Molecular-orbital Calculations on Cluster Compounds of Gold

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Molecular-orbital calculations on $[Au_6]^{2+}$ and $[Au_9]^{3+}$ clusters have shown that the overlap of the gold 6*s* orbitals makes a dominant contribution to the bonding. Co-ordination of ligands to these ' bare ' metal clusters encourages a more favourable hybridisation of the metal orbitals and results in stronger radial metal–metal bonding. The electronic factors responsible for the breakdown of the Polyhedral Skeletal Electron Pair rules when applied to the gold clusters are discussed.

AN analysis of the structural, stereochemical, and reactivity features of metal cluster compounds is clearly a prerequisite to an evaluation of these compounds as viable models for metal surfaces involved in catalytic processes. The determined synthetic efforts of Chini[1] and Lewis[2] and their co-workers have resulted in the isolation and characterisation of metal carbonyl cluster compounds with four to 15 metal atoms. Generally these complexes have metal atoms situated on the surface of the polyhedron and therefore do not represent unambiguously the closer-packed arrangement which characterises a metal surface. No doubt such centred compounds will become more numerous when larger clusters are synthesised (see ref. 1 for such an example). The gold clusters $[Au_{11}(PPh_3)_7(SCN)_3]$ and $[Au_9(PPh_3)_8]^{3+}$ provide examples of such centred clusters,[3-10] but their chemical and catalytic properties have not been reported in any great detail. As part of a more general study of the bonding in metal cluster compounds, molecular-orbital (m.o.) calculations have been completed on this type of gold cluster and on the related octahedral cluster $[Au_6(PPh_3)_6]^{2+}$.[11,12] This study was aimed at delineating the electronic factors responsible for the geometries and stabilities of these complex clusters.

In recent years the geometries of metal carbonyl cluster compounds have been systematised by a set of simple rules which have been described collectively as the Polyhedral Skeletal Electron Pair Theory.[13-17] These rules were derived from a perceptive analogy between isostructural borane and transition-metal cluster molecules[13] and have been widely used to rationalise and predict cluster and metallacarbaborane geometries. It has been shown that the molecular orbitals in isostructural polyhedral boranes and metal carbonyls are closely related because the contracted *d* orbitals of transition metals give very poor metal–metal overlaps and the orbital picture is dominated by the more effective overlap of the diffuse metal *s* and *p* orbitals.[18] Adherence to these rules also depends on the fact that axially symmetric $M(CO)_n$ fragments are isolobal † with B–H and C–H fragments and therefore present orbitals of like symmetry for polyhedral skeletal bond formation.[19,20] The polyhedral skeletal approach does have its limitations, however, and in particular it is not generally applicable to clusters of the Group 1B elements and of platinum.[17] The gold cluster complexes described above fall into this class and therefore this theoretical analysis was also undertaken in order to establish the electronic factors responsible for this breakdown.

CALCULATIONS

The molecular orbitals of the octahedral clusters Au_6 and $[Au_6(PPh_3)_6]^{2+}$ were computed using the overlap formulae and

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† Isolobal means that the number, symmetry properties, extent in space, and energies of the frontier orbitals of the fragments are similar. A fuller discussion of the bonding capabilities of $M(CO)_3$ and $M(\eta\text{-}C_5H_5)$ fragments is given in refs. 19 and 20.

[1] V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumulo, *J.C.S. Chem. Comm.*, 1974, 299.

[2] C. R. Eaddy, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **37**, C39.

[3] L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Chem. Comm.*, 1965, 212.

[4] L. Malatesta, L. Baldini, G. Simonetta, and F. Cariati, *Co-ordination Chem. Rev.*, 1966, **1**, 255.

[5] L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Inorg. Chim. Acta*, 1967, **1**, 24, 315.

[6] F. Cariati and L. Naldini, *Inorg. Chim. Acta*, 1971, **5**, 172.

[7] M. McPartlin, R. Mason, and L. Malatesta, *Chem. Comm.*, 1969, 334.

[8] V. G. Albano, P. L. Bellon, M. Manaserro, and M. Sansoni, *Chem. Comm.*, 1970, 1210.

[9] P. L. Bellon, M. Manaserro, and M. Sansoni, *J.C.S. Dalton*, 1972, 1481.

[10] P. L. Bellon, F. Cariati, M. Manaserro, L. Naldini, and M. Sansoni, *Chem. Comm.*, 1971, 1423.

[11] P. L. Bellon, M. Manaserro, L. Naldini, and M. Sansoni, *J.C.S. Chem. Comm.*, 1972, 1035.

[12] P. L. Bellon, M. Manaserro, and M. Sansoni, *J.C.S. Dalton*, 1973, 2423.

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

[14] K. Wade, *Chem. in Britain*, 1975, 177 and refs. therein.

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

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

[17] R. Mason and D. M. P. Mingos, *M.T.P. Internat. Rev. Sci., Phys. Chem., Series* II, ' Chemical Crystallography,' ed. J. M. Robertson, 1975, p. 121.

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

[19] M. Eilian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

[20] M. Eilian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *J. Amer. Chem. Soc.*, in the press.

assumptions discussed in some detail in a previous paper.[18] This type of calculation may be described as a Wolfsberg–Helmholtz or extended-Hückel treatment [21-24] and the constant, *k*, commonly employed in this type of calculation was set equal to 1.75.

The Au–Au distances were taken to be 3.02 Å {the average bond length determined [12] in the *X*-ray crystallographic study of $[Au_6(PPh_3)_6][BPh_4]_2$}. The Au–P overlap calculations were made for an internuclear distance of 2.29 Å. In order to satisfy computer limitations, sp^3 hybridisation was assumed for the phosphorus atoms, and the valence-state ionisation energy of the phosphine lone-pair orbital was assumed to be −12.30 eV.* The valence-state ionisation energies for the gold atom are: 5*d*, −11.85; 6*s*, −9.22; and 6*p*, −4.27 eV.[25] The gold–gold overlap integrals were computed using the multiple zeta wavefunctions suggested by Basch and Gray.[26] For phosphorus the exponents tabulated by Clementi [27] were used.

The $[Au_9(PPh_3)_8]^{3+}$ ion has D_{2h} symmetry and the peripheral gold–gold distances were set equal to the 2.850 Å average found in the *X*-ray crystallographic study of this ion.[10] These calculations were made using the ICON 8 extended-Hückel program at Cornell University. The Hückel calculations, using the 6*s* orbitals of gold as a basis set, were made on the ICL 1904 computer at this College.

RESULTS AND DISCUSSION

The molecular orbitals formed when the gold atoms aggregate to form a polyhedral cluster will naturally reflect the orbital overlaps and valence-state ionisation energies of the valence orbitals. Therefore, before discussing the cluster molecular orbitals in any detail, some attention will be drawn to trends in overlap integrals and valence-state ionisation energies. Table 1 gives the calculated *d*-orbital-overlap integrals for gold and cobalt [18] at distances appropriate for clusters of these metals, and Table 2 gives a similar comparison of *s*- and *p*-orbital overlaps for boron,[21] cobalt,[18] and gold.

TABLE 1

Calculated cobalt–cobalt and gold–gold *d*-orbital-overlap integrals

Integral	Co–Co (r = 2.50 Å)	Au–Au (r = 3.00 Å)
(d_σ, d_σ)	0.062	0.026
(d_π, d_π)	0.048	0.011
(d_δ, d_δ)	0.010	0.001

TABLE 2

Calculated cobalt–cobalt, gold–gold, and boron–boron, *s*- and *p*-orbital-overlap integrals

	B–B (r = 1.76 Å)	Co–Co (r = 2.50 Å)	Au–Au (r = 3.00 Å)
(s, s)	0.40	0.421	0.120
(p_σ, p_σ)	0.33	0.228	0.242
(p_π, p_π)	0.24	0.462	0.048

The *d*–*d*-overlap integrals for cobalt and gold (Table 1) are small to the point of being almost insignificant. Therefore, the energy spread of the molecular orbitals generated will be rather small when these atomic orbitals combine in a cluster. This feature is a characteristic of the later transition elements and arises primarily from a contraction of the *d* orbitals due to inefficient screening effects as the atomic number increases across the transition series.[28]

The cobalt and boron *s*- and *p*-orbital overlaps are comparable and large and will lead to a wide spectrum of m.o. energies. It is this similarity which forms a theoretical basis for the polyhedral skeletal electron rules which govern the geometries of borane and metal carbonyl clusters.[13-18] For gold the $6p_\sigma$–$6p_\sigma$ overlap is similar to the corresponding cobalt overlap, but the 6*s*–6*s* and $6p_\pi$–$6p_\pi$ overlaps are much smaller than those for the lighter elements. The very small $6p_\pi$–$6p_\pi$ overlap arises from the high sensitivity of this type of overlap to increases in internuclear distance.[29] It is clear from this analysis that the cluster molecular orbitals for $[Au_6(PPh_3)_6]^{2+}$ are expected to bear little resemblance to those of the isostructural $[Co_6(CO)_{14}]^{4-}$ and $[B_6H_6]^{2-}$ ions where all the *s* and *p* orbitals make a significant contribution in forming delocalised molecular orbitals with large electron densities on the faces and at the centre of the octahedron. Therefore, electron-counting schemes based on analogies between gold and borane clusters are likely to have limited value.

The co-ordination numbers and geometries of mononuclear gold(I) complexes are greatly influenced by the large 6*s*→6*p* promotion energy of the free atom,[30] and similar effects seem to influence the cluster molecular orbitals in gold aggregates. In particular, *s*–*p*-hybridisation effects which would be encouraged by the reasonable $6s$–$6p_\sigma$ gold overlaps are found to be minimal for the isolated Au_6 cluster because of the large energy difference separating these orbitals.

These qualitative conclusions are supported by the m.o. calculations on the octahedral Au_6 cluster which are illustrated in Figure 1. The gold 5*d* orbitals combine to form a narrow band of 30 molecular orbitals at lowest energies. At higher energies there are six molecular orbitals with predominantly 6*s* character, and, at higher energies still, 18 orbitals with predominantly 6*p* character. The $A_{1g}(s)$, $T_{1u}(s)$, and $E_g(s)$ orbitals are illustrated schematically in Figure 2 and their relative orderings can be easily understood in terms of the signs of the adjacent (*cis*-) gold–gold 6*s*–6*s* overlaps. The small contributions of the 5*d* orbitals to these molecular orbitals do not seem to contribute significantly to their energies. The *trans*-6*s*–6*s* overlap integrals are almost negligible (0.011) and therefore the

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* 1 eV ≈ 1.60×10^{-19} J.

[21] H. C. Longuett-Higgins and M. de V. Roberts, *Proc. Roy. Soc.*, 1954, **A224**, 336.

[22] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 1964, **3**, 10.

[23] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, 1952, **20**, 837.

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

[25] C. E. Moore, ' Atomic Energy Levels,' Nat. Bur. Standard, circular 467, 1952 (vol. II), 1958 (vol. III).

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

[27] E. Clementi, *J. Chem. Phys.*, 1964, **40**, 1944.

[28] C. S. G. Phillips and R. J. P. Williams, ' Inorganic Chemistry,' Oxford University Press, London, 1966, vol. 2.

[29] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493.

[30] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273.

$T_{1u}(s)$ molecular orbitals are essentially non-bonding (see Figure 2).

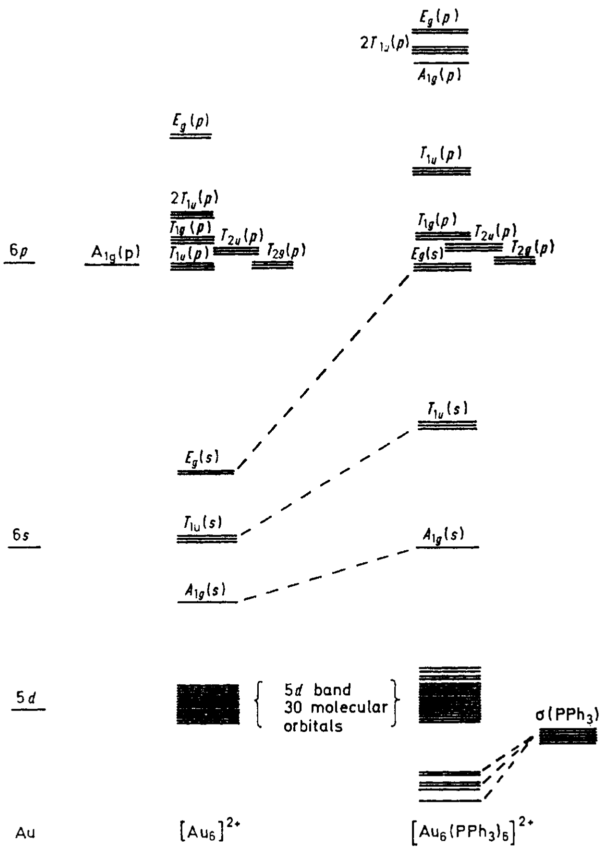

FIGURE 1

The uncomplexed $[Au_6]^{2+}$ cluster has 64 valence electrons and therefore it will have the ground-state electronic configuration [5*d* band]$^{60}[A_{1g}]^2[T_{1u}]^2$. It is clear that such a cluster is very weakly bound because it has only a single electron pair in a strongly bonding molecular orbital $[A_{1g}(s)]$. The remaining electrons occupy the mildly repulsive *d* band and the non-bonding $T_{1u}(s)$ molecular orbitals.

More effective gold–gold bonding is encouraged by co-ordination of triphenylphosphine ligands to the vertices of the cluster because the lone-pair orbitals of these ligands overlap effectively with the metal 6*s*, 6*p*, and 5*d* orbitals and encourage a more favourable in-pointing hybridisation of the gold orbitals. The stabilising effect of the phosphine ligands can be seen in the m.o. correlation diagram calculated for $[Au_6(PPh_3)_6]^{2+}$ and illustrated on the right-hand side of Figure 1. The additional electron pairs introduced by the phosphine ligands occupy the lowest-lying A_{1g}, E_g, and T_{1u} orbitals which are strongly metal–metal and metal–phosphorus bonding. This bonding feature is made possible by effective s–d_{z^2} hybridisation of the metal orbitals and results in strong radial metal–metal and metal–ligand bonding. The importance of this type of hybridisation in mononuclear linear gold complexes was first recognised by Orgel.[31,32]

Metal–phosphorus bonding also introduces more 6*p* character into the higher lying $A_{1g}(s)$, $E_g(s)$, and $T_{1u}(s)$ molecular orbitals and this effect is illustrated schematically in Figure 3. The higher proportion of *p* character introduced into these orbitals results in a larger energy spread and a shift to higher energies. The relative ordering of the energy levels is not affected, however. The ground state of the molecule is therefore still . . . $[A_{1g}(s)]^2[T_{1u}(s)]^2$ and presumably paramagnetic if the idealised geometry is retained. The highest-lying $T_{1u}(s)$ level is now somewhat antibonding (see Figure 1) and therefore a distortion which would relieve this antibonding character may be anticipated. The *X*-ray crystallographic analysis of $[Au_6(PPh_3)_6][BPh_4]_2$ [11,12] has shown that the molecule has an almost idealised D_{3d} cluster geometry derived by compressing the octahedron along a three-fold axis. The six crystallographically independent edges of the octahedron can thus be divided into two classes: two opposite faces related by an inversion centre have edges of mean length 3.073 Å, whereas the remaining edges are shorter (mean 2.965 Å). This type of distortion could presumably remove the orbital degeneracy of the highest-occupied molecular orbital and give rise to a singlet ground state and diamagnetic properties. Unfortunately, this cluster has not been prepared in sufficient quantities to be fully characterised and its magnetic properties have not been studied. The possibility that the cluster has bridging hydrogen ligands which would

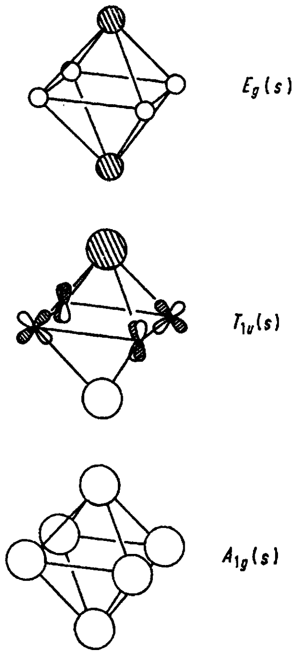

FIGURE 2

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[31] L. E. Orgel, *J. Chem. Soc.*, 1958, 4186.

[32] L. E. Orgel, ' An Introduction to Transition Metal Chemistry,' 2nd edn., Methuen, London, 1966.

contribute additional electrons to the skeletal bonding scheme cannot be excluded by the present limited *X*-ray crystallographic structural evidence.

The radial type of bonding which is an important feature of this type of cluster can be enhanced by the incorporation of a small main-group atom at the centre of the cluster. (The hole at the centre of an octahedral cluster is clearly too small to accommodate another gold atom.) The $A_{1g}(s)$ and $T_{1u}(s)$ orbitals of $[Au_6(PPh_3)_6]^{2+}$ are ideally hybridised to overlap with the $2s$ and $2p$ orbitals of a central carbon atom (see Figure 3). The correlation diagram for $[Au_6C(PPh_3)_6]^{2+}$ (Figure 4) indicates that the four valence electrons contributed by the carbon atom would lead to a very stable closed-shell electronic configuration. Similar carbido-clusters have been reported for Group 8 metal carbonyl cluster compounds, *e.g.* $[Ru_6C(CO)_{17}]$,[33] and presumably owe their remarkable stabilities to the operation of similar electronic effects.[34]

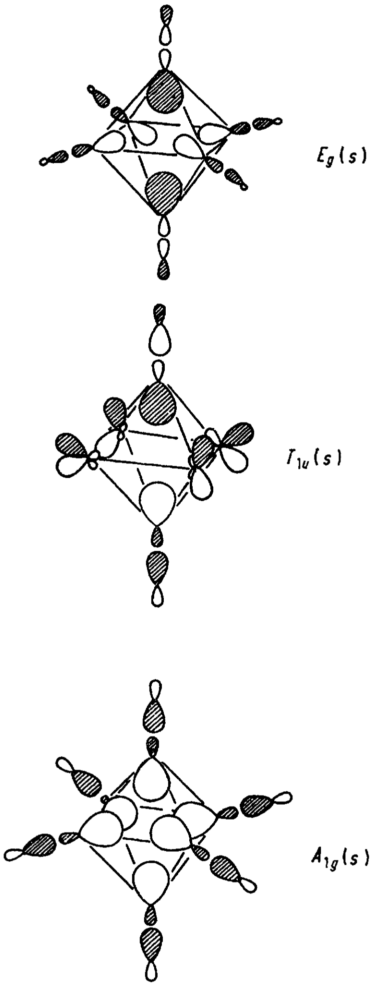

FIGURE 3

For the larger cluster compounds, centred gold structures do become a possibility and are indeed found in $[Au_9(PPh_3)_8]^{3+}$ and $[Au_{11}(PPh_3)_7X_3]$ (X = SCN or I).[3-10] The skeletal geometries of these clusters (Figure 5) may be derived from a common parent, the centred cosahedron. The complex $[Au_9(PPh_3)_8]^{3+}$, (I), which has D_{2h} symmetry, can be obtained by removing two pairs of adjacent vertices from opposite sides of the icosahedron, and $[Au_{11}(PPh_3)_7X_3]$, (II), by replacing a triangular set of adjacent vertices of the icosahedron by a single vertex.[10]

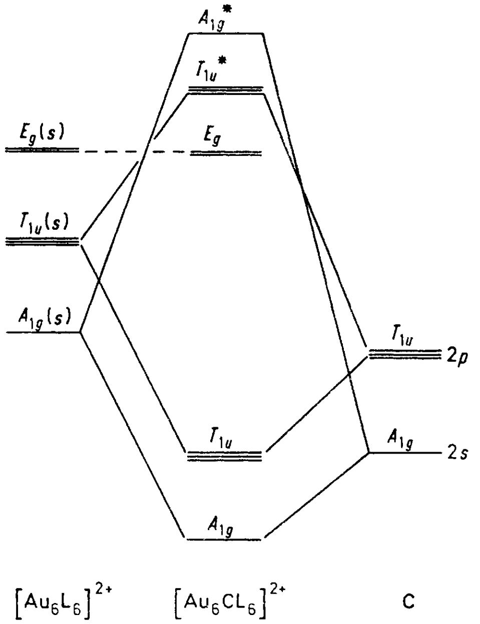

FIGURE 4

The results of extended-Hückel m.o. calculations on the centred D_{2h} cluster (I) are shown in Figure 6. The small *d–d* overlaps result in a somewhat wider band of *d*-type molecular orbitals than that noted above for the Au_6 cluster because of the larger basis set of orbitals. At lower energy than the *d* band there is a molecular orbital of A_g symmetry which has predominantly $6s$ character on the central atom and a mixture of $6s$ and $5d$ character on the peripheral atoms. Above the *d* band there are eight molecular orbitals which also have predominantly $6s$ character and are localised mainly on

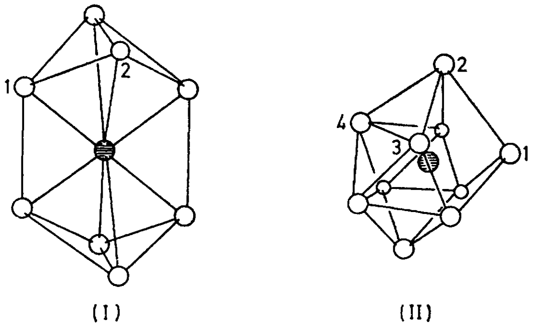

FIGURE 5

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[33] B. F. G. Johnson, J. Lewis, and R. D. Johnston, *J. Chem. Soc.* (*A*), 1968, 2865.

[34] P. S. Braterman, *Structure and Bonding*, 1972, **10**, 57.

the peripheral atoms. The molecular orbitals with 6*p* character are of even higher energy and have been omitted from Figure 6. The $[\mathrm{Au}_9]^{3+}$ cluster has 96 valence electrons and these can be nicely accommodated in all the bonding molecular orbitals to give the diamagnetic closed-shell electronic ground-state configuration $[A_g]^2[5d\ \mathrm{band}]^{90}[B_{1u}]^2[B_{3u}]^2$, ^1A_g. It is noteworthy that the energy gap separating the highest-occupied and lowest-empty orbitals is substantial (*ca.* 1.7 eV). Computer limitations prevented a full calculation on the $[\mathrm{Au}_9(\mathrm{PPh}_3)_8]^{3+}$ cluster, but the experience gained with the $[\mathrm{Au}_6(\mathrm{PPh}_3)_6]^{2+}$ ion suggests that the same ordering of levels will be retained in the complexed cluster. At the same time co-ordination of the phosphine ligands will stabilise the cluster by encouraging more effective radial gold–gold bonding.

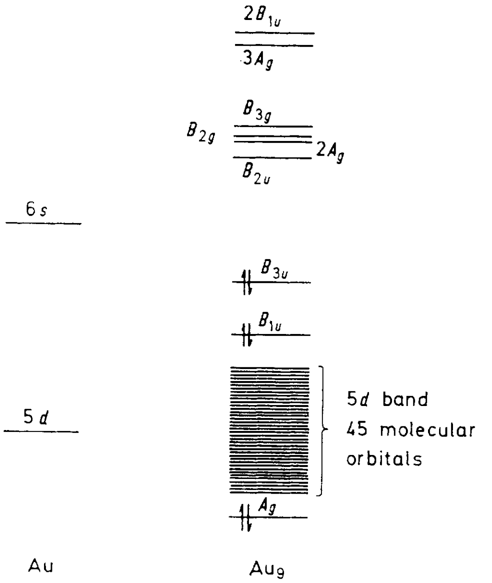

FIGURE 6

The dominant role of the gold 6*s* orbitals in the 'bare' gold clusters suggests a simpler and computationally much less demanding Hückel m.o. model. As the 6*s* orbitals have no directional overlap preferences, and the 6*s*–6*s* overlaps for non-adjacent gold atoms are negligible (0.01), Hückel resonance integrals for bonded gold atoms may be set equal to β and those for non-bonded gold atoms may be neglected.[35] The result of such a Hückel calculation on the centred $[\mathrm{Au}_9]^{3+}$ cluster, (I), is shown in Figure 7. The m.o. level orderings and the magnitudes of the splittings closely follow those obtained from the more sophisticated extended-Hückel calculation (Figure 6). Figure 7 also shows the results of the Hückel calculation for the uncentred gold cluster $[\mathrm{Au}_8\mathrm{L}_8]^{2+}$ with the same polyhedral geometry. A comparison of the two calculations gives a clear illustration of the stabilising effect of the central atom. The A_g molecular orbital is in fact stabilised to such a large extent that its energy is depressed to below that of the 5*d* band (Figure 6). In general, the degree of extra stabilisation introduced by the central atom will reflect its co-ordination number, the higher the co-ordination number the larger the number of positive resonance-energy terms. Similarly the contribution to the total energy made by the bonding between peripheral gold atoms will depend on the number of adjacent bonded gold atoms; this stabilisation will be greatest for closed polyhedra with triangular faces.[36,37] However, if the polyhedron has less than 12 metal atoms, the hole at the centre of the closed polyhedron is not sufficiently large to accommodate a similar atom. For the smaller $[\mathrm{Au}_9(\mathrm{PPh}_3)_8]^{3+}$ cluster, a suitable compromise is obtained by utilising a part of the icosahedron, which has triangular faces, rather than the closed dodecahedron which has too small a central cavity.[38]

A Hückel m.o. calculation for a hypothetical centred dodecahedral cluster suggests that the *s* orbitals combine to form four bonding and five antibonding molecular orbitals. A closed-shell electronic configuration for this geometry therefore requires an additional electron pair. The disparate electronic requirements for (I) and the dodecahedron will discourage a distortion of the D_{2h} polyhedron (I) towards the dodecahedron. A carbido-centred cluster such as $[\mathrm{Au}_8\mathrm{C}(\mathrm{PPh}_3)_8]^{4+}$ would satisfy the electronic and steric requirements for a dodecahedral gold geometry.

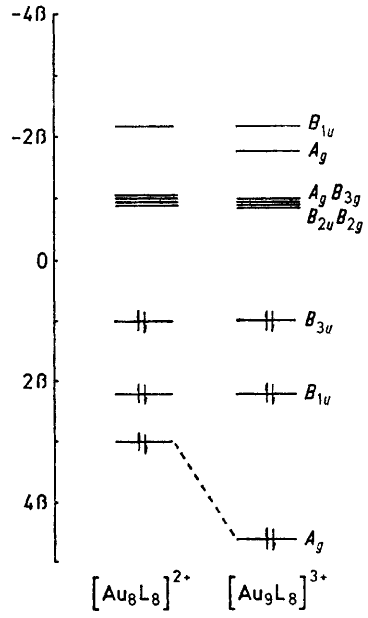

FIGURE 7

A similar calculation for the $[\mathrm{Au}_{11}]^{3+}$ cluster based on the idealised C_{3v} geometry (II) leads to the m.o. correlation diagram in Figure 8. For this geometry the

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[35] F. A. Cotton, 'Chemical Applications of Group Theory,' 2nd edn., Wiley, New York, 1971.

[36] R. B. King, *J. Amer. Chem. Soc.*, 1970, **92**, 6460.

[37] R. B. King, *Progr. Inorg. Chem.*, 1971, **15**, 287.

[38] S. J. Lippard, *Progr. Inorg. Chem.*, 1967, **8**, 109.

118 valence electrons can be assigned to the *5d* band orbitals and all the bonding *6s* molecular orbitals, to give the closed-shell electronic ground-state configuration . . . $[A_1]^2[5d\ \text{band}]^{110}[E]^4[A_1]^2$, $^1A_1$. The polyhedron shown in (II) does not have triangular faces exclusively, and therefore the peripheral gold–gold interactions are not maximised. The bicapped square antiprism does satisfy this requirement but it has a less satisfactory central cavity. A Hückel calculation for a hypothetical centred D_{4d} bicapped square antiprism has shown that it also has four bonding and seven antibonding molecular orbitals and a slightly larger total stabilisation energy. The idealised polyhedron (II) might therefore be expected to show distortions towards a bicapped square-antiprismatic geometry and these are indeed observed. Bellon *et al.*[9,11] have discussed the nature of these distortions in some detail. In the clusters $[Au_9(PPh_3)_8]^{3+}$,[10] $[Au_{11}I_3(PR_3)_7]$, and $[Au_{11}(PPh_3)_7(SCN)_3]$[9] the peripheral gold–gold distances (2.75—3.18 Å) are consistently longer than the radial gold–gold distances (2.60—2.73 Å). These bond-length differences presumably reflect the relative importance of the peripheral- and radial-bonding components discussed above.

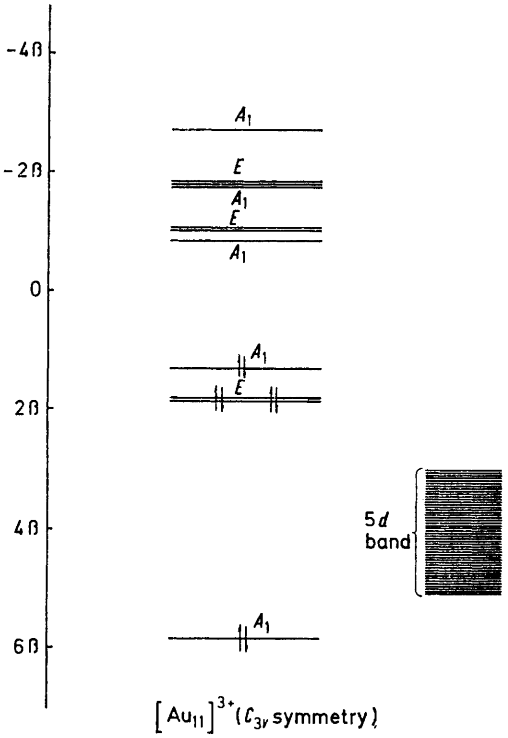

FIGURE 8

The fact that both (I) and (II) may be derived from a centred icosahedron leads naturally to an investigation of the electronic requirements for stabilising the parent compound. A Hückel m.o. calculation on this cluster geometry has shown that the 6*s* orbitals combine to form four bonding and nine antibonding molecular orbitals (see Figure 9). A stable closed-shell electronic configuration for this closed symmetrical cluster would be satisfied therefore by an $[Au_{13}]^{5+}$ ion. Accommodating such a high positive charge on the cluster could prove to be problematical unless it is complexed with some very good electron-donating ligands. Additional calculations have shown that the icosahedron would produce a greater stabilisation energy than the alternative bicapped pentagonal prism, cube octahedron, and truncated tetrahedron polyhedra.

The calculated charge distributions in the $[Au_9]^{3+}$ and $[Au_{11}]^{3+}$ centred clusters are given in Table 3. For the $[Au_9]^{3+}$ cluster the close agreement obtained for the Hückel and extended-Hückel calculations is very satisfactory. For both clusters the highest positive charge is associated with the central atom. Unfortunately, there have not been any *X*-ray photoelectron or Mössbauer studies on these complexes which would test the validity of the calculated charge distributions. It is interesting to note, however, that ^{13}C n.m.r. studies on carbido-centred clusters have indicated that the central carbon atom bears quite a large positive charge.[39] The peripheral gold atoms in the gold clusters show a large variation in build up of calculated positive charge, especially in the $[Au_{11}]^{3+}$ cluster. These charges will of course be reduced when the bare cluster is complexed to PPh_3 or halide ligands. It is significant that in the $[Au_{11}I_3(PPh_3)_7]$ complex the negatively charged ligands co-ordinate to the most positively charged peripheral gold atoms [3 in Table 3, and Figure 5 (II)].

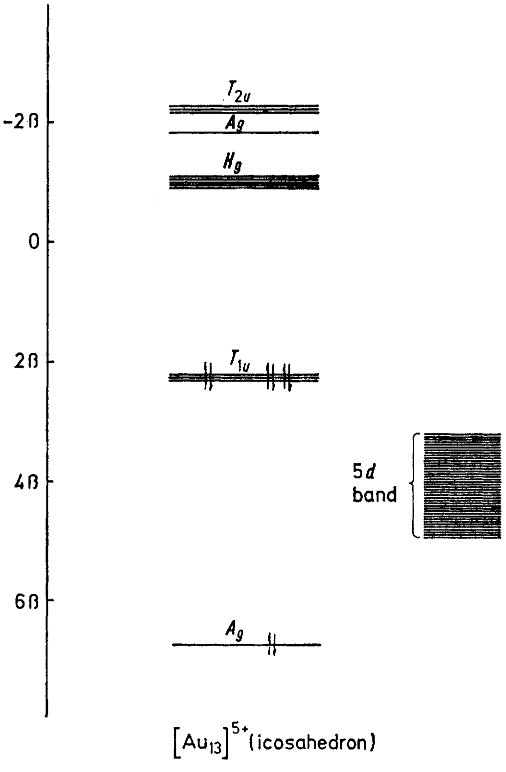

FIGURE 9

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

In clusters such as $[Au_{11}(PPh_3)_7X_3]$ the presence of adjacent metal atoms with different charges could have important catalytic implications and I would encourage a more systematic study of the chemical properties of these compounds.

TABLE 3

Calculated charge distributions in the $[Au_9]^{3+}$ and $[Au_{11}]^{3+}$ clusters

	$[Au_9]^{3+}$			$[Au_{11}]^{3+}$
	Extended Hückel	Hückel		Hückel
Central Au	0.46	0.47	Central Au	0.53
Au(1) *	0.21	0.18	Au(1)	0.04
Au(2)	0.42	0.46	Au(2)	0.21
			Au(3)	0.32
			Au(4)	0.27

* See (I) and (II) (Figure 5) for the numbering scheme used to distinguish gold atoms which are not symmetry related.

Conclusions.—The centred gold clusters owe their stability to the simultaneous formation of metal–metal bonds on the periphery of the polyhedron and to somewhat stronger radial interactions between the peripheral atoms and the atom at the centre of the polyhedron. Phosphine ligands co-ordinated to the vertices of the polyhedron play an important role in stabilising the cluster by encouraging a more favourable hybridisation of the gold valence orbitals. Other workers have drawn attention to the possible importance of radial [7,26,27] and surface-bonding effects [11,12] in these clusters, but have not emphasised the importance of both factors occurring concomitantly. In order to draw attention to the dual roles of the peripheral atoms, it may be useful to describe these gold compounds and the related carbidometal carbonyl compounds as co-ordination-cluster compounds.*

The Skeletal Electron Pair Theory approach has been shown to be inappropriate for these compounds because the gold valence orbitals do not generate a set of strongly bonding molecular orbitals which are tangential to the polyhedral surface. This arises largely from the very poor $6p_\pi$–$6p_\pi$ overlaps for gold atoms separated by 2.8—3.0 Å and the large $6s \rightarrow 6p$ promotion energy. The molecular orbitals of the isolated clusters can be faithfully reproduced using a simple Hückel model which uses the 6*s* orbitals of gold as a basis set and which neglects non-nearest-neighbour interactions. This model should serve as a useful basis for rationalising the electronic structures of other gold triphenylphosphine cluster compounds which will be synthesised in the future, and for giving a reliable indication of the charge distributions in these complexes.

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* R. B. King (ref. 37) has suggested the name porcupine compounds for the gold clusters discussed in this paper.