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POLYHEDRAL SKELETAL ELECTRON PAIR THEORY: ITS EXTENSION TO NON-CONICAL ML_2 FRAGMENTS

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Summary

Molecular orbital calculations on platinum metal tertiary phosphine cluster compounds have indicated how they may be encompassed within the framework of the polyhedral skeletal electron pair theory.

In many cluster compounds of the transition metals it has proved possible to relate the geometry of the cluster to the number of skeletal electron pairs required to fill all the bonding metal–metal molecular orbitals [1]. The complex of ideas, which has been collectively described as the polyhedral skeletal electron pair theory [2], has proved particularly useful for describing the structures of clusters based on conical $M(CO)_3$ and $M(\eta\text{-}C_5H_5)$ fragments, because of the isolobal nature of these fragments and main group fragments such as B–H [3]. This approach has however proved to have very limited applicability for cluster compounds of palladium, platinum and gold. This deficiency has been noted widely and attributed in the most general terms either to the fact that these metals do not conform to the 18 electron rule, or to the large *d–p* promotion energies of these metals in their atomic states [4], but firm recommendations for predicting structures in this rapidly growing area of cluster chemistry [5] have not been proposed. Molecular orbital calculations which we have completed [6] have suggested that the electronic structures can be interpreted in terms of the bonding capabilities of the angular $Pt(PH_3)_2$ fragment.

A comparison of the frontier molecular orbitals of $M(CO)_3$ and $Pt(PH_3)_2$ fragments [7] (see Fig. 1) shows that although both fragments have similar Hy(s–z) and Hy(xz) outpointing hybrid orbitals suitable for skeletal bonding, the Hy(yz) orbital of $M(CO)_3$ is replaced by a lower lying d_{yz} and a much higher lying p_y orbital in the $Pt(PH_3)_2$ fragment. The overlap between d_{yz} orbitals on adjacent platinum atoms is too small to make a significant contribution to the total metal–metal bonding, but the overlap between p_y orbitals on adjacent metal atoms is large. Therefore the Hy(s–z), Hy(xz) and p_y orbitals of the $Pt(PH_3)_2$ fragments have the potential to form radial and tangential MO's which are entirely equivalent to those formed by $M(CO)_3$ fragments in an analogous polyhedral cluster. However the

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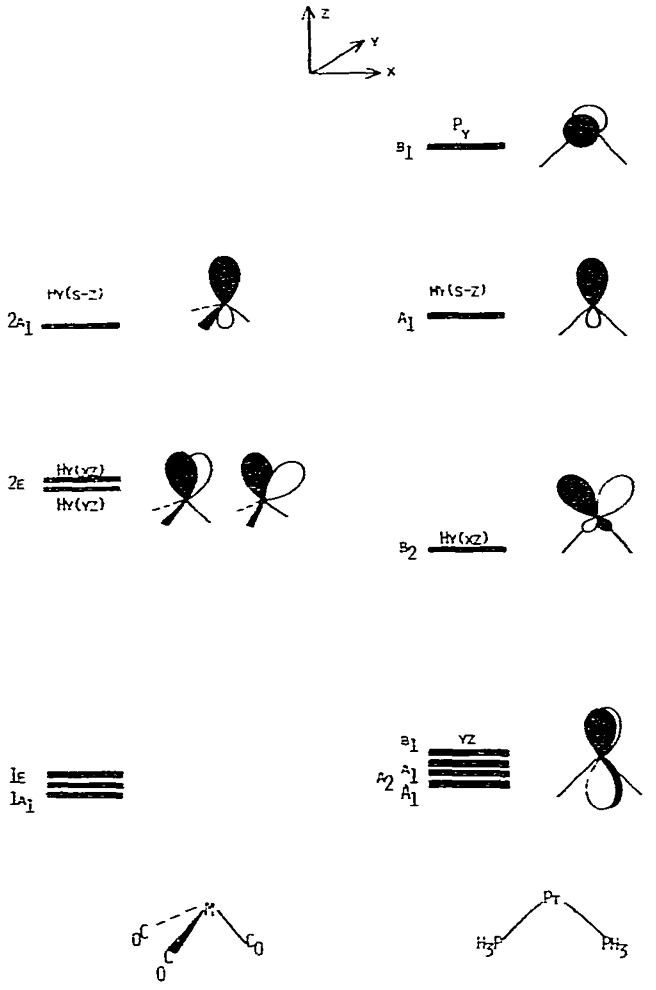


Fig. 1. A comparison of the frontier molecular orbitals of $Pt(PH_3)_2$ and $M(CO)_3$.

bonding molecular orbitals which are derived from the p_y orbitals are not sufficiently stable for electron occupation (see Fig. 2). Consequently, the bonding in platinum clusters is dominated by the symmetries and energies of the skeletal molecular orbitals formed from the Hy(s–z) and Hy(xz) frontier orbitals. The latter depend markedly on the conformations adopted by the PtL_2 fragments relative to the principal axis of the polyhedron. Consideration of the latitudinal and longitudinal conformers illustrated in Fig. 2 leads to a considerable simplification of the quantum mechanical problem since it permits the application of first order perturbation theory arguments to the recently published surface π-orbitals of metal polyhedra [8,9]. Full details of our analysis will be presented elsewhere and only the more important conclusions for $[Pt(PH_3)_2]_n$ ($n = 3$–5) will be summarised here.

The symmetry transformation properties of the π-surface skeletal molecular orbitals for the latitudinal and longitudinal conformers when added together match those of the π-surface molecular orbitals of an isostructural $[M(CO)_3]_n$ cluster. For example, the π-surface molecular orbitals of a triangular cluster are in order of increasing energy E', A''_2, E'', and A'_2 [8,9] which represent the sum of the bonding and antibonding skeletal molecular orbitals derived from Hy(xz) for the latitudinal (E' and A'_2) and longitudinal (A''_2 and E'') conformers (see Fig. 2). The skeletal MO's for tetrahedral and trigonal bipyramidal clusters shown in this Figure are amenable to a similar type of analysis.

The unequal number of bonding and non-bonding molecular orbitals derived from Hy(xz) for the two conformers shown in Fig. 2 implies that the total electron count resulting from the occupation of these levels will vary in the following manner:

Triangular	$Pt_3(PH_3)_6$	latitudinal	- 42 electrons;	longitudinal	- 40 electrons
Tetrahedral	$Pt_4(PH_3)_8$	latitudinal	- 56 electrons;	longitudinal	- 54 electrons
Trigonal Bipyramidal	$Pt_5(PH_3)_{10}$	latitudinal	- 66 electrons;	longitudinal	- 68 electrons

The calculations demonstrate that the more stable conformer is that which has the larger number of bonding and non-bonding skeletal molecular orbitals derived from Hy(xz), i.e. latitudinal for Pt_3 and Pt_4 and longitudinal for Pt_5 (see Fig. 2). Typical computed energy differences separating the two conformers are: 1.1 eV for $Pt_3(PH_3)_6$, 2.1 eV for $Pt_4(PH_3)_8$ and 0.4 eV for $Pt_5(PH_3)_{10}{}^{2-}$. These differences originate in part from the larger σ-component to overlap integrals between Hy(xz) orbitals of $Pt(PH_3)_2$ fragments which are coplanar. The large energy difference for the tetrahedral cluster also reflects the substantial steric repulsions generated between phosphine ligands in the longitudinal conformer. Recent X-ray crystallographic studies on $Pt_3H_3(PR_3)_3(\mu\text{-}H)_3$ and $Pt_4H_4(PR_3)_4(\mu\text{-}H)_4$ have suggested that these complexes have geometries close to the latitudinal geometries predicted by the calculations, although unambiguous confirmation will require additional neutron diffraction experiments [10]. Our calculations also indicate a further complication introduced by the bridging hydrido-ligands in the former compound, which interact primarily with the Hy(xz) orbitals of the $Pt(PH_3)H$ fragments. Such interactions are maximised when the bond angle made between two bridging hydrido-ligands and the metal approximates to 90°. The attainment of this bond angle requires some rotation of the $Pt(PH_3)H$ fragments about the Pt-cluster centroid vector. Small rotations of this kind are discernable in the crystal structure of $Pt_3H_3(PR_3)_3(\mu_2\text{-}H)_3$, and are more pronounced in the isoelectronic rhodium cluster compound $Rh_3(P(OMe)_3)_6(\mu_2\text{-}H)_3$ [5], where the steric requirements of the terminal ligands are more demanding.

For clusters based on the triangle the more stable latitudinal conformer has six fewer electrons than that anticipated by analogy with $Os_3(CO)_{12}$ [11], and the more stable conformers of the tetrahedral and trigonal bipyramidal clusters have four fewer electrons than that predicted by the polyhedral skeletal electron pair approach. This conclusion is supported by the following examples of cluster compounds from the recent literature [5,10]:

Triangular	$Os_3(CO)_{12}$	48 valence electrons	$Pt_3H_6(PR_3)_3$ $Rh_3H_3(PR_3)_6$	42 valence electrons
Tetrahedral	$Ir_4(CO)_{12}$	60 valence electrons	$Pt_4H_8(PR_3)_4$ $Rh_4H_4(PR_3)_8$	56 valence electrons

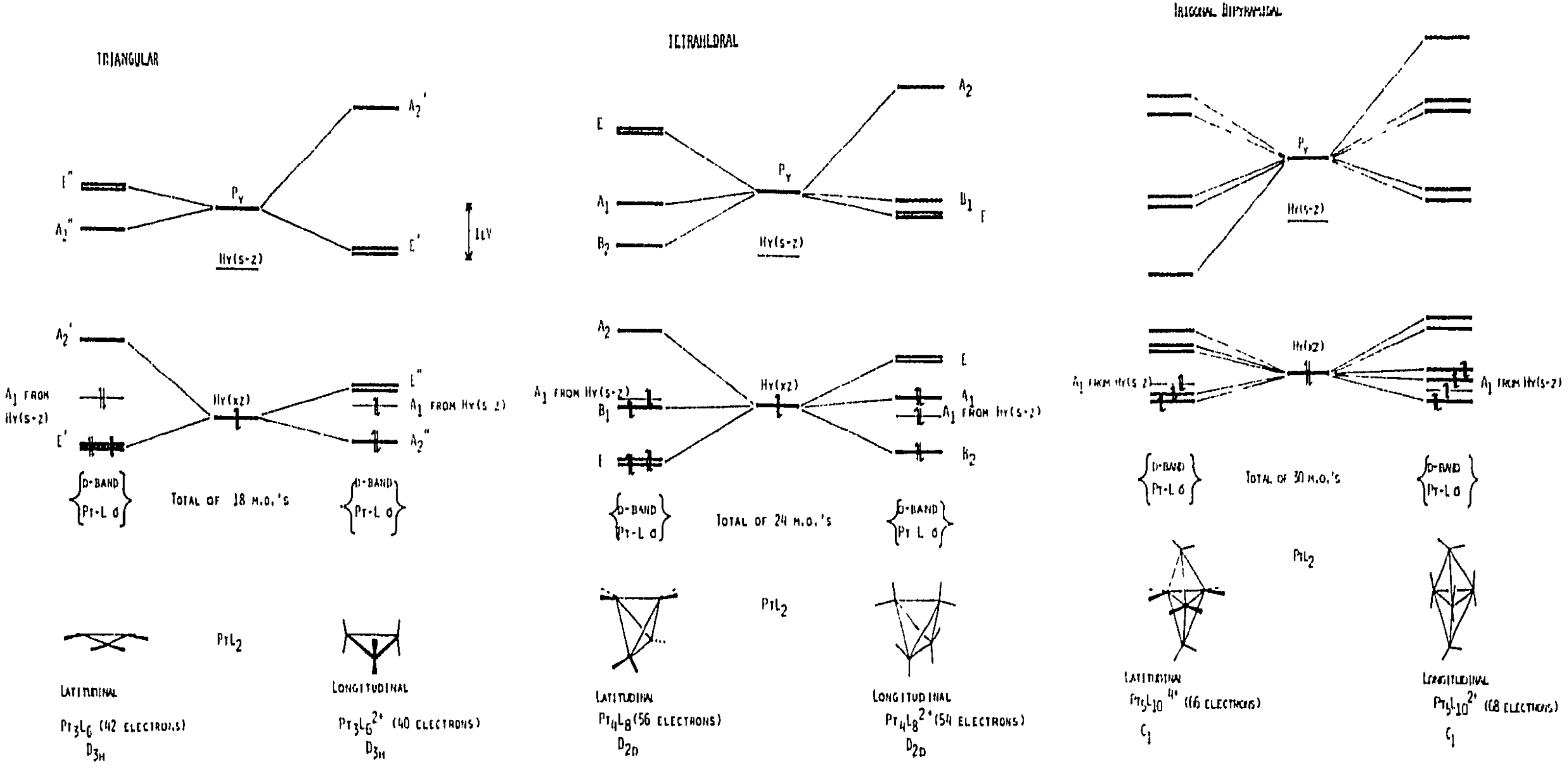


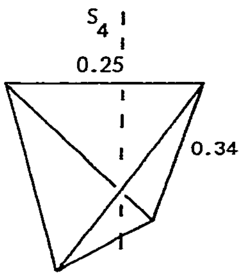
Fig. 2. Schematic representation of the skeletal molecular orbitals for latitudinal and longitudinal conformers of Pt_nL_{2n}, where L = PH_3. Particularly noteworthy is the complementary nature of the surface π-molecular orbitals for the alternative conformers. When taken together the molecular orbitals derived from Hy(*xz*) for the two conformers correspond to the analogous molecular orbitals derived for an isostructural polyhedron with conical fragments at the vertices.

Trigonal bipyramidal	$Os_5H(CO)_{15}^-$	72 valence electrons	$Pt_5H_8(PR_3)_5$	68 valence electrons

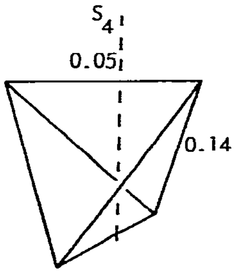
If these electron counts are exceeded then the additional electron pairs have by necessity to occupy antibonding skeletal molecular orbitals derived from the Hy(*xz*) orbitals of the $Pt(PH_3)_2$ fragments, unless there are alternative low lying molecular orbitals derived from the π^* orbitals of the terminal and bridging ligands. The latter situation has been discussed in the context of $Pt_3(CO)_6^{2-}$ (44 valence electrons) by several workers [12]. Occupation of antibonding skeletal molecular orbitals derived from Hy(*xz*) molecular orbitals leads to analogous distortional modes to those which have been noted previously for compounds which conform to the polyhedral skeletal electron pair theory. Consequently, these lower symmetry polyhedral entities maintain the same relationships as noted above, i.e. six electrons fewer for triatomic clusters and four electrons fewer for tetra- and penta-atomic clusters. The following compounds illustrate this general principle:

Open triangle	$Os_3(CO)_{12}I_2$	50 valence electrons	$Pt_3Ph(PPh_3)_2(PPh_2)_3$	44 valence electrons
Butterfly	$Os_4H_3I(CO)_{12}$	62 valence electrons	$Pt_4(CO)_5(PR_3)_4$	58 valence electrons
Edge bridged tetrahedron	$Os_5H_2(CO)_{16}$	74 valence electrons	$Pt_5(CO)_6(PR_3)_4$	70 valence electrons

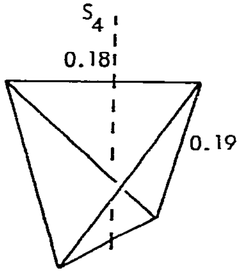
Besides accounting for the total electron count in cluster compounds of the platinum metals the molecular orbital calculations which we have completed can also account for subtler aspects of their structures. For example, the computed Mulliken overlap populations for the latitudinal conformers of $Pt_4(PH_3)_4H_4^{4-}$, $Pt_4(PH_3)_4H_4(\mu_3\text{-}H)_4$ and $Pt_4(PH_3)_4H_4(\mu_2\text{-}H)_4$ which are reproduced below suggest a substantial asymmetry in the strengths of the metal–metal bonds, particularly for the first two compounds.



$Pt_4(PH_3)_4H_4^{4-}$

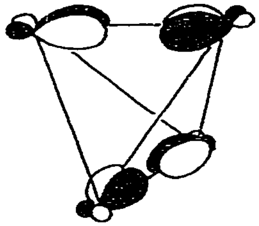


$Pt_4(PH_3)_4H_4(\mu_3\text{-}H)_4$



$Pt_4(PH_3)_4H_4(\mu_2\text{-}H)_4$

This asymmetry can be attributed to the loss of spherical symmetry in the surface molecular orbitals which results from the fact that the $Pt(PH_3)H$ fragment presents only a single Hy(*xz*) orbital for tangential cluster bonding. Indeed the nodal characteristics of the highest lying $1B_1$ molecular orbital derived from Hy(*xz*) and illustrated below are such that it is antibonding along the Pt_4 bonds bisected by the S_4 axis. In the μ_3 hydrido-cluster the asymmetry is more pronounced because this molecular orbital retains its metal character, whereas the low lying A_1 and E orbitals derived from Hy(*xz*) interact with the face bridging hydrogens and become more delocalised. X-ray crystallographic studies on tetranuclear 56 electron platinum and rhodium clusters have confirmed the occurrence of large asymmetries in the metal–metal bond lengths in the directions indicated by the overlap populations



above [5,10]. Furthermore, the calculations clearly favour the triply bridged hydrido-structure. This bridging mode has been demonstrated for $Rh_4(\mu\text{-}H)_4(COD)_4$ [13], and the calculations suggest that this is also the preferred geometry for $Pt_4(\mu\text{-}H)_4H_4(PPr_2{}^iPh)_4$ [10] where the hydrido-ligands have not been located by X-ray techniques.

For mixed metal clusters which contain both $M(CO)_3$ fragments and $Pt(PR_3)_2$ fragments the total electron count depends markedly on the number of platinum atoms but lies within the limits set out above for the homonuclear situations. The following compounds illustrate the gradation in total electron count for tetrahedral clusters: $Ir_4(CO)_{12}$ (60 electrons), $Os_3PtH_2(CO)_{10}(PR_3)$ (58 electrons), and $Pt_4H_8(PR_3)_4$ (56 electrons) and for the butterfly clusters: $Os_4H_3I(CO)_{12}$ (62 electrons), $Os_3PtH_2(CO)_{10}(PR_3)_2$ (60 electrons), $Os_2Pt_2H_2(CO)_8(PR_3)_2$ (58 electrons) and $Pt_4(CO)_5(PR_3)_4$ (58 electrons) [11,14]. For triangular clusters the replacement of $Pt(PR_3)_2$ groups by isolobal fragments derived from $Fe(CO)_4$ [4] leads to a more regular change in the total number of valence electrons since the number of bonding skeletal molecular orbitals (three) remains constant. This is illustrated by the series $Fe_3(CO)_{12}$ (48 electrons), $Fe_2Pt(CO)_8(PR_3)_2$ (46 electrons), $FePt_2(CO)_5(PR_3)_3$ (44 electrons) and $Pt_3H_6(PR_3)_3$ (42 electrons) [11,14].

Acknowledgment

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References

1 K.M. Thomas, R. Mason and D.M.P. Mingos, J. Amer. Chem. Soc., 95 (1973) 3802; D.M.P. Mingos and M.I. Forsyth, J. Chem. Soc. Dalton Trans., (1977) 610.

2 K. Wade in B.F.G. Johnson (Ed.), Transition Metal Clusters, J. Wiley (Chichester), 1980, p 193; D.M.P. Mingos, Nature (London) Phys. Sci., 236 (1972) 99.

3 M. Elian, M.M.L. Chen, R. Hoffmann and D.M.P. Mingos, Inorg. Chem., 15 (1976) 1148; D.M.P. Mingos, Adv. Organometal. Chem., 15 (1977) 1.

4 F.G.A. Stone, Inorg. Chim. Acta, 50 (1981) 33; B.F.G. Johnson and J. Lewis, Adv. Inorg. Radiochem., 24 (1981) 225.

5 R.K. Brown, J.M. Williams, A.J. Sivak and E.L. Muetterties, Inorg. Chem., 19 (1980) 370; M.D. Fryzuk, Organometallics, 1 (1982) 408.

6 Details of the type of calculation employed and the relevant parameters are to be found in D.M.P. Mingos, J. Chem. Soc. Dalton Trans., (1977) 602.

7 D.M.P. Mingos, J. Chem. Soc. Dalton Trans., (1977) 602; M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.

8 A.J. Stone, Inorg. Chem., 20 (1981) 563.
9 A.J. Stone, Mol. Phys., 41 (1980) 1339.
10 D. Gregson, J.A.K. Howard, M. Murray and J.L. Spencer, J. Chem. Soc. Chem. Commun., (1981) 716; P.W. Frost, J.A.K. Howard, J.L. Spencer and D.G. Turner, ibid., (1981) 1104.
11 P.R. Raithby, in B.F.G. Johnson (Ed.), Transition Metal Clusters, J. Wiley (Chichester) 1980, p 5.
12 J.W. Lauher, J. Amer. Chem. Soc., 100 (1978) 5305; J. Evans, J. Chem. Soc. Dalton Trans., (1980) 1005; D.G. Evans, G.R. Hughes, D.M.P. Mingos, J.M. Basset and A.J. Welch, J. Chem. Soc. Chem. Commun., (1980) 1255.
13 M. Kulzick, R.T. Price and E.L. Muetterties, Organometallics, in press.
14 A. Dedieu and R. Hoffmann, J. Amer. Chem. Soc., 100 (1978) 2074, and B.E.R. Schilling and R. Hoffmann, J. Amer. Chem. Soc., 101 (1979) 3456 give a discussion of the bonding in binuclear and hetero-nuclear complexes derived from PtL_2.