechanics calculations. [c] Total energies computed using extended Hückel calculations.

A_1- and A_0-type interactions will arise at relatively higher energy for d rather than for s and p orbitals. Overlap effects can roughly be evaluated, in a similar way, in all the other situations but, unfortunately, variables like the 'real' position of the HOMO–LUMO gap and the shape of the cluster orbitals cannot be determined *a priori*, in spite of their importance. Thus, computations only allow the assignment of a particular interaction to the $\mathbf{B}_0$ or $\mathbf{B}_1$ type, by showing that a given i.a. orbital has a better energy and overlap match with some valence (rather than some virtual) cluster orbital. However, even if an unambiguous assignment cannot be made *a priori*, a tendency is clear; on raising the energy of one i.a. orbital there is a fluctuation in the number of c.v. orbitals it contributes; as a consequence, a fluctuation in the number of c.v. orbitals, contributed by the different chemical elements on moving along a row of the Periodic Table, is expected. On filling an electronic subshell, the orbitals become more and more stable and contracted, and exhibit most of the different (C–A of Fig. 1) interaction types. This should be particularly evident for the d orbitals on moving from early- to late-transition elements and, even if the lack of experimental data on interstitial early-transition metals hampers a direct observation of the 'fluctuating' behaviour, the few data available about interstitial late-transition elements agree with the proposed scheme. For instance, the icosahedral anions $[Ni_{10}Sb_2(\mu_{12}\text{-}Ni)(CO)_{18}\{Ni(CO)_3\}_2]^{n-}$,[11] and $[Ni_{10}Bi_2(\mu_{12}\text{-}Ni)(CO)_{18}]^{n-}$ (n = 2–4)[4] have four or five c.v. orbitals more than $[Ni_{12}(\mu_{12}\text{-}Sn)(CO)_{22}]^{2-}$,[3] essentially because the interstitial Ni d orbitals are too contracted (five $\mathbf{A}_1$-type interactions).[11] Moreover, a detailed MO analysis of $[Ag_{12}(\mu_{12}\text{-}Ag)\{Fe(CO)_4\}_8]^{4-}$,[7] which possesses a cuboctahedral core, has clearly shown that it is closely related to the $[Cu_{12}S_8]^{4-}$ anion,[6] and that the six c.v. orbitals in excess originate from the i.a. d (five $\mathbf{A}_1$-type interactions) and s (one $\mathbf{B}_1$-type interaction) orbitals.

The fact that even a strongly interacting s orbital can afford a new c.v. orbital, rules out any possible *general* statement about interstitial atoms and suggests that the nature of the cage atoms, the shape of the cage and the stereochemistry of the ligand envelope must always be taken into account, since they determine the position of the HOMO–LUMO gap and the shape of the cluster orbitals.

Interstitial main-group elements normally work as 'internal ligands' not affecting the number of c.v. orbitals (because their s and p orbitals strongly interact in a A_0-type mode); some, however (for instance B, Si, Ge and Sn), have p orbitals with the right energy for setting up $\mathbf{B}_1$- or $\mathbf{C}_1$-type interactions and could behave 'abnormally', at least in principle, if suitable orbitals were present in the empty cluster. Also, oxygen and fluorine s orbitals are stable and contracted enough to be involved in $\mathbf{A}_1$-type interactions.

The interaction schemes outlined in Fig. 1, together with a close analysis of the energy and diffuseness of the atomic orbitals of the possible i.a.s, might give other possible 'exceptions' but, owing to the versatility of co-ordination of the external CO ligands, there are so many combinations of free charges, ligand numbers and stereochemistries that it is prohibitive to test all the different possibilities for the shape and energies of the 'empty' cluster orbitals. Hence it is thought that Fig. 1 will be mainly relevant in the *a posteriori* classification of the observed behaviours.

The relevance of the ligand stereochemistry in determining the cluster–i.a. interactions can also be proved by tackling the problem from the opposite point of view and, in the next section, how the shape of the ligand envelope is affected by the presence (or absence) of an interstitial atom is considered.

Influence on the Ligand Stereochemistry. A Working Example.—The weakness of a purely steric model of the ligand envelope has been recently pointed out by simulating most of the known octahedral carbonyl clusters with molecular mechanics (MM) and comparing 'theoretical' and experimental geometries.[17] Here, octahedral clusters of general formula $[M_6C_{1-n}(CO)_{14}]^{4n-}$ (M = Co, Rh or Ir; n = 0 or 1) (whose stoichiometries are in accordance with the usual electronic requirements of 86 c.v.e.s[1]) are considered, in order to test if the presence of the interstitial carbon atom does or does not influence the ligand stereochemistry.

The three most reasonable candidate stereogeometries for a $M_6(CO)_{14}$ cluster are: **I**, of O_h symmetry, with eight COs μ_3-bridging all the faces and one terminal CO per metal atom [Fig. 2(*a*)]; **II**, of C_{3v} symmetry, with two COs μ_3-bridging two opposite faces and two terminal COs per metal atom [Fig. 2(*b*)]; and **III**, of C_{2v} symmetry, with four asymmetric and two symmetric μ-CO [Fig. 2(*c*)].[17]

Stereoisomers **I**–**III** have been built using Allinger's MM2 program,[18] modified for handling metal carbonyl clusters,[17] and the computer-generated geometries have been used in the EH computations for the hypothetical $[Rh_6(CO)_{14}]^{4-}$ and $[Rh_6C(CO)_{14}]$ clusters (SUP 56909). The stereoisomers were built using the parameter set E of ref. 17 corresponding to a M–M bond distance of 2.80 Å [the average Rh–Rh bond distance in $Rh_6(CO)_{16}$ being 2.78 Å]. Since the octahedral cavity is large enough to accommodate the interstitial carbon atom without any relevant distortion, it is possible to compare the EH computations of $[Rh_6(CO)_{14}]^{4-}$ and $[Rh_6(\mu_6\text{-}C)(CO)_{14}]$ using exactly the same stereogeometry. The choice of a smaller cage for a straight comparison with the known cobalt derivatives (see below) would be hampered by the need to impose large distortions on the metal cage of the carbide species. The parameters for the EH computations were taken from ref. 19.

The results of MM and EH computations, reported in Table 2, clearly confirm the earlier suggestion that *intramolecular steric interactions are not the leading term in determining the metal carbonyl cluster stereogeometries.*[17,*] In fact, the relative energies obtained through MM, which only account (in the present form) for intramolecular steric interactions, are much smaller (and suggest opposite conclusions) than those obtained through EH computations, which also account for stereoelectronic effects.

The comparison between the EH relative energies (Table 2) of empty and C-centred clusters clearly indicates that the *interstitial carbon atom has a determining role in driving the ligand stereochemistry.* In fact for the empty $[Rh_6(CO)_{14}]^{4-}$ the most stable stereoisomer is **I** while for the C-centred $[Rh_6C(CO)_{14}]$ the most stable one is **III**. Accordingly stereogeometry **I** has been observed in the empty $[Co_6(CO)_{14}]^{4-}$ anion,[21] stereogeometry **II** (suggested by MM) has not yet been observed, while stereogeometry **III** has been found in the C-centred $[Co_6C(CO)_{14}]^-$ anion {note however that [Co₆C-

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[*] Some early work on the relative importance of cluster and ligand-sphere interactions in determining cluster geometries is given in refs. 20(*a*)–(*d*). The possible relevance of electronic factors on ligand stereochemistry has been raised in ref. 20(*e*).

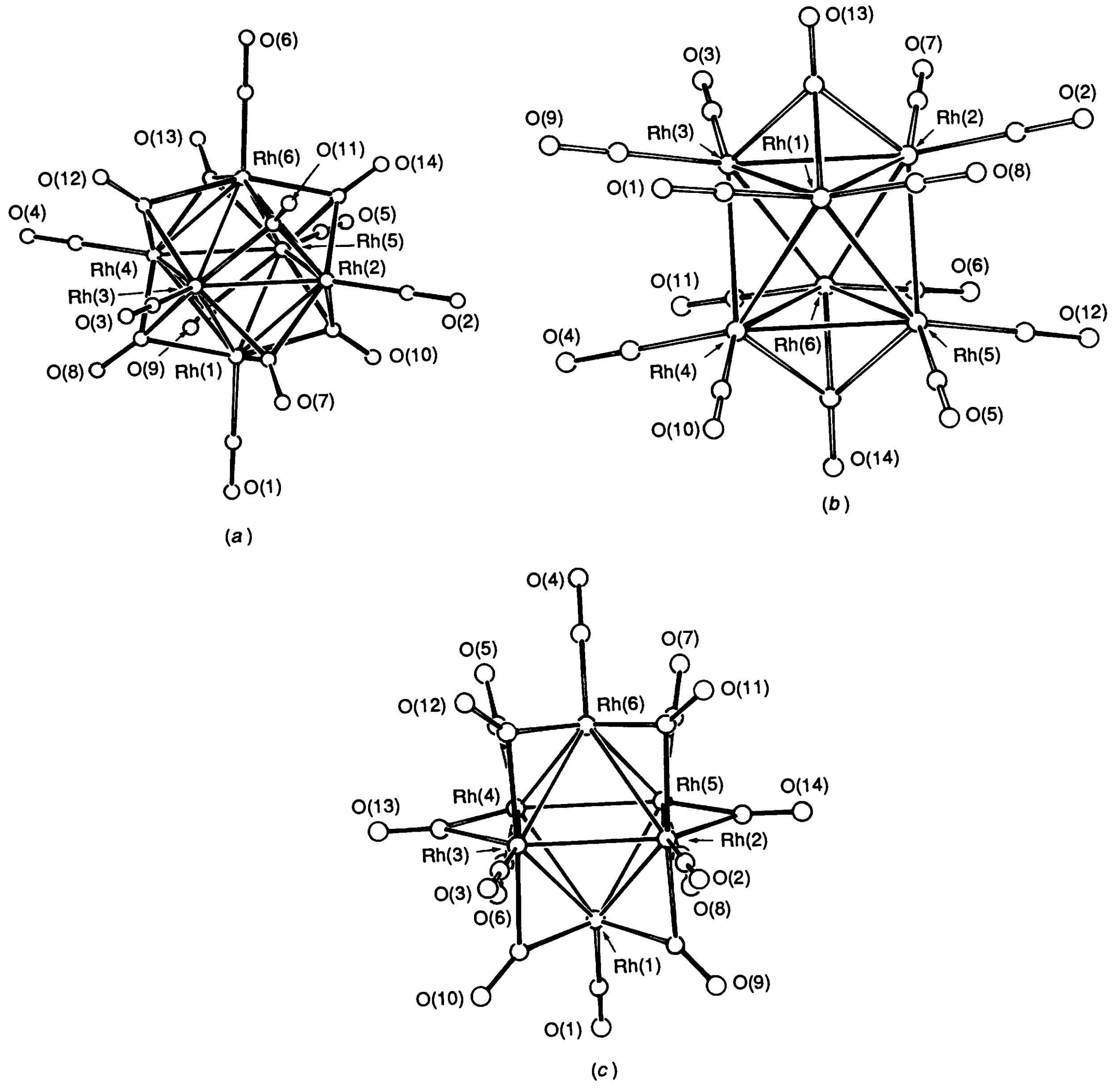

Fig. 2 The three most reasonable candidate stereogeometries for a $M_6(CO)_{14}$ cluster; (*a*) stereoisomer **I**, of O_h symmetry (eight COs μ_3-bridging all the faces and one terminal CO per metal atom); (*b*) stereoisomer **II**, of C_{3v} symmetry (two COs μ_3-bridging two opposite faces and two terminal COs per metal atom); (*c*) stereoisomer **III**, of C_{2v} symmetry (four asymmetric and two symmetric μ-COs and one terminal CO per metal atom)

$(CO)_{14}]^-$ is paramagnetic, has 87 c.v.e.s and a highly distorted metal polyhedron}.[22]

The orbital interaction diagrams[23] between the inner carbon and the empty $[Rh_6(CO)_{14}]$ cluster, for both stereogeometries **I** and **III**, are reported in Fig. 3, in order to show how the different nature (symmetry, shape and energy) of the interacting cluster orbitals results in highly dissimilar interaction patterns. A detailed description of Fig. 3 is not relevant in this context,* rather it is important to realize that in the present case: (*i*) the ligand stereochemistry, controlling the nature of the cluster frontier orbitals, ultimately controls the i.a.–cage interactions; or alternatively; (*ii*) the optimization of the i.a.–cage interactions influences the ligand stereogeometry.

Conclusion

Even if the reported EH computations concern only a particular case, the assumption that the ligand stereogeometry controls the shape of the cluster frontier orbitals applies in all situations and, *in general*, a strong influence of the interstitial atoms on the ligand stereogeometry could be expected. For instance, on a different system,[11] it had been concluded that the *real* $[Ni_{12}(\mu_{12}\text{-}Ge)(CO)_{12}(\mu\text{-}CO)_6(\mu_3\text{-}CO)_4]^{2-}$ and the *hypo-*

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* Participation of the interstitial atom is observed all along the energy range, reflecting that metal–i.a. interactions cannot be rationalized using a localized bonding scheme. Nevertheless, it is clear that the i.a. orbitals (which have energies below the cluster HOMO–LUMO gaps) are well suited to A_0-type interactions because the empty and the filled clusters have the same number of occupied orbitals in each symmetry class. Stereogeometry **III** is clearly unstable in the 'empty' form (having a small high-lying HOMO–LUMO gap) but is greatly stabilized in the 'filled' form because of the transfer of electrons from its high-lying frontier orbitals to the C-based ones. This is less true for **I** as shown by a close analysis of the ⟨cage|i.a.⟩ group overlap integrals, which indicates that 'empty' **III** has more suitable frontier orbitals (*i.e.* larger ⟨cage|i.a.⟩ integrals) than 'empty' **I** to interact with the i.a.. Hence, even if **III** is less stable than **I** in the 'empty' form (*i.e.* the **I**→**III** ligand reorganization is unfavourable) the frontier orbital rehybridization promoted by the ligand reorganization is more important and, as a result, **III** is more stable than **I** in the 'filled' form (Table 2).

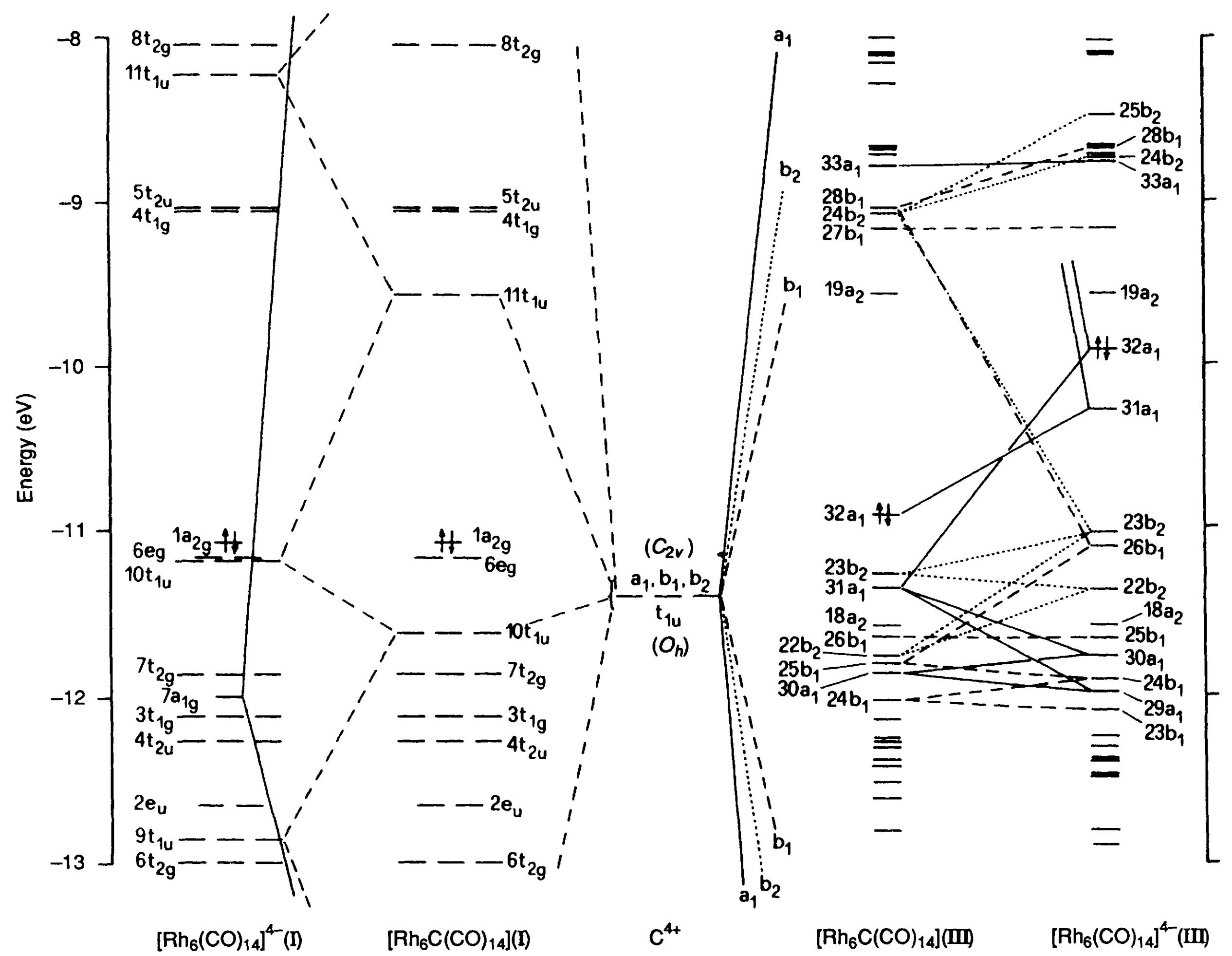

Fig. 3 Orbital interaction diagrams for the $[Rh_6(\mu_6\text{-}C)(CO)_{14}]$ clusters. Left, stereogeometry I (O_h symmetry); right, stereogeometry III (C_{2v} symmetry). The μ_6-C 2s atomic orbital is not shown, being off-scale. Both $[Rh_6(CO)_{14}]^{4-}$ and $[Rh_6(\mu_6\text{-}C)(CO)_{14}]$ have 86 c.v.e.s; for the sake of clarity only the HOMO has been represented as being occupied by two electrons. Lines correlating orbitals not matching the symmetry of the i.a. orbitals have been omitted

thetical empty and μ_{12}-Ni derivatives would not have been isoelectronic if they had had the same ligand stereogeometry.

The above considerations, together with the earlier suggestion that interstitial carbides can exert some 'steric repulsion' on μ_3 hydrides,[24] show that interstitial atoms can affect both the cluster electronic requirements and the ligand stereochemistry and cannot merely be considered *innocent* 'internal ligands'. However, the energy and the shape of the cluster orbitals depend on the details of the ligand stereochemistry and the exact relationship between the inner interstitial atom, the cluster stoichiometry, and the outer ligand geometry needs to be determined for each individual case.

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