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Preliminary communication

BONDING IN CONDENSED POLYHEDRAL CLUSTER COMPOUNDS OF PLATINUM

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Summary

The structures of condensed platinum cluster compounds containing tertiary phosphine ligands have been rationalised using the cluster condensation generalisation derived from molecular orbital calculations.

Recently we proposed a general methodology for evaluating the number of cluster valence molecular orbitals in low symmetry metal carbonyl clusters generated from the condensation of triangular, tetrahedral and deltahedral metal cluster fragments [1]. The fundamental condensation modes considered are

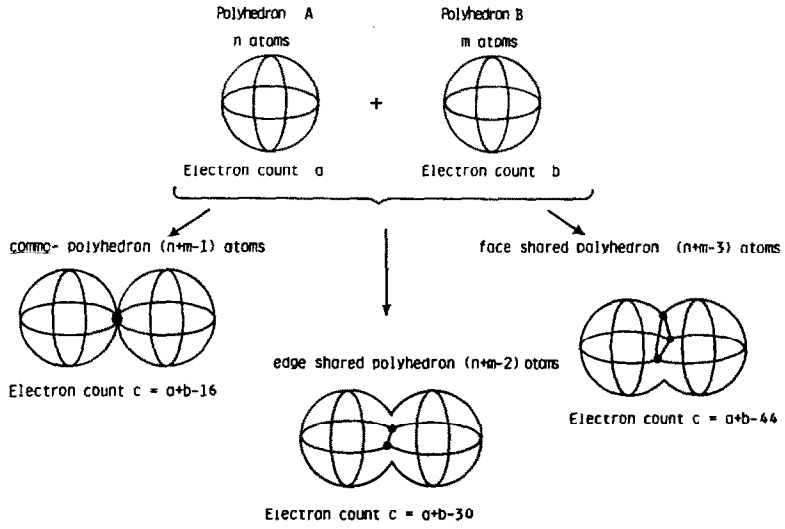

Fig. 1. Summary of condensation generalisation for platinum clusters.

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those illustrated in Fig. 1, and the results of a molecular orbital analysis which we have completed suggested the following generalisation:

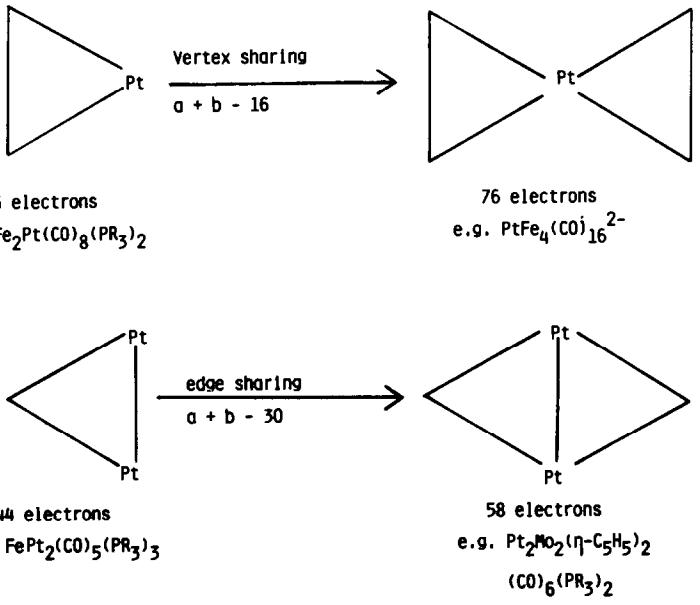
The total electron count in a condensed polyhedron C is equal to the sum of the characteristic electron counts for the parent polyhedra A and B minus the electron count characteristic of the atom, pair of atoms or face of atoms common to both polyhedra.

For metals which utilise all nine valence orbitals for bonding the electron counts summarised on the left hand side of Table 1 are characteristic.

However, for many platinum metal clusters, and particularly those containing tertiary phosphines the number of cluster valence molecular orbitals is determined by the utilisation of only eight valence orbitals and the Table summarises the relevant electron counts for these clusters derived from molecular orbital calculations [2].

Utilising these characteristic electron counts and the condensation generalisation it is a simple matter to account for the number of bonding cluster valence molecular orbitals in the condensed platinum clusters illustrated in Fig. 2 [3]. Particularly impressive is the way in which the generalisation accounts for the bonding in these clusters even though many have low symmetries and high nuclearities.

The methodology can also be extended to mixed metal clusters where the condensation processes occur through platinum atoms as the following examples illustrate:



It is a simple matter to extend these processes to describe the bonding in complex mixed metal raft clusters such as $[Pt_3Fe_3(CO)_{15}]^{2-}$ [4].

For condensed mixed metal clusters where the condensation occurs through metal atoms which utilise nine valence orbitals then the electron counts on the left hand side of the Table are utilised, as the example on top of p. C16 illustrates.

TABLE 1

SUMMARY OF CHARACTERISTIC ELECTRON COUNTS FOR METAL CLUSTER COMPOUNDS

	Metals which utilise 9 valence orbitals	Metals which utilise 8 valence orbitals
Mononuclear	18	16
Binuclear	34	30
Triangular	48	44
Tetrahedral	60	56[a]
Trigonal bipyramidal	72	68[a]

[a] For these clusters the electron count depends on the conformation of the ML_2 fragments, that shown represents the electron count for the more stable conformer.

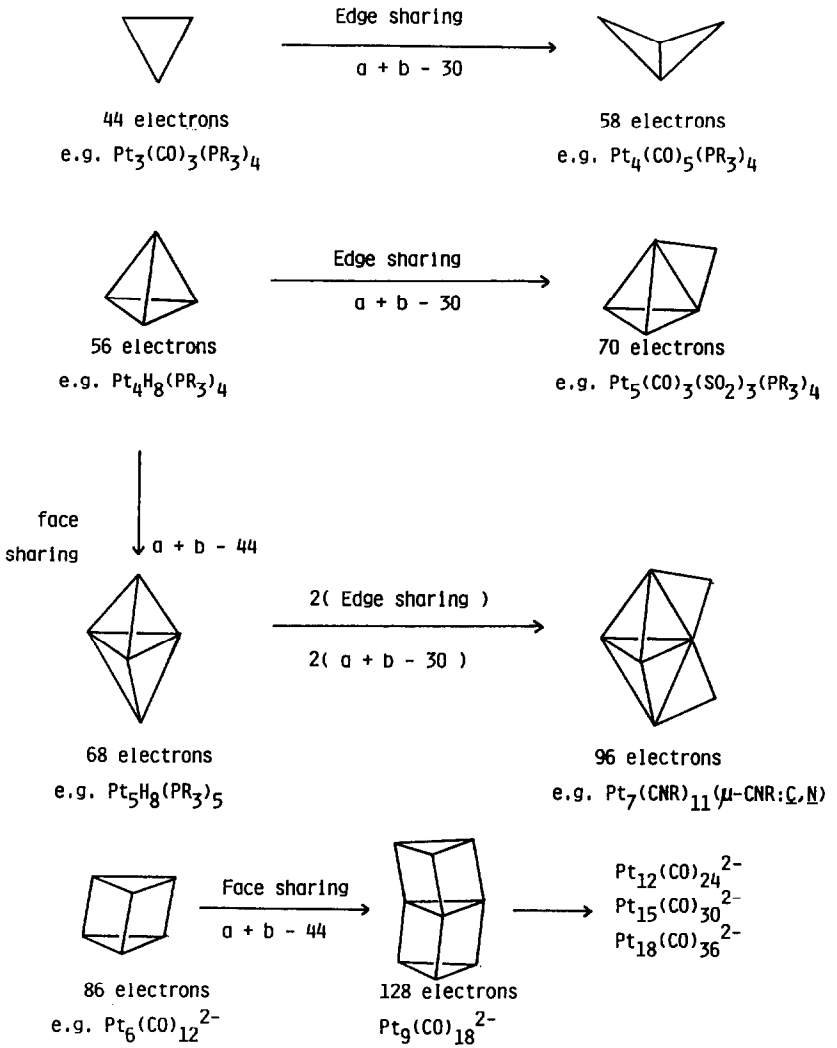
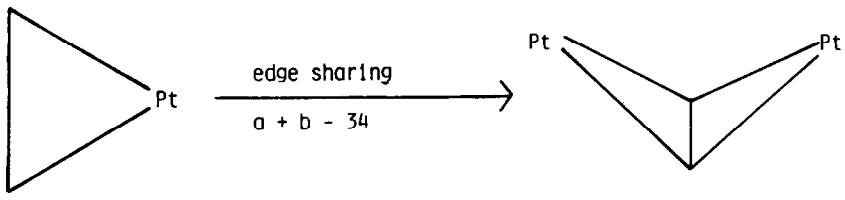


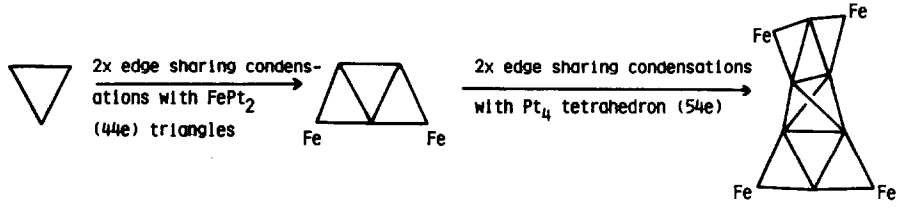
Fig. 2. Illustrations of the application of the condensation generalisation to platinum clusters.



46 electrons
e.g. $Fe_2Pt(CO)_8(PR_3)_2$

58 electrons
e.g. $Fe_2Pt_2H_2(CO)_8(PR_3)_2$

The bonding descriptions given above have been derived without considering the alternative conformational possibilities open to $[PtL_2]_x$ clusters [2], because the occurrence of bridging carbonyl ligands effectively diminishes the importance of these conformational differences. The only example which we have encountered where the conformational aspect is significant is $[Pt_6Fe_4(CO)_{22}]^{2-}$ [4]. In this instance the generally less favoured longitudinal conformation [2] is imposed by the Fe_2Pt bridging fragments and therefore the central tetrahedral fragment is characterised by 54 rather the more usual 56 valence electrons characteristic of the latitudinal conformation (see below).



44 electrons
e.g. $Pt_3(CO)_6^{2-}$

72 electrons

138 electrons
e.g. $Fe_4Pt_6(CO)_{22}^{2-}$

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References

1 D.M.P. Mingos, J. Chem. Soc., Chem. Commun., in press.
2 D.G. Evans and D.M.P. Mingos, J. Organomet. Chem., 240 (1982) 321.
3 For recent reviews dealing with the structures of platinum cluster compounds see: F.G.A. Stone, Inorg. Chim. Acta, 50 (1981) 33; D.A. Roberts and G.L. Geoffroy, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Chapter 40, Pergamon, Oxford, 1982.
4 G. Longoni, M. Manasserro and M. Sansoni, J. Am. Chem. Soc., 102 (1980) 7973.