and tris(ethylenediamine)metal(III) ions. The results were consistent with the previously proposed model that, in the racemic adsorption of $M(phen)_3^{2+}$, the Λ and Δ enantiomers were closely located on a clay surface with their phenanthroline ligands stacked stereoselectively.[1] For a pair of $M(phen)_3^{2+}$ and $M(phen)_3^{3+}$ ions, such stereoselective pairing was not realized because the electrostatic repulsion between the chelates overcame the attractive interaction due to the dispersive force between the phenanthroline ligands. For a pair of $M(phen)_3^{2+}$ and $M(en)_3^{3+}$ ions, attractive interaction might occur to a lesser extent between the phenanthroline ligands in $M(phen)_3^{2+}$ and the ethylenediamines in $M(en)_3^{3+}$.

Circular dichroism studies demonstrated that labile metal complexes such as $Co(phen)_3^{2+}$ and $Fe(phen)_3^{2+}$ antiracemized when adsorbed by an ion-exchange adduct of a clay and optically active $M(phen)_3^{2+}$, e.g. Λ-$Ru(phen)_3^{2+}$–montmorillonite. The results indicated that the empty sites on a clay in the state shown in (1) not only accepted the opposite enantiomer of a primary adsorbed $M(phen)_3^{2+}$ but also stabilized the configuration of an adsorbate against racemization. For the case of $Fe(phen)_3^{2+}$, about 80% of initially added $Fe(phen)_3^{2+}$ converted to the Λ enantiomer, being adsorbed by Δ-$Ni(phen)_3^{2+}$–montmorillonite. The results implied that the equilibrium constant between Δ-$Fe(phen)_3^{2+}$ and Λ-$Fe(phen)_3^{2+}$, K, were displaced from 1 to 4 in the presence of the clay adduct. This was a remarkably large shift of equilibrium in comparison with that of the previously known Pfeifer effects in solution phases. Davies and Dwyer reported that Δ-$Ni(phen)_3^{2+}$ was enriched with $K = 1.14$ at 25 °C in the presence of 2% cinchonium sulfate in 0.10 N H_2SO_4.[15] The large value of K presently observed was ascribed to the participation of a macromolecule of a colloidal clay. On such a clay surface, the adsorbed molecule might be protected from racemization as though it were separated from a bulk solution as a solid crystal.

The above tendency to select and stabilize only one enantiomer of a chelate by an adduct of an optically active chelate–montmorillonite might be of potential utility for asymmetric syntheses. That is, when some achiral molecule reacted at an empty site of a clay at the state shown in (1), the molecule would change to an optically active compound under the stereoselective control due to the preadsorbed optically active chelates. This possibility was strengthened by the facts that (i) racemic $Cu(PAN)_2$ became optically active in its electronic absorption spectrum (Figure 12) under the influence of Δ-$Ni(phen)_3^{2+}$ and that (ii) an achiral molecule, the N-substituted acridine orange cation, formed an optically active aggregate when it was adsorbed by Δ-Ni-$(phen)_3^{2+}$–montmorillonite. In fact, such an effect was observed when a metal ion (Co^{2+}) was added to a solution of Δ-Ni-$(phen)_3^{2+}$–montmorillonite that had adsorbed PAN ligands. Optically active $Co(PAN)_2^+$ was produced as a product.[16] The results were regarded as an indication that the adsorbed PAN ligands were in positions asymmetric with each other just as the acridine orange cations in the present case.

(15) Davies, N. R.; Dwyer, F. P. *Trans. Faraday Soc.* **1954**, *50*, 24.

(16) Yamagishi, A. *J. Chem. Soc., Chem. Commun.* **1984**, 119.

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Six- and Five-Vertex Organometallic Clusters

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The electronic structure of closo square-bipyramidal M_4E_2 clusters (M = metal atom in an ML_3 local coordination and E = PR, GeR, S, Te, ...) is analyzed. Two electron counts are possible: there are eight or seven skeletal electron pairs whether a low-lying metal–metal π antibonding MO is occupied or not. The role of 3d orbitals of the E fragment is emphasized, and the E···E bonding interaction is analyzed. The electron count in other related closo and nido clusters is also discussed. Particularly, the possibility of six or seven electron pairs is predicted for M_4E_2 clusters where M is in an ML_2 local coordination.

The polyhedral skeletal electron pair (PSEP) theory has proved to be a powerful tool in the understanding and prediction of the structure of organometallic clusters.[1] Its simple rules have been derived on the basis of the structural and bonding pattern of polyhedral borane and carborane clusters, taking advantage of the isolobal analogy[2] of B–H and C–H fragments with d^8 and d^9 ML_3 units.

As general and fundamental as it is, the PSEP theory sometime fails,[3] as all models do. This paper deals with a family of six-vertex closo-M_4E_2 compounds, which often do not conform with the PSEP theory.

The structurally characterized clusters of this family are listed in Table I.[4–14] They can be well represented by the model **16**,
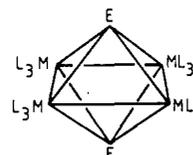
16

where the ligand E is GeR, PR, AsR, S, or Te. In the compounds of Table I the transition metal is in an ML_3 local coordination

(1) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1; "Transition Metal Clusters"; Johnson, F. B. G., Ed.; Wiley: New York, 1980; p 193. (b) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99. (c) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (d) Grimes, R. N. *Acc. Chem. Res.* **1978**, *11*, 420.

(2) For a general discussion of the isolobal analogy see: Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

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‡Cornell University.

Table I. Crystallographically Characterized M_4E_2 Clusters

no.	compd	E···E dist, Å[a]	n[b]	ref
1	(CO)₃Co / GeMe / Co(CO)₂ / CO / (CO)₃Co / GeMe / Co(CO)₂	2.926	8	4[d]
2	(CO)₃Fe / P-p-Tol / Fe(CO)₂ / CO / (CO)₃Fe / P-p-Tol / Fe(CO)₂	2.636 (4)	7	5
3	(CO)₃Fe / P-p-Tol / Fe(CO)₂ / CO / P(OMe)₃(CO)₂Fe / P-p-Tol / Fe(CO)₂	2.646 (8)	7	6
4	(CO)₃Fe / P-p-Tol / Fe(CO)₃ / (CO)₃Fe / P-p-Tol / Fe(CO)₃	2.598 (3)	8	6
5	(CO)₃Fe / PPh / Co(CO)₂ / CO / (CO)₃Fe / PPh / Fe(CO)₂	2.566	8	7
6	(CO)₃Fe / PMe / NiCp / (CO)₂Co / PMe / Fe(CO)₃	2.558	8	8
7	(CO)₂Co / PPh / Co(CO)₂ / OC / CO / (CO)₂Co / PPh / Co(CO)₂	2.537 (6)	8	9
8	(CO)₃Co / PPh / Co(CO)PPh₃ / OC / CO / PPh₃(CO)Co / PPh / Co(CO)₂	2.540 (5)	8	9
9	(CO)₂Co / PPh / Co(CO)₂ / H / CO / (CO)₂Co / PPh / Co(CO)₂		8	10
10	(CO)₃Ru / PPh / Ru(CO)₂ / CO / (CO)₃Ru / PPh / Ru(CO)₂	2.76 (3)	7	11
11[c]	(COD)Rh / PPh / Rh(COD) / (COD)Rh / PPh / Rh(COD)	2.679 (4)	6	12
12	(CO)₂Co / AsPh / Co(CO)₂ / OC / CO / (CO)₂Co / AsPh / Co(CO)₂		8	10
13	(CO)₃Fe / S / Co(CO)₂ / CO / (CO)₃Fe / S / Co(CO)₂		8	7a
14	(CO)₂Co / S / Co(CO)₂ / OC / CO / (CO)₂Co / S / Co(CO)₂	2.74 (2)	8	13
15	(CO)₂Co / Te / Co(CO)₂ / OC / CO / (CO)₂Co / Te / Co(CO)₂	3.30	8	9a

[a] When available. [b] Skeletal electron pair number. [c] COD = Cyclooctadiene. [d] Syntheses of other M_4Ge_2 clusters have been recently reported.[14]

with the ligands L being either terminal or briding. The exceptions **6** and **11**, which possess ML_2 subunits, will be discussed later.

(3) See for example: (a) Cox, D. N.; Mingos, D. M. P.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1981**, 1788. (b) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219. (c) Wade, K.; O'Neill, M. *Inorg. Chem.* **1982**, *21*, 461.
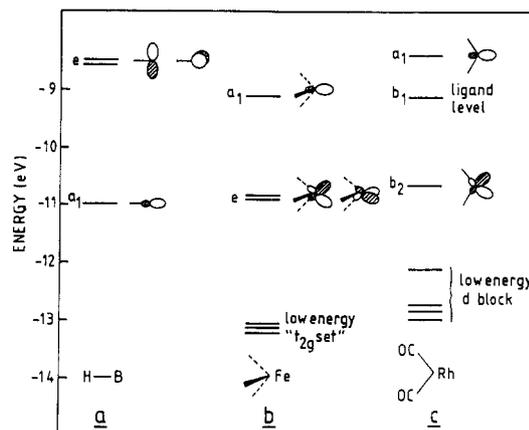
Figure 1. Comparison of the frontier orbitals of BH, $Fe(CO)_3$, and $Rh(CO)_2$ fragments.
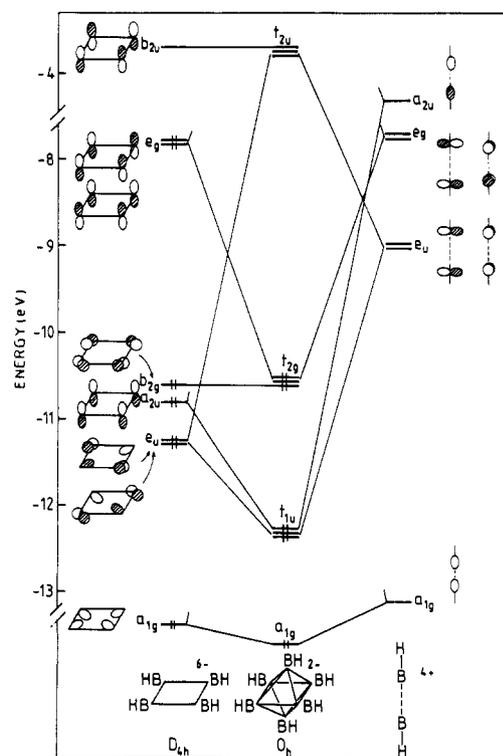
Figure 2. Orbital interaction diagram for $B_6H_6^{2-}$.

According to the PSEP theory, closo *n*-vertex clusters are expected to be stable for $n + 1$ skeletal electron pairs. Thus a normal count of seven skeletal pairs is anticipated for our compounds, as in their borane analogue, $B_6H_6^{2-}$. This is not the case for most of the clusters in Table I, which possess eight electron pairs.[15]

(4) Foster, S. P.; Mackay, K. M.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1982**, 1156.
(5) Vahrenkamp, H.; Wolters, D. *J. Organomet. Chem.* **1982**, *244*, C17. Vahrenkamp, H.; Wucherer, E. J.; Walter, D. *Chem. Ber.* **1983**, *116*, 1219.
(6) Vahrenkamp, H.; Walter, D. *Organometallics* **1982**, *1*, 874.
(7) (a) Vahrenkamp, H.; Wucherer, E. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 680. (b) Vahrenkamp, H.; Wucherer, E. J.; Walter, D. *Chem. Ber.* **1983**, *116*, 1219.
(8) Vahrenkamp, H.; Müller, M. *Chem. Ber.* **1983**, *116*, 2765.
(9) (a) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. (b) Ryan, R. C.; Pittman, C. U.; O'Connor, J. P.; Dahl, L. F. *J. Organomet. Chem.* **1980**, *193*, 247.
(10) Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046.
(11) Field, J. S.; Haines, R. J.; Smit, D. N. *J. Organomet. Chem.* **1982**, *224*, C49.
(12) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251.
(13) Wei, C. H.; Dahl, L. F. *Cryst. Struct. Commun.* **1975**, *4*, 583.
(14) Gusbesh, P.; Vahrenkamp, H. *J. Organomet. Chem.* **1983**, *252*, C93.

Another particular feature of these compounds is that they have a short E···E nonbonded interatomic distance, only ~15–20% larger than a normal simple E–E bond. Let us examine the reasons for the stabilization of the eight-electron-pair count.

The $B_6H_6^{2-}$ Analogue to the Metal Clusters

Let us consider first the electronic structure of $B_6H_6^{2-}$.[1a,16] One way in which the electronic structure of this analogue of the M_4E_2 clusters may be constructed is from the starting point of a hypothetical square-planar $B_4H_4^{6-}$ (which isostructural with the cyclobutadiene dianion, $C_4H_4^{2-}$). $B_4H_4^{6-}$ is an arachno species with $n = 4$ cluster atoms and $n + 3 = 7$ skeletal electron pairs. These seven pairs are located in seven bonding or nonbonding MO's constructed from the FMO's of the four main-group B–H units, illustrated in Figure 1a. The molecular orbitals of the $B_4H_4^{6-}$ arachno species are shown on the left side of Figure 2.

The seven bonding or nonbonding orbitals are separated from the b_{2u} antibonding LUMO by a large energy gap. The skeletal MO's of $B_6H_6^{2-}$, shown in Figure 2, can be constructed with those of $(B_4H_4)^{6-}$ and two $(B-H)^{2+}$ capping units. The derivation of the seven occupied levels of $B_6H_6^{2-}$ from those of $B_4H_4^{6-}$ is clear: six of them are bonding combinations of six of the occupied MO's of $B_4H_4^{6-}$ with the six FMO's of the HB···BH bicapping moiety. The seventh is the unperturbed b_{2g} level of $B_4H_4^{6-}$. The HOMO–LUMO separation in $B_6H_6^{2-}$ is even larger than the one in $B_4H_4^{6-}$. Note that one component of the triply degenerate LUMO of $B_6H_6^{2-}$ is the unperturbed b_{2u} level of $B_4H_4^{6-}$.

In the composite $B_6H_6^{2-}$ cluster the calculated overlap population between two nonbonded boron atoms is −0.256. From our experience such large negative overlap populations are indicative of substantial repulsion. The B···B antibonding can be traced to strong interactions of the HB···BH a_{1g} (B···B bonding) and a_{2u} (B···B antibonding) orbitals with corresponding $B_4H_4^{6-}$ orbitals. The result is depopulation of a_{1g} (an FMO analysis gives only 1.21 electrons in the composite MO which reside in the HB···BH fragment) and occupation of a_{2u} (by 0.88 electron). Both electron occupations make for HB···BH antibonding.

M_4E_2 Clusters with ML_3 Subunits

We now go back to the clusters of type **16**. Like its analogous borane, our chosen model $Fe_4(CO)_{12}(PH)_2$ (**17**) can be divided

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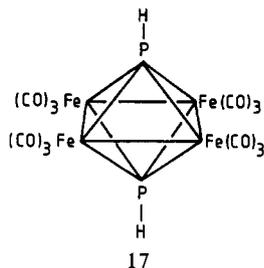
into a square-planar $Fe_4(CO)_{12}$ fragment and a bicapping HP···PH unit. The frontier orbitals of the well-known conical $Fe(CO)_3$ fragment[17] are illustrated in Figure 1b. Since $Fe(CO)_3$ and BH are isolobal, $Fe_4(CO)_{12}$ displays seven bonding or nonbonding skeletal MO's of the same symmetry as those of B_4H_4 (see the left side of Figure 3). But the large gap between these seven MO's and the π antibonding one has now disappeared. The b_u π^* MO, the first M–M antibonding MO of the $Fe_4(CO)_{12}$ units, is now not so high in energy. Note that the entire set of π orbitals (a_u, e_g, b_u) are not split much in energy. It appears that the π-type
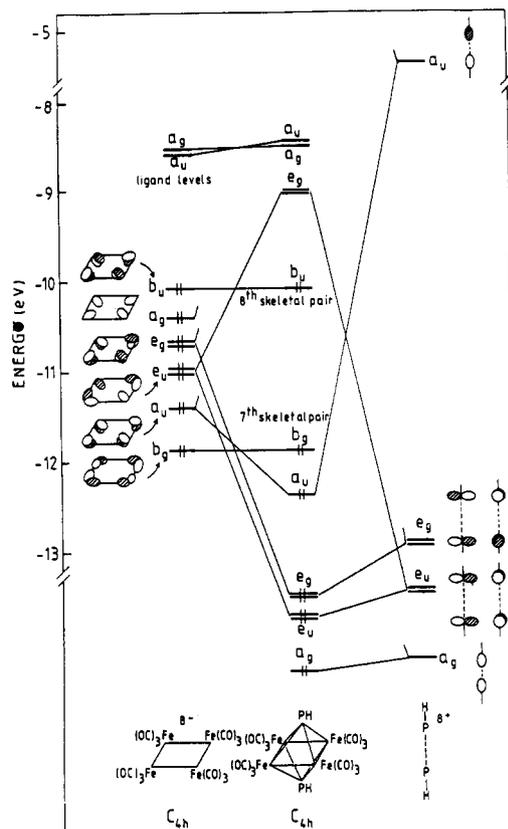
Figure 3. Orbital interaction diagram for $Fe_4(CO)_{12}(PH)_2$.

overlap in this metallacyclobutadiene is not as high as in the related borane or cyclobutadiene.

From the level scheme of the metal tetramer it would appear that if M_4L_{12} arachno square-planar species were to exist they should have six, seven, or eight electron pairs. The lower electron counts might be high spin or easily susceptible to a second-order Jahn–Teller deformation. In fact only seven-electron-pair arachno butterflies of this type have been observed.[18]

Neglecting at first the role played by 3d phosphorus orbitals, we can consider that a PH group (or S, Te atoms) provides a set of FMO's identical in number and symmetry with the orbital set of the BH unit. Thus, the orbital correlation diagram of $Fe_4(C-O)_{12}(PH)_2$ is similar to that of $B_6H_6^{2-}$ (see Figure 3), but now the unperturbed b_u MO sits in the middle of a large energy gap. This pattern suggests the possibility of either seven or eight skeletal

(15) Some eight-skeletal-pair nido-M_4E_2 clusters have been reported. Their structure is based on a pentagonal bipyramid with an unoccupied basal vertex. Here the two capping units are metal fragments and the E atoms are located in the basal plane with no E–E bond: Adams, R. D.; Yang, L.-W. *J. Am. Chem. Soc.* **1983**, *105*, 235. Adams, R. D.; Horvath, I. T.; Mathur, P. *J. Am. Chem. Soc.* **1983**, *105*, 7202.

(16) Longuet-Higgins, H. C. *Q. Rev., Chem. Soc.* **1957**, *11*, 121.

(17) For a detailed discussion of ML_3 fragments see for example: (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

(18) (a) For a theoretical analysis of M_4 clusters see: Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305. (b) Some seven-skeletal-electron-pair M_4 arachno clusters have been reported. See: Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 1919. Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 7417. Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541, 4542. Tachikawa, M.; Stein, J.; Muetterties, E. L.; Teller, R. G.; Beno, M. A.; Gebert, E.; Williams, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 6649. Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485. Bradley, J. S.; Ansell, G. B.; Leonowicz, M. E.; Hill, E. W. *J. Am. Chem. Soc.* **1981**, *103*, 4968. Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1978**, 673. Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2985. Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1572. Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825. Davis, J. H.; Beno, M. A.; Williams, J. M.; Zimmie, J.; Tachikawa, M.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 668. Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1774. Carty, A. J.; Taylor, N. J.; Sappa, E.; Tiripicchio, A. *Inorg. Chem.* **1983**, *22*, 1871. Carty, A. J.; McLaughlin, S. A.; Taylor, N. J. *J. Chem. Soc., Chem. Commun.* **1981**, 476. Kreter, P. E.; Meek, D. W.; Christoph, G. G. *J. Organomet. Chem.* **1980**, *188*, C27. Brun, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaün, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 1357. Sappa, E.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Chem. Commun.* **1979**, 254.
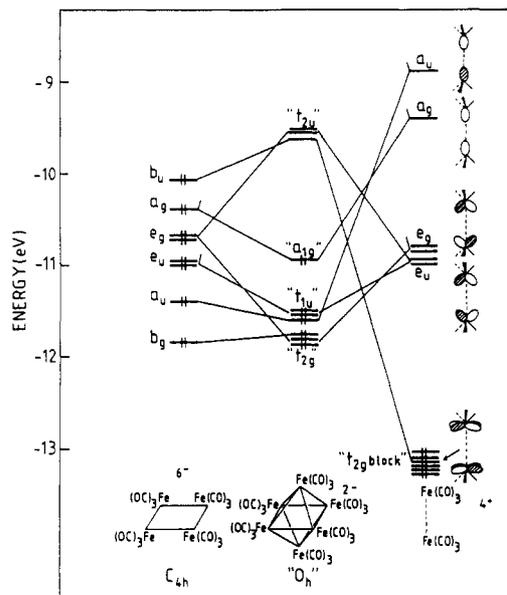
Figure 4. Orbital interaction diagram for the pseudooctahedral $Fe_6(CO)_{18}$ cluster. The labeling of the molecular levels of the M_6 cluster was kept in O_h group symmetry.

pairs for this family of compounds, in total agreement with experiment (see compounds **1–5** and **7–14** in Table I).

However, a careful examination of this table indicates that most of these clusters bear eight rather than seven skeletal pairs, for instance compound **4**, almost identical to our model $Fe_4(CO)_{12}$-$(PH)_2$ (**17**). A stabilization of b_u, thus increasing the gap between it and the higher unoccupied orbitals, is hinted at. It can be achieved by introduction of d orbitals on phosphorus. b_u is stabilized as shown in **18**.
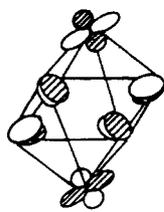
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A remarkable result of the calculation is that in $Fe_4(CO)_{12}(PH)_2$ the P···P interaction is attractive. The P···P overlap population is $+0.226$ ($+0.501$ with P 3d orbitals).

We can ask why this interaction is attractive while the corresponding B···B interaction in $B_6H_6^{2-}$ is repulsive. Since the atomic orbitals of the phosphorus atoms are diffuse, the σ FMO's on each PH unit can strongly feel each other at rather large P···P separation. There results a large splitting between their bonding a_g and antibonding a_u combinations, which brings these orbitals far away from the skeletal orbitals of the $Fe_4(CO)_{12}$ fragment. Consequently, their interaction with the corresponding a_g and a_u metallic levels is smaller than the corresponding interactions in $B_6H_6^{2-}$. The occupied a_g MO of $Fe_4(CO)_{12}(PH)_2$ is mainly P···P bonding, and the occupied a_u has a dominant iron character (the population analysis of this cluster leads to an occupation of 1.93 electrons for the a_g FMO and 0.77 electron for the a_u FMO of the HP···PH moiety).

If the occupation of a_u of $Fe_4(CO)_{12}(PH)_2$ does not significantly affect the P···P interaction, why do compounds **4–9**, having eight skeletal pairs, have shorter P···P separations than compounds **2**, **3**, and **10**, which bear seven pairs? The eighth skeletal MO, b_u, cannot be behind this observation, for its P···P bonding character is poorly developed—it is of δ character. Anyway, even if the overlap were significant, this orbital is P···P antibonding.

Interatomic distances in a cluster are a compromise between all interatomic interactions. Thus, the P···P distance depends not only on the direct P···P interaction but also on M–P and M–M

separations. Metal–phosphorus bonding for seven or eight electron pairs is strong, and M–P distances should be similar, as they are in the observed structures.

If M–P is constant, the P···P separation depends on the M–M distance. The larger this distance, the shorter should be the P···P separation. For an eight-skeletal-pair count the M–M distance is expected to be longer because of the rather antibonding character of the b_u level. It follows that a smaller P···P distance should occur.

But the metal–metal distances in the metallic plane are also affected by the nature of the metal atoms and ligands and by the presence of bridging ligands. It seems dangerous to correlate the magnitude of the P···P distance only to the skeletal electron count.

Other Related Clusters

The question that arises now is why all the known octahedral M_6 clusters[19,20] (these M_6 clusters are well typified by model **19**) possess seven skeletal electron pairs, never eight. These com-
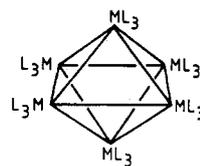
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pounds can be derived from our M_4E_2 model by substituting the two nonmetallic units by two isolobal ML_3 fragments. The answer resides in the MO diagram of $Fe_6(CO)_{18}^{2-}$ [21] constructed from

(19) (a) Albano, V.; Chini, P.; Scaturin, V. *J. Organomet. Chem.* **1968**, *15*, 423. (b) Albano, V.; Bellon, P. L.; Chini, P.; Scaturin, V. *J. Organomet. Chem.* **1969**, *16*, 461. (c) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1979**, 735. (d) McPartlin, M.; Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1976**, 883. (e) Corey, E. R.; Dahl, L. F.; Beck, W. *J. Am. Chem. Soc.* **1963**, *85*, 1202. (f) Albano, V. G.; Ciani, G.; Chini, P. *J. Chem. Soc., Dalton Trans.* **1974**, 195. (g) Famagalli, A.; Martinengo, S.; Chini, P.; Albinati, A.; Bruckner, S.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* **1978**, 195. (h) Churchill, M. R.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 5670. (i) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; Machin, P.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1976**, 945. (j) Ceriotti, A.; Ciani, G.; Garlaschelli, L.; Sartorelli, U.; Sironi, A. *J. Organomet. Chem.* **1982**, *229*, C9. (k) Demartin, F.; Manessero, M.; Sansoni, M.; Garlaschelli, L.; Sartorelli, U.; Tagliabue, F. *J. Organomet. Chem.* **1982**, *234*, C39. (l) Ciani, G.; Sironi, A.; Chini, P. *J. Organomet. Chem.* **1981**, *213*, C37. (m) Paquette, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 6621. (n) Slovokhotov, Yu. L.; Struchkov, Yu. L.; Lopatin, V. E.; Gubin, S. P. *J. Organomet. Chem.* **1984**, *266*, 139.

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the fragment orbitals of $Fe_4(CO)_{12}$ and $(OC)_3Fe\cdots Fe(CO)_3$ and shown in Figure 4. In this case the bicapping moiety possesses a low-lying antibonding combination of d δ orbitals part of the "t_{2g}" set of the $Fe(CO)_3$ monomers.[22] This FMO, of symmetry b_u in C_{4h}, destabilizing the b_u level of the square fragment, giving a large HOMO-LUMO gap for a seven-electron-pair count.

Clusters with mixed bicapping units, such as **20**, are also observed.[23] All the compounds of this family possess seven skeletal electron pairs.

20
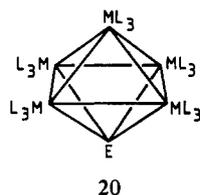
Monocapped nido clusters, such as **21** and **22**, are intermediate cases between the square-planar M_4 arachno species and the bicapped closo complexes **16** or **19**. Their bonding or nonbonding

21 **22**
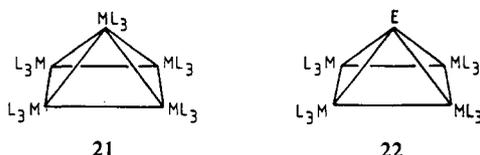
orbitals can be derived from those of the M_4 metallic entity in the same way as those of **16** or **19**.

In analogy to **19**, our calculations on $Fe_5(CO)_{15}^{4-}$ anticipate a seven-electron-pair count for compounds of the class **21**. However, the calculated HOMO-LUMO gap is rather small (0.9 eV), suggesting a relative instability for this kind of compound. Indeed, no compound of this kind has been reported to date, to our knowledge. Compounds such as **23**, presenting a carbido

23
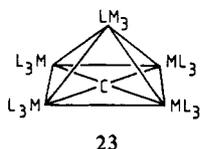
main-group atom in the middle of the square face, are well-known.[24] They all bear seven skeletal pairs. Calculation of $Fe_5(CO)_{15}C$ shows that the incoming C^{4+} nucleus in $Fe_5(CO)_{15}^{4-}$ stabilizes all its occupied skeletal MO's, leaving untouched the "b_u" LUMO (see in Figure 4 on the left side). The result is a larger HOMO-LUMO separation (1.5 eV), rendering the complex more stable.

Figure 5. Orbital interaction diagram for $Rh_4(CO)_8(PH)_2$.

To our knowledge, no compound related to **22** exists. Calculations on the model $Fe_4(CO)_{12}(PH)$ predict a stable complex for eight skeletal electron pairs. Even without use of 3d phosphorus orbitals, the "b_u" molecular orbital does not lie far above the seven other skeletal MO's (0.7 eV), while a large HOMO-LUMO energy gap (1.4 eV) is observed. The introduction of 3d orbitals leads to values of 0.3 and 1.9 eV, respectively, for these gaps. From this perspective nothing would seem to hinder the existence of such compounds. They should be able to be synthesized.[25]

M_4E_2 Clusters with ML_2 Subunits

Compounds **6** and **11** are exceptions in the series of clusters listed in Table I, in that they are part of ML_2 fragments. We can easily admit that the electronic structure of **6**, which possesses three ML_3 and only one ML_2 subunit and bears eight skeletal pairs, is not that different from that of clusters of type **16**. This is not obviously the case for **11**, which possesses four ML_2 subunits and only six skeletal pairs. As illustrated in Figure 1c, an ML_2 fragment has one less frontier MO available for polyhedral bonding than an ML_3 or a BH group. This difference has already been exploited by Evans and Mingos in their work concerning the extension of the PSEP theory to nonconical fragments.[26]

Figure 5 gives the orbital correlation diagram for the model $Rh_4(CO)_8(PH)_2$ (**24**) used in our calculations. Since an ML_2

24
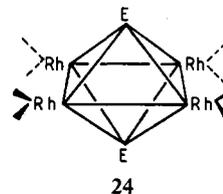
unit has, compared to ML_3, a "missing" π-type in-plane orbital,[2,26,27] the $Rh_4(CO)_8$ fragment, vis-à-vis the $Fe_4(CO)_{12}$ entity,

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(25) To our knowledge only two M_4E clusters have been reported with E in the square plane of the pyramid. See: Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. Süss-Fink, G.; Thewalt, U.; Klein, H.-P. *J. Organomet. Chem.* **1984**, *262*, 315.
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(27) Hoffman, D. M.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1982**, 1471.

Table II. Extended Hückel Parameters

| orbital | H_{ii}, eV | exponents[a] | |
		ζ_1	ζ_2
H 1s	−13.60	1.30	
B 2s	−15.2	1.3	
2p	−8.5	1.3	
C 2s	−21.40	1.625	
2p	−11.40	1.625	
O 2s	−32.30	2.275	
2p	−14.80	2.275	
P 3s	−18.60	1.6	
3p	−14.00	1.60	
3d	−7.00	1.4	
Fe 4s	−9.10	1.90	
4p	−5.32	1.90	
3d	−12.60	5.35 (0.5366)	1.80 (0.6678)
Rh 5s	−8.09	2.135	
5p	−4.57	2.10	
4d	−12.50	4.29 (0.5807)	1.97 (0.5685)

[a] Two Slater exponents are listed for the 3d functions. Each is followed in parentheses by the coefficient in the double-ζ expansion.

will have "missing" MO's, those constructed with the "missing" monomer orbitals. Thus, the total number of bonding or nonbonding orbitals of $Rh_4(CO)_8$ is reduced to six, the "b_{2g}" bonding orbital of the $Fe_4(CO)_{12}$ fragment "lacking". Of course, the π-type b_{2u} antibonding orbital is still here, now in the middle of the FMO block. The highest FMO at the left in Figure 5 is now e_u, for it has lost most of its bonding character. However, it still has some in-plane π-type metal character derived from the predominantly ligand-based b_1 level of the $Rh(CO)_2$ fragment (see Figure 1c). Except for the "missing" "b_{2g}" MO, there is no great difference between the MO diagram of $Rh_4(CO)_8(PH)_2$ and that of Fe_4-$(CO)_{12}(PH)_2$. Consequently, there are two possible electron counts for **24**, six or seven pairs depending on whether the π-antibonding b_{2u} MO is vacant or not. For our model a six-pair count is more favorable without the inclusion of 3d phosphorus orbitals (see Figure 5), but calculations including these polarization functions suggest that the two possible electron counts are both feasible. Note also that the b_{1g} HOMO of the complex is not derived from the frontier MO's of the two interacting fragments but is an antibonding combination of in-plane low-lying d-block orbitals of the $Rh(CO)_2$ unit.

As in $Fe_4(CO)_{12}(PH)_2$, the P···P interaction is attractive. The corresponding overlap population for six skeletal pairs is +0.177 (+0.412 if 3d phosphorus functions are included).

From the above discussions, it follows that the favorable electron count for the hypothetical nido compound **25** should be six or seven skeletal electron pairs.
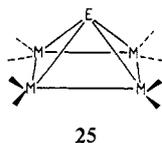
25

At this point, the interesting square-planar $Pt_4(OAc)_8$ compound[28] should be noted. This four-skeletal-pair cluster can be schematized by **26** with M = Pt(II) (d^8).

(28) De C. T. Carrondo, M. A. A. F.; Skapski, A. *J. Chem. Soc., Chem. Commun.* **1976**, 410.
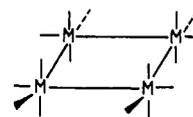
26

Just like an ML_2 fragment, the C_{2v} ML_4 unit provides two FMO's of symmetry a_1 and b_2.[2-26] The difference between **26** and the M_4 fragment of **11** or of our model **24** is that the b_2 orbitals of the four ML_4 subunits lie in the plane of the square in **26**, while in the $M_4(CO)_8$ fragment, the corresponding orbitals lie perpendicular to this square. As for $Rh_4(CO)_8$, the skeletal MO's of **26** are related to those of $Fe_4(CO)_{12}$ (see Figure 3). This time, the "missing" MO's are π type. From the seven plus one lower skeletal MO's of the $Fe_4(CO)_{12}$ entity only four remain, all strongly σ bonding, in accordance with the electron count of $Pt_4(OAc)_8$ and its short observed Pt–Pt bond lengths. $Pt_4(OAc)_8$ is a stable, isolable compound (as already pointed out by Mingos et al.,[26] the inorganic equivalent of cyclobutane). On the other hand, a fragment like $Rh_4(CO)_8$ has little chance to be stable, whatever its charge, but with its π-type orbitals, is prepared for bonding with appropriate capping units.[29,30]

Appendix

The calculations have been carried out within the extended Hückel formalism[31] using the weighted H_{ij} formula.[32] The atomic parameters utilized are listed in Table II. The calculations on clusters containing P atoms have been made with and without inclusion of 3d phosphorus orbitals (see text). When not specified, results always refer to calculations without 3d phosphorus orbitals. An octahedral symmetry was assumed for the borane $B_6H_6^{2-}$ with B–B = 1.70 Å and B–H = 1.20 Å. All the calculations on compounds of type **16** and **19–23** were based on the same $C_{4h}Fe_4(CO)_{12}$ fragment. The following bond distances (Å) and angles (deg) were used: Fe–Fe = 2.70; Fe–P 2.29; P···P = 2.54; Fe–C = 1.80; C–O = 1.15; P–H = 1.40; Fe–$C_{carbido}$ = 1.91; OC–Fe–CO = 90.

Calculations on $Rh_4(CO)_8(PH)_2$ were made by assuming D_{4h} point group symmetry, with the following bond distances (Å) and angles (deg): Rh–Rh = 2.84; Rh–P = 2.42; P···P = 2.70; Rh–C = 1.90; C–O = 1.15; P–H = 1.40; OC–Rh–CO = 100.

Registry No. **1**, 84601-33-2; **2**, 95617-00-8; **3**, 95646-72-3; **4**, 95646-73-4; **5**, 95617-01-9; **6**, 95617-02-0; **7**, 58092-22-1; **8**, 73804-98-5; **9**, 95617-03-1; **10**, 95617-04-2; **11**, 95646-74-5; **12**, 95617-05-3; **13**, 95617-06-4; **14**, 57034-21-6; **15**, 95673-65-7.

(29) Other planar tetrametallic systems, having an ML_4 local coordination around the metals, are known. See for example: McCarley, R. E.; Ryan, T. R.; Torardi, C. C. *ACS Symp. Ser.* **1981**, *No. 155*, 41. Ryan, T. R.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 2072. Moiseev, I. I.; Stromnova, T. A.; Vargaftig, M. N.; Mazo, G. J.; Kuz'mina, L. G.; Struchkov, Yu. T. *J. Chem. Soc., Chem. Commun.* **1978**, 27; *Koord. Khim.* **1979**, *5*, 1558. Rudyi, R. .; Cherckashina, N. V.; Moiseev, I. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 1866. See also ref 25b and references therein.

(30) A tetrahedral $(ML_2)_4$ cluster has been reported. See: Vargaftig, M. N.; Stromnova, T. A.; Moiseev, I. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1690.

(31) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872.

(32) Ammeter, J. H.; Burgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.