Journal of Organometallic Chemistry, 352 (1988) 397–413
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Molecular orbital analysis of the bonding in some triangular platinum clusters with 42 to 48 valence electrons

David G. Evans

Department of Chemistry, University of Exeter, Stocker Road, Exeter, EX4 4QD (Great Britain)

(Received March 17th, 1988)

Abstract

The electronic and structural features of triangular platinum clusters have been analysed by Extended Hückel molecular orbital calculations. The prevalence of planar triangular clusters with a 42 electron count is rationalised, and the way in which the cluster bonding orbitals are markedly stabilised by edge-bridging ligands is discussed in terms of a general model. In such clusters, the metal *p* orbitals play a minor role, but the calculations indicate how incorporation of out of plane capping carbonyl ligands induces a greater role for these *p* orbitals and facilitates the formation of clusters with electron counts of between 42 and 48. The calculations lead to a rationalisation of the way in which the synergism between ligand orbitals on opposite sides of the metal triangle determines the detailed structural features observed in a series of clusters based on the $[Pt_3(dppm)_3]$ core, recently reported by Puddephatt.

Introduction

In recent years the cluster chemistry of low-valent platinum has attracted considerable synthetic [1], structural [2] and spectroscopic [3] interest, and has been the subject of a comprehensive review [4]. The majority of reported clusters contain both carbonyl and tertiary phosphine ligands, although many high nuclearity homoleptic carbonyl clusters have been structurally characterised [5], as have a number of smaller clusters containing isocyanide [6] or hydride ligands [7]. The common structural feature of these clusters is the Pt_3 triangular unit, since the structures of the larger clusters may be derived by the fusion of these triangles [4]. We have outlined the theoretical basis of this polyhedral fusion process elsewhere [8].

There have been a number of other papers in the literature that have discussed the electronic structure of various platinum clusters. Triangular clusters of the type $[Pt_3(CO)_6]^{2-}$ have been analysed by Evans [9] and Woolley [10], and the way in which such units may be combined to form stacked 'tinker-toy' clusters has been

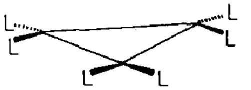
0022-328X/88/$03.50

elegantly formulated by Hoffmann et al. [11]. Mealli [12] has shown how the bonding molecular orbitals in clusters of the type $[Pt_3L_6]$ are stabilised by bridging ligands and we [13,14] have analysed the bonding in a series of platinum phosphine hydride clusters [7] and rationalised the observed cluster electron counts and conformational preferences exhibited by the ligands.

The majority of known triplatinum clusters are of the type $[Pt_3L_6]$. Examples are $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$ [15], $[Pt_3(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu\text{-}SO_2)(PPh_3)_3]$ [17] amongst others [4]. In each case the Pt_3 triangle is approximately equilateral with the Pt–Pt distances in the range 2.6–2.75 Å, corresponding to a single bond. The polyhedral electron count in such species is 42. A minority of triplatinum clusters with a 44 electron count are known however. In the species $[Pt_3(\mu\text{-}CO)_3(CO)_3]^{2-}$ [18] and $[Pt_3(\mu\text{-}CO)_3(PCy_3)_4]$ [19] the additional electron pair is accommodated without a disruption of the pseudo-equilateral metal framework. The 44 electron cluster $[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$ [20] has an isosceles triangle of metals, however, with two Pt–Pt distances of 2.79 Å and the third, at 3.63 Å, corresponding to a non-bonding interaction [11].

In terms of the polyhedral skeletal electron pair approach [21], transition metal carbonyl ring clusters with n vertices should be characterised by $16n$ electrons. Thus $[Os_3(CO)_{12}]$ with 48 electrons has an equilateral triangle of metals [22]. Replacement of the $Os(CO)_4$ fragments with PtL_2, their isolobal analogues, leads to a decrease in valence electron count of two per fragment [13], accounting for the observed electron count of the majority of $[Pt_3L_6]$ clusters. It is the purpose of this paper to explore the way in which triplatinum clusters can adopt electron counts between 42 and 48 by incorporation of additional ligands. It can be anticipated that such species might be relevant as potential intermediates in a catalytic cycle [23]. We begin, however, with a discussion of the parent $[Pt_3L_6]$ clusters. Our analysis is based on elementary symmetry and perturbation theory arguments, supported by Extended Hückel [24] molecular orbital calculations, with the parameters given in the Appendix.

The electronic structure of $[Pt_3L_6]$ clusters may best be discussed in terms of the frontier orbitals of the angular C_{2v} PtL_2 fragment, which are well known [13], and illustrated in Fig. 1. The occupied set of orbitals in a d^{10} ML_2 fragment consists of four closely spaced levels of essentially metal d character together with the higher lying HOMO, which is an outpointing in plane hybrid of d_{xz} and p_x, denoted hy(xz), destabilised by an antibonding interaction with the σ-donor ligand orbitals. The unoccupied set of orbitals consists of an out-pointing hybrid of s, p_z and d_{z^2}, denoted hy(s–z), together with a higher-lying out of plane p_y orbital. As shown in Fig. 2, combination of three such PtL_2 fragments [$L = PH_3$ in this case] to form a triangular $[Pt_3L_6]$ cluster **1** with the latitudinal [13,14] conformation, generates four cluster bonding molecular orbitals. One of these is derived from hy(s–z) (S^σ in the Tensor Surface Harmonic Theory due to Stone [25]), two from hy(xz) [$P^\pi_{c,s}$] and one from p_y [P^π_0]. The latter orbital is unavailable for occupation however as a consequence of the high lying nature of the platinum $6p$ orbitals [13]. The cluster



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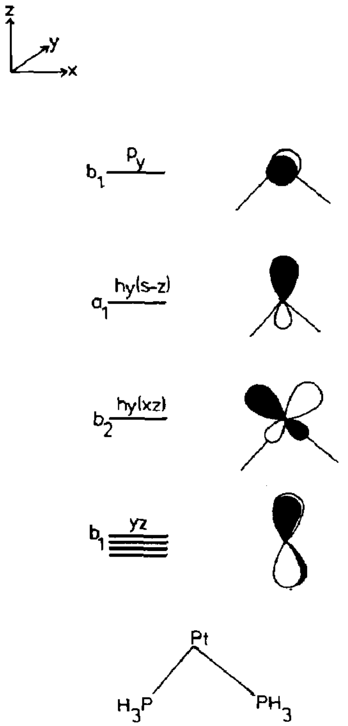


Fig. 1. The frontier orbitals of the angular $Pt(PH_3)_2$ fragment.

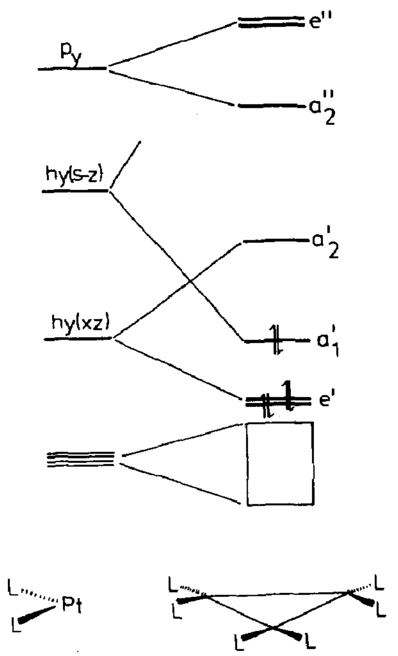
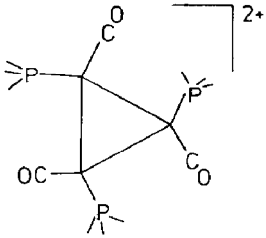


Fig. 2. The molecular orbitals of the latitudinal Pt_3L_6 cluster derived from the frontier orbitals of three PtL_2 fragments. Although there are four cluster bonding molecular orbitals, one of these (a_2'') is too high-lying to be occupied, so that there are three skeletal bonding electron pairs.

therefore has three occupied metal–metal bonding molecular orbitals and a total of 42 valence electrons.

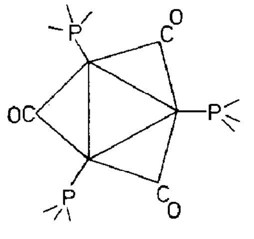
The frontier orbitals of the angular Pt(PH_3)(CO) fragment, illustrated on the left of Fig. 3 are very similar to those of the Pt(PH_3)$_2$ fragment (Fig. 2). The main difference arises from the presence of low lying π-acceptor orbitals on the carbonyl ligand. The out of plane CO $\pi^\star$ orbital mixes with the platinum p_y orbital to give two MO's of b_1 symmetry (although the symmetry of Pt(PH_3)$_2$ is C_s, the labels of C_{2v} symmetry are retained for the sake of consistency). The lower orbital is predominantly localised on the carbonyl ligands and the higher one predominantly on the metal. The MO scheme for the [$Pt_3(CO)_3(PH_3)_3$] cluster in the latitudinal conformation **2** is given in Fig. 3 and is directly analogous to that for [$Pt_3(PH_3)_6$] (see Fig. 2). The LUMO in [$Pt_3(CO)_3(PH_3)_3$] is the a'' orbital (P_0^π), derived from



(2)

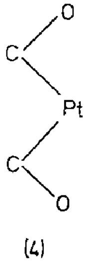
the in phase combination of the b_1 orbitals located mainly on the $\pi^\star$ orbitals of the carbonyl groups in the Pt(PH_3)(CO) fragments.

There is of course an alternative geometry for such a [$Pt_3(CO)_3(PH_3)_3$] cluster, involving bridging CO ligands as shown in **3**. The ability of CO, as opposed to



(3)

phosphine, to coordinate in this fashion is a consequence of in plane $\pi^\star$ orbitals in the former, making it effectively isolobal with the bridging methylene group. We have proposed previously [26] that the bonding in clusters such as **3** may be analysed by treating the μ-CO ligand as two one-electron donor ligands, denoted L′. Thus **3** may be considered to be derived from three T-shaped d^8 M(CO)(L′)$_2$ fragments. Such a fragment may effectively be formed by taking a Pt(PH_3)(CO)$_2$ fragment in which the CO groups are distorted to adopt their bridging geometry as shown in **4**. Subsequently Mealli [12] discussed the role of cluster bridging ligands



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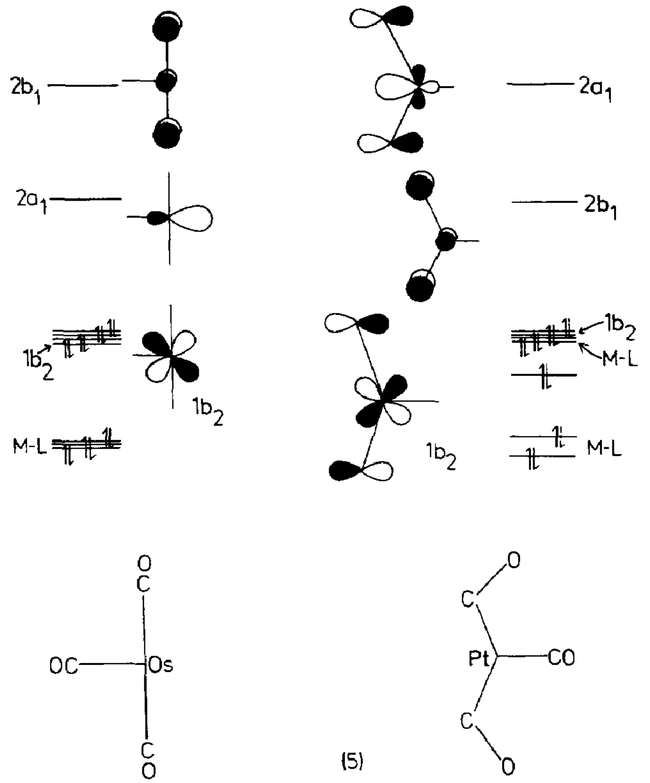
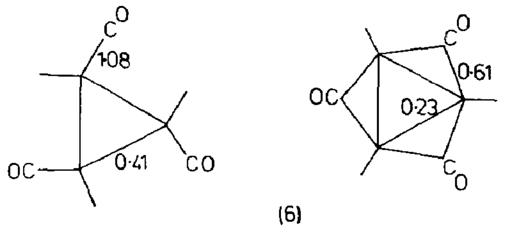


(5)

in a somewhat related fashion and Minot [27] has also illustrated the importance of the local geometry of ligand σ-orbitals around a metal atom in determining cluster bonding.

The frontier orbitals calculated for **4** are illustrated in **5** and are analogous to those reported elsewhere [9] for the $Ni(CO)_3$ fragment with this geometry. The well-documented description of the orbitals of the T-shaped $M(CO)_3$ fragment is also illustrated in **5** to highlight the similarity between the two fragments.

More revealing in the context of the trinuclear clusters, however, is the similarity between the angular $Pt(PH_3)(CO)$ fragment and **4**. As shown in Fig. 3, the frontier orbitals of the two fragments are very similar. The major differences involve the parentage of the a_1 and b_2 frontier orbitals, which have a much greater proportion of d character in **4**. This is particularly true in the case of the b_2 orbitals. As a consequence these orbitals are more stable than their counterparts in the angular fragments, but the overlap between them on forming the cluster is diminished because of the somewhat contracted nature of the platinum 5d orbitals. Thus the direct metal–metal overlap is less in the case of **3** than **2**, but the total metal–carbon overlap is larger in the former by virtue of its greater σ-character. This is reflected in the computed Mulliken overlap populations for the two clusters reproduced in **6**.



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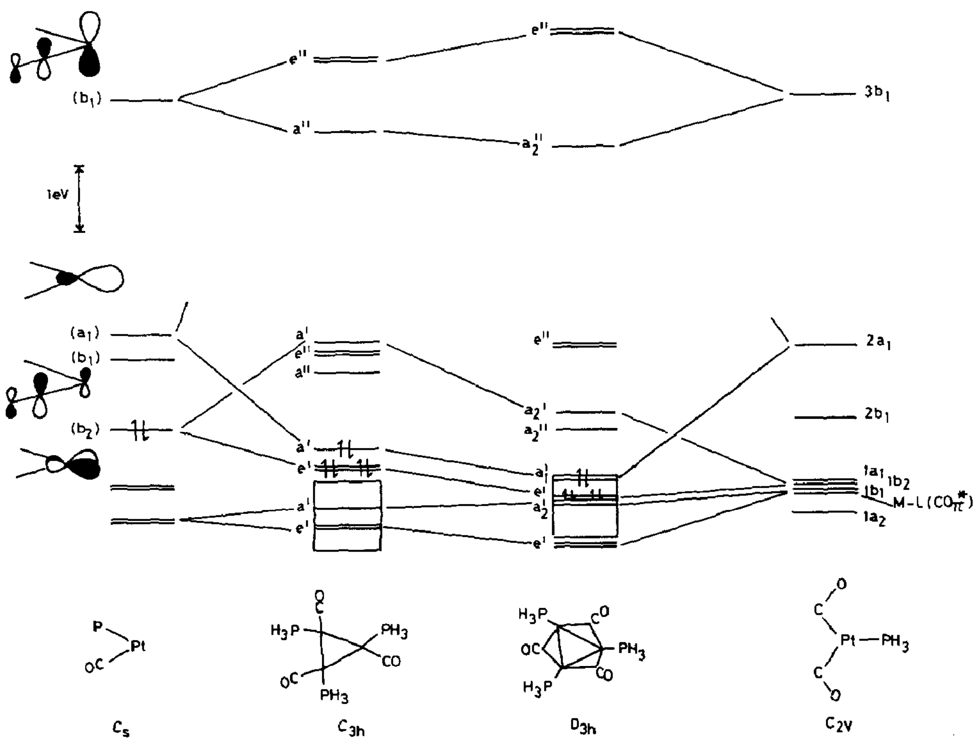


Fig. 3. A comparison of the molecular orbitals of triangular $[Pt_3(CO)_3(PH_3)_3]$ and $[Pt_3(\mu\text{-}CO)_3(PH_3)_3]$ clusters derived from $Pt(CO)(PH_3)$ and $Pt(CO)(L')_2$ fragments, respectively. Each cluster has three bonding skeletal molecular orbitals (e' and a_1') but those in the bridged cluster are more stable by virtue of their greater d character.

Overall the calculations suggest that the bridging carbonyl geometry is 1.8 eV more stable than **2**, similar to the conclusion reached by Mealli [12] for $[Pt_3(CO)_6]^{2-}$, primarily as a consequence of the greater stability of the $2e'$ $(P^{\pi}_{c,s})$ and $1a_1'$ (S^{σ}) metal–metal bonding orbitals and the more effective metal–carbon bonding. Furthermore, occupation of $1e'$ and $1a_2'$ in **3**, which represent the bonding combinations of in plane carbonyl π^* and metal orbitals, is energetically more favourable than occupation of their counterparts in **2**, which have purely π-character (and therefore lower overlap integrals) with respect to metal–carbon interaction.

The calculated energy difference between the terminal and bridged isomers is consistent with the observations that all known $[Pt_3L_6]$ clusters adopt the latter geometry and that it has been unambiguously demonstrated by NMR [28] that there is no interchange between terminal and bridging carbonyl ligands in clusters of the type $[Pt_3(\mu\text{-}CO)_3(CO)_3]_n{}^{2-}$ even at high temperatures.

The planar geometry of the $[Pt_3L_6]$ unit in the trinuclear clusters discussed above facilitates on steric, and as we shall see, electronic grounds the introduction of face capping (triply bridging) ligands. The molecular orbitals for the cluster $[Pt_3(dppm')_3]$ **7**, (dppm' = $H_2PCH_2PH_2$) are illustrated on the left of Fig. 4 and are as expected from the discussion above.

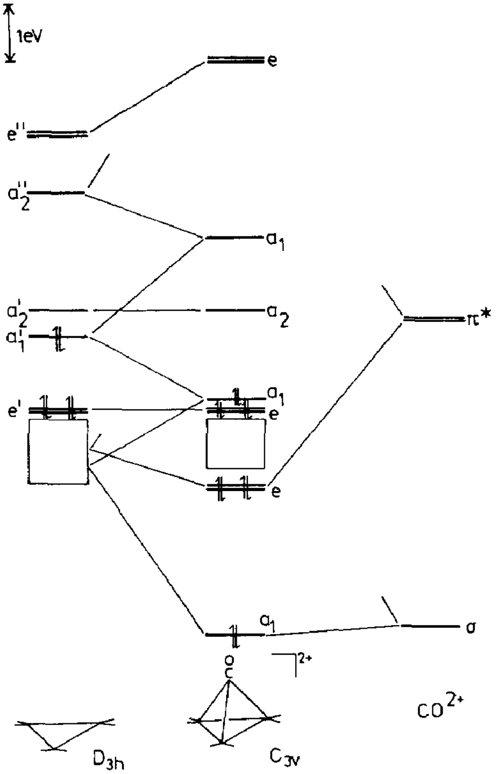
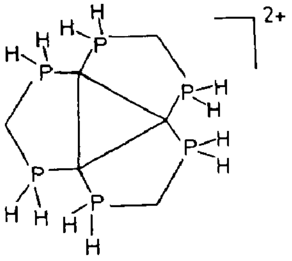
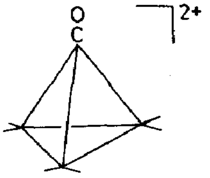


Fig. 4. Molecular orbital diagram for the interaction of a capping CO^{2+} fragment with $Pt_3(dppm')_3$. The capping ligand stabilises existing cluster bonding molecular orbitals so that a 42 electron count is maintained, and induces a mixing between the platinum *d*, *s* and *p* orbitals of a_1 symmetry in the cluster $[Pt_3(dppm')_3(\mu_3\text{-}CO)]^{2-}$.



(7)

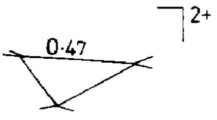
The effect of introducing a triply bridging CO^{2+} ligand to form $[Pt_3(dppm')_3(\mu_3\text{-}CO)]^{2+}$, **8** is shown schematically in Fig. 4. The CO^{2+} 5σ LUMO interacts weakly



(8)

with an appropriate combination of orbitals from the metal d band, whilst the CO^{2+} $\pi^{\star}$ orbitals interact much more effectively with suitable d orbitals. The $e'(P^{\pi}_{c,s})$ skeletal bonding MO's are essentially unaffected by the capping process but the a_1 (S^{σ}) skeletal bonding HOMO is strongly stabilised. This may be understood as follows. The capping ligand reduces the symmetry of of the cluster from D_{3h} to C_{3v} thus inducing a mixing between the S^{σ} orbital (a_1' in D_{3h}) and the $P_0^{\pi}(a_2''$ in D_{3h}), which both span a_1 in C_{3v}. The consequent stabilisation of the S^{σ} orbital induces its mixing with the lower lying a_1 combination of $d_{x^2-y^2}$ orbitals, which prevents the energy of the former from falling more than 1.3 eV and it remains the HOMO of the $[Pt_3(dppm')_3(\mu_3\text{-}CO)]^{2+}$ cluster. As the central component of such a three-orbital interaction, it is only weakly metal–metal bonding however. Similar conclusions have been reached by Mealli [12] in his discussion of $[Pt_3(CO)_6]$ clusters.

The effects of the capping CO^{2+} ligand are therefore two-fold. Firstly, existing bonding molecular orbitals are stabilised by the capping process and no additional low-lying orbitals are generated, so that a 42 electron count is maintained. Secondly the direct metal–metal overlap is reduced, primarily because of the mixing of S^{σ} described above, but this is more than offset by the gain in metal–carbon bonding. The computed Mulliken overlap populations for $[Pt_3(dppm')_3]$, **7**, and $[Pt_3(dppm')_3(\mu_3\text{-}CO)]^{2+}$, **8**, are shown in **9** and **10** respectively. The net stabilisation of the cluster by the capping process is therefore substantial. Puddephatt [29] has recently reported the synthesis of $[Pt_3(dppm)_3(\mu_3\text{-}CO)]^{2+}$ and its palladium analogue which do indeed have this geometry and electron count.



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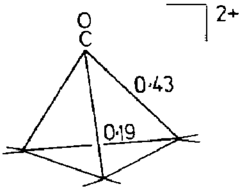
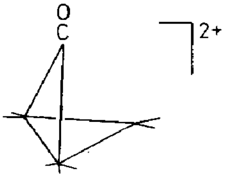


(10)

Puddephatt [29] also poses the question of whether the coordination mode of the CO (triply rather than doubly bridging) is determined primarily by steric or electronic factors. To examine this question we have performed calculations on $[Pt_3(dppm')_3(\mu_2\text{-}CO)]^{2+}$, **11**, with the results shown in Fig. 5. Comparison of Figs. 4 and 5 shows that although the overall bonding pictures for **8** and **11** are similar, the former is 1.5 eV energetically more favourable. This energy difference has two main contributing factors. Firstly, the three orbital interaction between S^{σ}, P_0^{π} and the $a_1(d_{x^2-y^2})$ orbitals is much less effective in **11**, so that the central component derived from S^{σ} (the cluster HOMO) is much less strongly stabilised in **11**.



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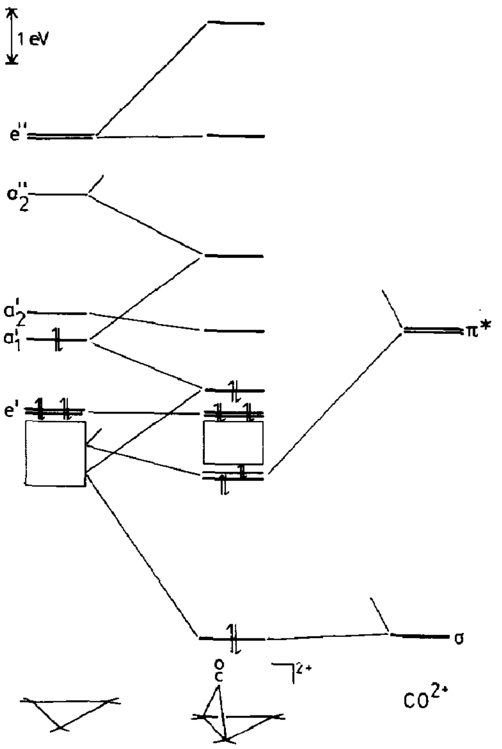
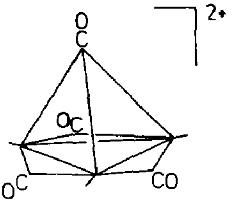


Fig. 5. Molecular orbital diagram for the interaction of an edge-bridging CO^{2+} fragment with $Pt_3(dppm')_3$. The resulting occupied cluster bonding orbitals are much less strongly stabilised than the analogous orbitals in $[Pt_3(dppm')_3(\mu_3\text{-}CO)]^{2+}$ (compare Fig. 4).

Secondly, the CO^{2+} π^* orbitals overlap less effectively with the metal *d* orbitals, so that the bonding combination is less strongly stabilised.

Although greater unfavourable steric effects would be observed if the CO adopted a μ_2-bridging position as in **11**, it is clear that there are also strong electronic factors militating against such a structure, and that the triply-bridged structure is the more favourable on both steric and electronic grounds. We will return to the electronic structures of clusters derived from both **8** and **11** later in this paper.

The similarity between the electronic structures of $[Pt_3L_6]$ and $[Pt_3(\mu_2\text{-}L)_3L_3]$ noted earlier (see Fig. 3) prompted us to consider whether $[Pt_3(\mu_2\text{-}CO)_3(PH_3)_3]$ might be capped by a triply bridging CO ligand, to form a cluster **12**, analogous to **8**. The MO interaction diagram for the formation of **12** is shown in Fig. 6 and is similar to that for **8** (see Fig. 4). The major difference between the two cases is that whereas the high-lying S^σ orbital in $[Pt_3(dppm')_3]$ is very strongly stabilised by the



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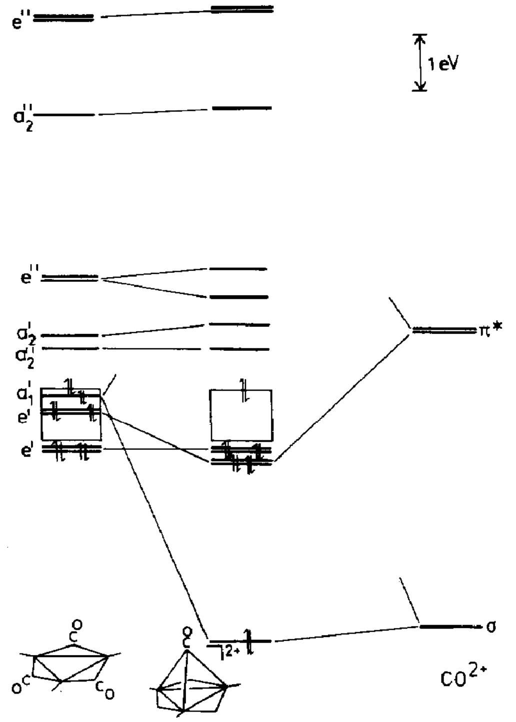
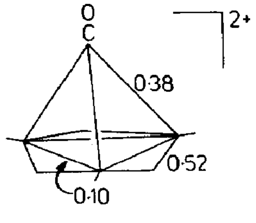


Fig. 6. Molecular orbital diagram for the interaction of a capping CO^{2+} fragment with $Pt_3(\mu\text{-}CO)_3(PH_3)_3$. The stabilisation of cluster molecular orbitals by the capping process suggests that the synthesis of such a cluster is a viable proposition.

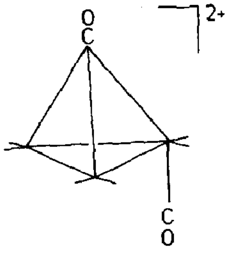
capping ligand as discussed above, the corresponding orbital in $[Pt_3(\mu_2\text{-}CO)_3(PH_3)_3]$ is already stabilised by the edge bridging ligands (see Figure 3) and the triply bridging ligand does not bring about a significantly greater stabilisation. Nevertheless, the capping process again brings about a substantial overall stabilisation of the occupied orbitals in $[Pt_3(\mu_2\text{-}CO)_3(PH_3)_3]$. The computed overlap populations for the cluster **12** are illustrated in **13**. The calculations suggest that the synthesis of



(13)

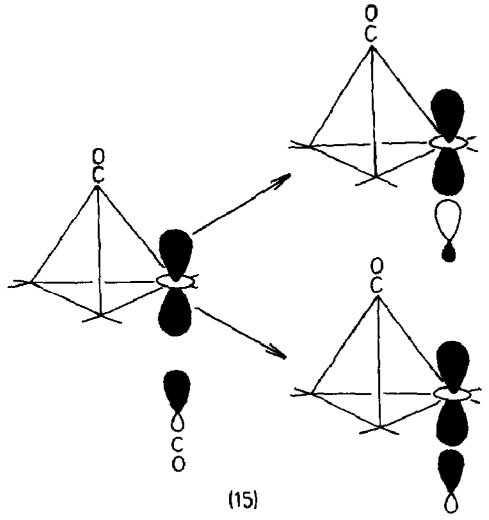
such a cluster is a viable proposition, although to date no such cluster has been reported. Other clusters containing a capped $[Pt_3(\mu_2\text{-}CO)_3(PH_3)_3]$ unit have been synthesised however – for example [30] $[Pt_3Au(CO)_3(PCy_3)_4]^+$ has a capping $[Au(PCy_3)]^+$ unit. The bonding in such species has been discussed by Gilmour and Mingos [31].

We now consider the effect of introducing additional terminal carbonyl ligands on the opposite face of the triangle to the triply bridging carbonyl ligand. Consider first the case of the 44 electron cluster $[Pt_3(dppm')_3(\mu_3\text{-}CO)(CO)]^{2+}$, **14**, derived from $[Pt_3(dppm')_3(\mu_3\text{-}CO)]^{2+}$, **8**, and CO fragments. The $\sigma^\star$ HOMO of the



(14)

incoming terminal CO ligand interacts with a filled d_{z^2} orbital on the platinum atom giving rise to a four electron destabilising interaction shown schematically in **15**. The upper antibonding molecular orbital is stabilised by a mixing with a



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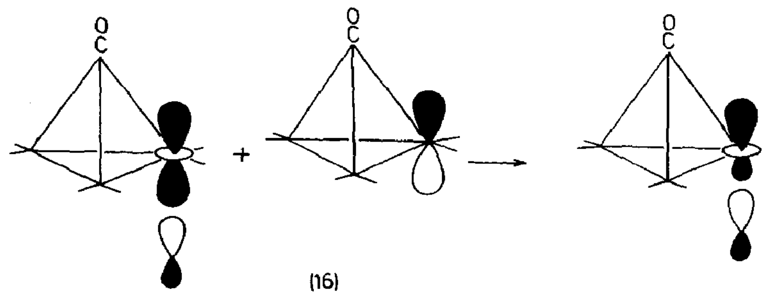
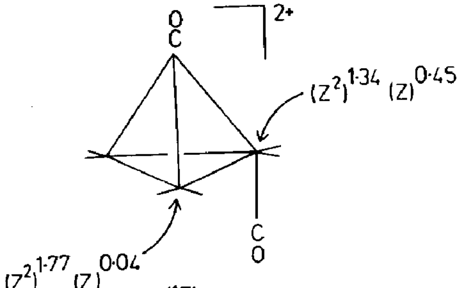
platinum p_z orbital, which is too high-lying to be occupied in the parent cluster **8** [13]. This gives rise to an overall three orbital four electron interaction with a central component as shown in **16**. Thus the introduction of the terminal CO ligand has



(16)

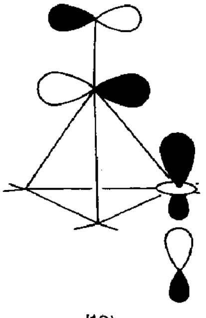
induced a mixing of the metal *d* and *p* orbitals, bringing about a greater involvement of the latter in **14** rather than **8**. The computed d_{z^2} and p_z atomic orbital occupations shown in **17** are consistent with this picture. The role of ligand-induced



(17)

d–p mixing has been discussed by us elsewhere [32]. The vacant π^* orbitals of the terminal ligand interact with and stabilise appropriate orbitals from the *d* band of $[Pt_3(dppm')_3(\mu_3\text{-}CO)]^{2+}$, **8**.

There are two main consequences of the three orbital interaction illustrated in **16**. The first is that the mitigation of the antibonding interaction between the metal d_{z^2} and CO HOMO results in a strong metal–CO bond and the second is that the back donation from the metal bearing the terminal CO into the π^* orbitals of the triply bridging CO is enhanced, as shown in **18**. As a consequence of this synergism it can be predicted that the triply bridging CO ligand should 'slip' towards the platinum atom bearing the terminal CO ligand. This is confirmed by the computed Mulliken overlap populations for $[Pt_3(dppm')_3(\mu_3\text{-}CO)(CO)]^{2+}$, **14**, shown in **19**.



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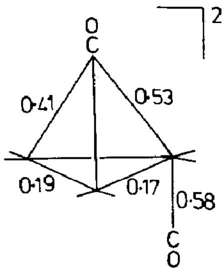
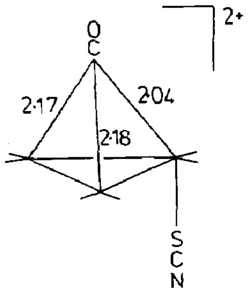


(19)

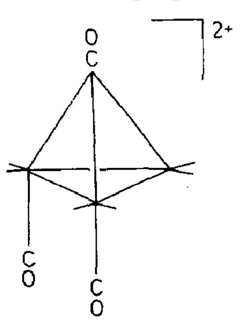
Puddephatt [33] has identified the species $[Pt_3(dppm)_3(\mu_3\text{-}CO)(CO)]^{2+}$ in solution on the basis of NMR experiments, but unfortunately the compound has not yet been isolated as a solid and comparison of the predicted and experimental geometries is not yet possible.

A closely related species has, however, been recently characterised by Puddephatt [34] viz. $[Pt_3(dppm)_3(\mu_3\text{-}CO)(SCN)]^+$. The triply bridging carbonyl ligand does indeed exhibit the slip distortion predicted above for the isoelectronic species $[Pt_3(dppm')_3(\mu_3\text{-}CO)(CO)]^{2+}$. The Pt–C(O) bond lengths for the thiocyanate cluster are shown in **20**.

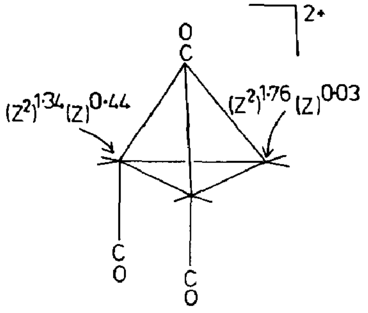


(20)

An exactly analogous bonding picture is found for the case of the 46 electron cluster $[Pt_3(dppm')_3(\mu_3\text{-}CO)(CO)_2]^{2+}$, shown in **21**. The ligand induced mixing of the d_{z^2} and p_z orbitals leads to a strong bond between terminal CO ligands and the metal triangle, and furthermore a slip distortion of the triply bridging CO ligand towards the two metal atoms bearing the terminal CO ligands. The metal d_{z^2} and p_z orbital populations and relevant overlap populations are shown in **22** and **23** respectively and the analogy with **17** and **19** is clear.



(21)



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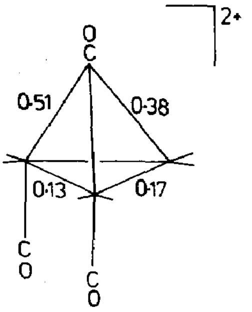
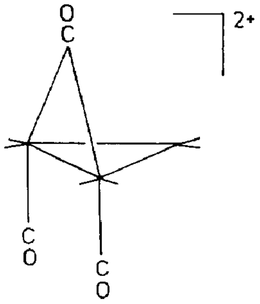


(23)

The calculations therefore suggest that the triply bridging CO ligand should slip towards a μ_2-coordination mode, analogous to that discussed above for $[Pt_3(dppm')_3(\mu_2\text{-}CO)]^{2+}$, **11**. Although **11** is unstable relative to the μ_3-CO ana-

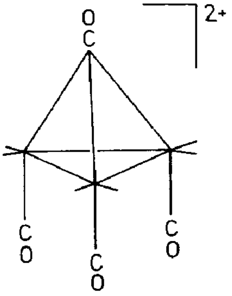


(24)

logue **8**, the calculations suggest that $[Pt_3(dppm')_3(\mu_2\text{-}CO)(CO)_2]^{2+}$, **24**, where the edge-bridging CO ligand is directly above the Pt–Pt edge, is some 0.2 eV more stable than the triply bridged isomer, **21**.

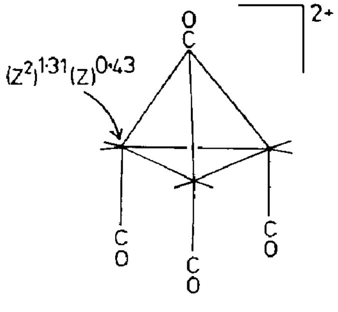
The cluster $[Pt_3(dppm)_3(\mu_2\text{-}CO)(CO)_2]^{2+}$ has been studied in solution by Puddephatt [33] and it has been clearly demonstrated that at low temperature, where the fluxional processes have been frozen out, the structure involves an edge-bridging rather than face capping CO ligand. Furthermore the isoelectronic cluster $[Pt_3(dmpm)_4(\mu_3\text{-}CO)]^{2+}$, which has a bridging dmpm ligand in place of the two terminal carbonyl ligands has been structurally characterised [35] and shown to have exactly the geometry predicted for $[Pt_3(dppm')_3(\mu_2\text{-}CO)(CO)_2]^{2+}$, **24** above.

As can be expected by extension of these ideas, an analogous bonding picture is found for the case of the 48 electron cluster $[Pt_3(dppm')_3(\mu_3\text{-}CO)(CO)_3]^{2+}$, **25**, where each platinum atom is coordinated to a terminal CO ligand. The metal d_{z^2}

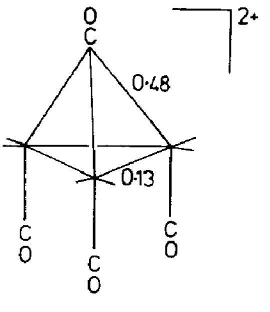


(25)

and p_z orbital populations and relevant overlap populations are shown in **26** and **27** and are as expected. For this D_{3h} cluster, any distortion of the capping CO ligand



(26)

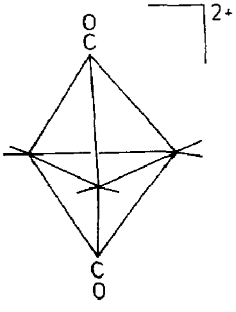


(27)

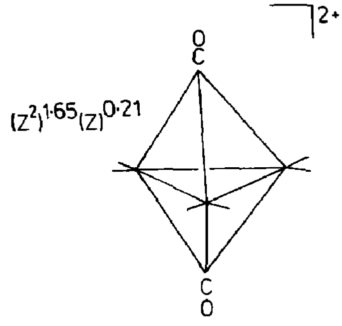
away from the symmetrical face-capping position is found to be energetically unfavourable, exactly as discussed above for the parent C_{3v} cluster $[Pt_3(dppm')_3(\mu_3\text{-}CO)]^{2+}$, **8**.

The calculations suggest that there is no electronic reason why such a cluster should not exist, although to date no such species has been identified, either in solution or the solid state. Such a species might possibly be synthesised in solution under high CO pressures, although replacement of the terminal CO ligands by a tripod phosphine might be expected to facilitate the isolation of an analogous cluster in the solid state.

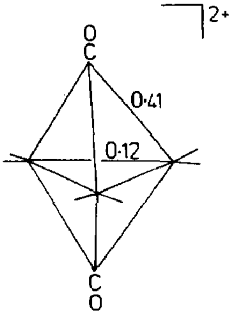
The structure of $[Pt_3(dppm')_3(\mu_3\text{-}CO)(CO)]^{2+}$ was discussed above. It is interesting to note that an alternative, more symmetrical, isomer of this compound is the doubly face-capped structure $[Pt_3(dppm')_3(\mu_3\text{-}CO)_2]^{2+}$, **28**. Molecular orbital calculations indicate that the qualitative features of the bonding in **28** and **14** are very similar but that the second triply bridging CO ligand induces a greater *d–p* mixing and a more effective utilisation of the metal *p* orbitals in **28** than does the terminal CO in **14**. This may be seen by comparing the computed d_{z^2} and p_z atomic orbital occupations and Mulliken overlap populations for **28**, shown in **29** and **30** respectively, with the corresponding results for **14** [see **17** and **19** above].



(28)



(29)



(30)

Overall the calculations suggest that **14** and **28** are of very similar energy – in essence the more effective metal–carbonyl bonding in **28** is offset by the less effective direct metal–metal bonding compared with **14**. This is consistent with the

Table 1

Parameters for non-metal atoms

Atom	Orbital	Slater component	H_{ii} (eV)
H	1*s*	1.30	−13.60
C	2*s*	1.63	−21.40
	2*p*	1.63	−11.40
O	2*s*	2.28	−32.30
	2*p*	2.28	−14.80
P	3*s*	1.60	−18.60
	3*p*	1.60	−14.00

Table 2

Parameters for platinum atom

Orbital	H_{ii} (eV)	ζ_1	c_1	ζ_2	c_2
6*s*	−9.80	2.55			
6*p*	−5.35	2.55			
5*d*	−10.61	6.01	0.633	2.70	0.551

results of Puddephatt [33] who has suggested, on the basis of IR and NMR results in solution that there is a rapid equilibrium between $[Pt_3(dppm)_3(\mu_3\text{-}CO)_2]^{2+}$ and $[Pt_3(dppm)_3(\mu_3\text{-}CO)(CO)]^{2+}$ in solution, even at −90 °C.

Appendix

All the calculations were performed using the Extended Hückel method with the relevant orbital parameters given in Tables 1 and 2. All the parameters conform to those which have been used to give reliable conclusions for organotransition metal compounds [36]. The off-diagonal terms in the Extended Hückel calculations were estimated from the expression $H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})/2$ [37].

The following bond lengths were used for the calculations:

Pt–Pt 2.63; Pt–P 2.28; Pt–C(O) (terminal) 1.81; Pt–C(O) (edge bridging) 2.05; Pt–C(O) (face capping) 2.09; P–C 1.85; P–H 1.42; C–H 1.05 Å. The calculations were performed on the ICL2988 computer at the South-West Universities Regional Computer Centre using the programs ICON8 and FMO [38].

Conclusions

The theoretical analysis presented here has demonstrated that it is possible to account for the structures of, and electron counts in, triangular clusters of platinum. There is a clear distinction between the planar $[Pt_3L_6]$ clusters and those involving additional, out of plane, ligands. In the former case, the platinum p_z orbitals play a relatively minor role by virtue of their high-lying nature, and an electron count of 42 is observed. Incorporation of additional out of plane ligands leads to a series of three orbital four electron interactions in which the metal *p* orbitals become hybridised into the bonding molecular orbitals, and electron counts of 44, 46 and possibly 48 may be observed. The synergistic interplay between the frontier orbitals of ligands on opposite sides of the metal triangle leads to specific ligand distortions being energetically favourable and these are observed in the experimental structures of such clusters.

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