A Molecular-orbital Study of some Di-μ-phosphido-bis(tricarbonyliron) Complexes. The Importance of Metal–Bridging Ligand Interactions in determining Molecular Geometry

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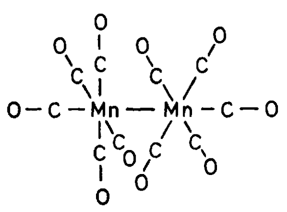
Extended Hückel molecular orbital (m.o.) calculations are used to examine the structures of $[Fe_2(CO)_6(\mu\text{-}AX_2)_2]$ systems (A = N, P, or As; X = a variety of organic ligands). The experimentally observed dramatic structural change, with a startling increase in metal–metal distance in the phosphido-bridged dimers when CF_3 replaces Me, H, or Ph as a bridging substituent (for A = P), is found to be due to the nature of the energetically highest-occupied m.o. (HOMO). This orbital, whilst metal–metal bonding, is metal–phosphorus antibonding, and the balance between these two forces controls the equilibrium geometry to a large extent. Replacement of X by CF_3 leads to stronger Fe–P repulsions in the HOMO and a longer Fe–Fe distance. The importance of Fe–P interactions stands out clearly in the calculations and these should be considered together with Fe–Fe interactions when viewing the structures of this and similar molecules. The geometry of these dimeric ' metal–metal-bonded ' systems is thus not determined purely by metal–metal interactions, as most previous studies have emphasised.

THE importance of direct metal–metal bonding in polynuclear transition-metal complexes has been a question of active interest to inorganic chemists for several years and one in which a clear but rather complex overall picture is just appearing. Clearly the metal–metal bonding is of vital importance in holding the two halves of the $[Mn_2(CO)_{10}]$ molecule (1) together even though



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the Mn–Mn bond length,[1] 2.92 Å, is rather long. However, at one stage the tendency of the radial CO groups to lean towards their counterparts in the neighbouring groups was taken [2] as evidence of incipient bridging-carbonyl formation. (A recent explanation [3] in terms of the preferred structure of the $[Mn(CO)_5]$ fragment is, however, much more convincing.)

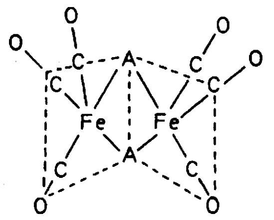
TABLE 1

Some structural data on bridged dimeric complexes

Complex	Ref.	Distance/Å		Angle/°	
		M–M	M–A	A–M–A	θ
$[Co_2(C_5H_5)_2(\mu\text{-}PPh_2)_2]$	*a*	2.56(1)	2.16(1)	83.7	105
$[Ni_2(C_5H_5)_2(\mu\text{-}PPh_2)_2]$	*a*	3.36(1)	2.15(1)	77.6	180
$[Fe_2(CO)_6(\mu\text{-}NH_2)_2]$	*b*	2.402(6)	1.98(1)	77.8	103.6
$[Fe_2(CO)_6\{(\mu\text{-}NCH_3)_2CO\}]$	*c*	2.391(7)	1.97(1)	64.8	92
$[Fe_2(CO)_6\{(\mu\text{-}NPh)_2CO\}]$	*d*	2.416(3)	1.996(6)	65.0	91.7
$[Fe_2(CO)_6\{C_6H_4(\mu\text{-}NPh)(\mu\text{-}NH)\}]$	*e*	2.372(2)	2.005(9)	72.9	95.4
$[Fe_2(CO)_6(\mu\text{-}PMePh)_2]$ [f]	*g*	2.619(1)	2.217(1)	80.5	101.4
$[Fe_2(CO)_6\{\mu\text{-}P(CF_3)_2\}_2]$	*h*	2.819(1)	2.193(1)	83.5	118.9
$[Fe_2\{As_2(\mu\text{-}AsMe)_2Me_2\}(CO)_6]$	*i*	2.664(5)	2.309(5)	77.6	124.5

[a] J. M. Coleman and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **88**, 542. [b] Ref. 4. [c] R. J. Doedens, *Inorg. Chem.*, 1968, **7**, 2323. [d] J. A. J. Jarvis, B. E. Job, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Comm.*, 1967, 1149. [e] P. E. Baikie and O. S. Mills, *Inorg. Chim. Acta*, 1967, **1**, 55. [f] Additional data on related molecules (R = Me, H, or Ph) show very similar structures (J. R. Huntsman and L. F. Dahl, unpublished work). [g] J. R. Huntsman and L. F. Dahl, unpublished work quoted in ref. 8. [h] Ref. 7. [i] B. M. Gatehouse, *Chem. Comm.*, 1969, 948.

A series of structures where the bridging groups are, because of their geometrical location, of obvious importance in holding the two halves of the structure together are the set of complexes $[Fe_2(CO)_6(AX_2)_2]$ [A = N, P, As, or S; X = a variety of organic ligands (H, Me, CF_3, Ph, *etc.*)], which form the subject of the present study. A summary of some relevant structural data is given in Table 1. These molecules consist of slightly distorted square-pyramidal $Fe(CO)_3A_2$ units joined along the A–A edge, (2).



(2)

Of particular interest is the variation of the Fe–Fe distance with the nature of A and the ligands attached to it. The Effective Atomic Number (e.a.n.) or 18-electron rule requires a single M–M bond. On a molecular-orbital (m.o.) basis this has been envisaged as follows.[4-6] The square-pyramidal d^7 $Fe(CO)_3A_2$ fragment {isoelectronic and isostructural with one half of

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[1] M. Bennett and R. Mason, *Nature*, 1965, **205**, 760.

[2] D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and R. M. Rawlinson, *J. Chem. Soc.* (*A*), 1971, 270; A. D. Berry, E. T. Carey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, 1970, **92**, 1940.

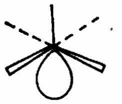
[3] J. K. Burdett, *J.C.S. Faraday II*, 1974, 1599.

[4] L. F. Dahl, W. R. Costello, and R. B. King, *J. Amer. Chem. Soc.*, 1968, **90**, 5422.

[5] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 1963, **2**, 328.

[6] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1.

$[Mn_2(CO)_{10}]\}$ contains one electron in an orbital of symmetry a_1 which projects out of the plane of the four equatorial groups, (3). On combining two such units to give the $[Mn_2(CO)_{10}]$ structure these two orbitals overlap linearly to give a Mn–Mn bond, but in the iron phosphido-dimer series a 'bent' M–M bond is the result, (4). Generally speaking, the metal–metal distance decreases in the order A = As (2.66—2.68) > P (with non-fluorine-containing ligands) (2.619—2.665) > S (2.51 —2.54) > N (2.372 —2.416 Å). Since this change in Fe–Fe distance is often associated with a concurrent change in Fe–A bond length, a useful parameter with which to describe the structural chemistry of the series is the dihedral angle θ [(5)] between the two planes formed by Fe^1AA and Fe^2AA. This angle grossly changes in the order N ~ S < P < As. A very interesting point is the recent determination[7] that when X = Me, H, or Ph is replaced as a bridging substituent by X = CF_3 in $[Fe_2(CO)_6(\mu\text{-}PX_2)_2]$, θ increases to 119° from just over 100° with a commensurate increase in Fe–Fe distance which some would describe as 'non-bonding' (Table 1). Most previous studies of the major structural effects governing the geometry in these systems have emphasised the importance of only the metal–metal bonding contributions. Whilst recent m.o. calculations[8] have demonstrated the existence of M–M and M–A bonding, the relative importance of each contribution in determining the overall geometry of the complex was not ascertained. In this study we concentrate on the effect of subtly changing the structure by varying the nature of the A or X groups since, as we have just noted, rather dramatic changes are sometimes seen and we hope to be able to qualitatively weight the influence of the Fe–Fe and Fe–A effects.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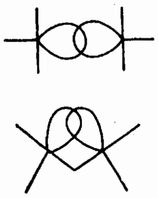
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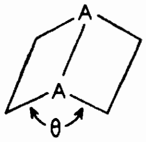

(5)

Summerville and Hoffmann,[9] in a very recent and extensive study of tetrahedrally (rather than square-pyramidal) based dimers, showed theoretically that in this series at least the geometries of the complexes are strongly influenced by the nature of the terminal and bridging ligands and that metal–metal bonding is a contributory but not overwhelmingly dominant effect.

The iron dimers form an excellent series with which to test theory against experiment since experimental data exist for some closely related systems where the effect of changing the nature of the X or A group is readily seen (Table 1).

THE STRUCTURE OF $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$

The m.o. diagrams discussed in this paper were derived using the Extended Hückel method,[10,11] a relatively simple orbital approach which is finding increasing favour as a method in structural transition-metal chemistry. Brief details of the parameters used for the calculations on the model compound are given in the Appendix. For simplicity, we chose to perform m.o. calculations on the molecule $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$, and initially focus our attention on the phosphorus series. Two idealised square-pyramidal units were used with C–M–C angles of 90° but maintaining the P–M–P angle found in the $P(CF_3)_2$ complex.[7] The interatomic distances within each unit remained fixed during variation of θ [(5)].

For molecules such as these with low symmetry and resulting from the fusion of simpler fragments $[2Fe(CO)_3 + 2PF_2]$ it is considerably easier to understand the complex m.o. diagram of the whole molecule in terms of its non-interacting constituents. The assembly of the m.o. diagram of the complex from those of the fragments is shown in Figure 1. Two $Fe(CO)_3$ fragments are combined to form $Fe_2(CO)_6$ which is then united with a suitably oriented P_2F_4 unit. One advantage of this method which will become apparent below is that we may readily compare the relative sizes of Fe–P and Fe–Fe interactions. The $Fe(CO)_3$ fragment has received a detailed examination from Elian and Hoffmann[12] and contains two types of frontier orbitals e and a_1 which point in the right direction for interaction with another $Fe(CO)_3$ unit or the offset P_2F_4 fragment. Both of these orbitals contain significant contributions from the $4p$ (in the case of the doubly degenerate pair) and the $4s$ and $4p$ orbitals (in the case of the d_{z^2} orbital of a_1 symmetry). In Figure 1(*a*) and (*b*) we see how the directional properties of these orbitals lead to Fe–Fe bonding–antibonding pairs in the $Fe_2(CO)_6$ molecule. The doubly degenerate pair form Fe–Fe π-bonding and π-antibonding combinations. The a_1 hybrid orbital gives rise to a corresponding pair of orbitals of the σ type. With four electrons overall in Fe–Fe bonding orbitals a net attraction exists between the two groups. Crudely, we would assign an M–M bond order of 2. The P_2F_4 molecule is of course capable of separate existence and with $P_2(CF_3)_2$ was the subject of a recent electron-diffraction study.[13] The most stable configuration in the gas phase is the *trans* arrangement compared to the eclipsed form existing in the present theoretically $(PF_2)_2$ and real $\{\mu\text{-}P(CF_3)_2\}_2$ complexes. The equilibrium P–P bond length in the gaseous phase is 2.20 Å compared to the much longer distance in $[Fe_2(CO)_6\{\mu\text{-}P(CF_3)_2\}_2]$ of 2.913 Å. The net bonding interaction between the phosphorus atoms in

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[7] W. Clegg, *Inorg. Chem.*, 1976, **15**, 1609.

[8] B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, 1975, **12**, 3103.

[9] R. H. Summerville and R. Hoffmann, *J. Amer. Chem. Soc.*, in the press.

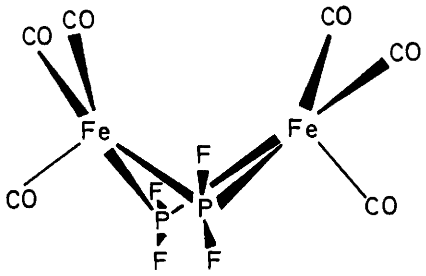
[10] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

[11] R. Hoffmann and W. R. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179, 3489; **37**, 2872.

[12] M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

[13] H. L. Hodges, L. S. Su, and L. S. Bartell, *Inorg. Chem.*, 1975, **14**, 599.

free P_2F_4 is readily understood with reference to Figure 2 where the frontier orbitals of the unit are shown schematically. Whereas both P–P bonding orbitals are occupied, only one of the antibonding orbitals is occupied. The observed bond length is that of a standard P–P single bond. In the $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$ complex [Figure 1(*c*)] all four of these orbitals [shown in energetic terms in Figure 1(*d*)] are depressed to lower energy and two electrons are transferred from the $Fe_2(CO)_6$ unit to this unoccupied P–P antibonding orbital. The net result is that the description of the iron becomes formally Fe^I and the occupation of the P–P antibonding orbital accounts for the increase in P–P distance in the complex compared to the free ligand. The dramatic shift of the P_2F_4 orbitals to lower energy (shown in qualitative terms in Figure 1) compared to the energy changes involved in metal–metal bond formation *via* overlap of the frontier Fe orbitals [Figure 1(*a*) and (*b*)] shows that the two $Fe(CO)_3$ units are held together more by strong Fe–P interactions rather than the direct Fe–Fe forces. In terms of bond-overlap populations, that between Fe and P is between one and two orders of magnitude larger than that between the two metal atoms. (That the M–P interactions are larger overall than M–M is quite expected, if only on the basis of the relative M–P and M–M distances.)



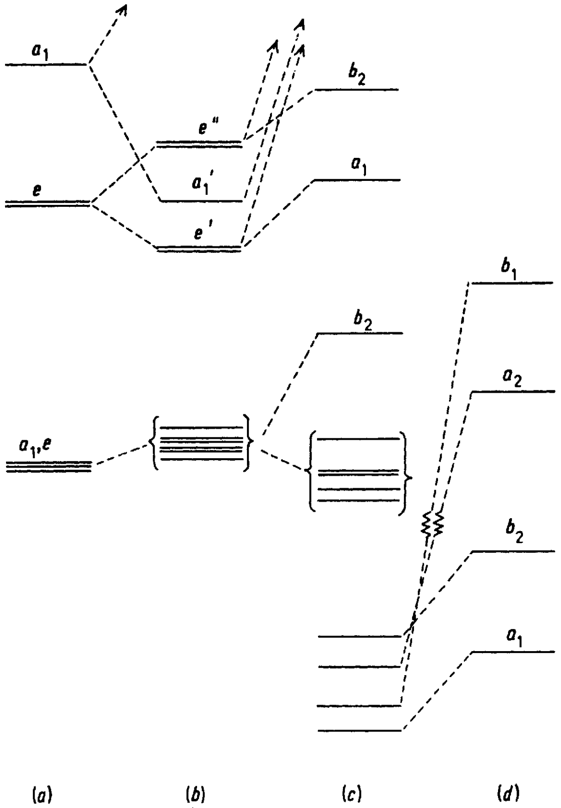


FIGURE 1 Fragment-formalism analysis of the m.o. structure of $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$: (*a*) frontier orbitals of the $Fe(CO)_3$ moiety; (*b*) two $Fe(CO)_3$ units combined to give $Fe_2(CO)_6$, the atoms occupying the same positions in space as in the $[Fe_3(CO)_6(\mu\text{-}PF_2)_2]$ molecule; (*c*) the result of interaction of the orbitals of (*b*) and (*d*), the frontier orbitals of the $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$ molecule; (*d*) the frontier orbitals of an eclipsed P_2F_4 molecule, the atoms occupying the same positions in space as in the $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$ molecule

The *d*-orbital region of the m.o. diagram thus consists at lowest energy of a group of five orbitals associated with the $Fe(CO)_3$ units. These (mainly *d*) orbitals [shown with a brace in Figure 1(*c*)] are oriented unfavourably with respect to either M–P or M–M overlap and thus remain approximately equienergetic from 1(*a*) to 1(*c*). Lying just above this group is a single orbital derived from one group of orbitals located poorly for M–M but better for M–P overlap. To higher energy lie two orbitals derived from the M–M bonding (*e'*) and antibonding (*e''*) of the asymmetrically sited P_2F_4 unit. The other components of these *e'* and *e''* orbitals are pushed to much higher energy. The resulting m.o. picture is very similar to that recently produced by Teo *et al.*[8] using a more sophisticated m.o. model. As pointed out by Hoffmann and his co-workers,[14] the description and occupation of the valence orbitals of the $M(CO)_3$

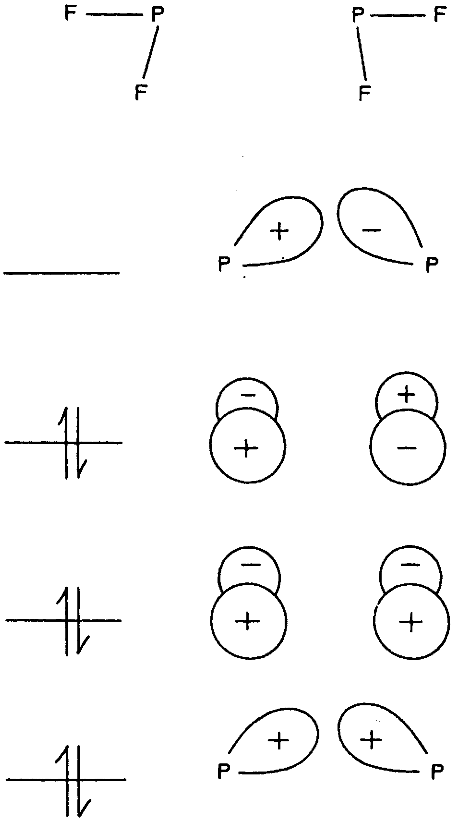


FIGURE 2 Frontier orbitals of the P_2F_4 unit with a geometry identical to that observed in the complex, showing occupation of both the P–P bonding orbitals and of one of the P–P antibonding orbitals

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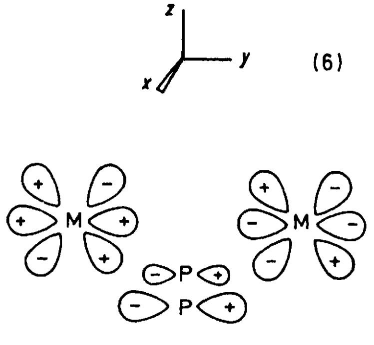
[14] J. W. Lauher and R. Hoffmann, *J. Amer. Chem. Soc.*, in the press.

fragment are very similar to the orbitals of the $M(C_5H_5)^-$ fragment (they are isolobal). Thus all the m.o. arguments described here for the carbonyl systems carry over directly into the two known $[M_2(C_5H_5)_2(\mu\text{-}PX_2)_2]$ systems of Table 1 in a qualitative fashion. However, quantitatively we would expect to find different amounts of mixing between *d,s*, and *p* orbitals.

The structure of the diagram of Figure 1 suggests that three series of molecules might be expected to exist. (*i*) With 12 '*d*' electrons (32 valence electrons), the lowest-energy group of six *d* orbitals will be filled. There are no structural data on possible examples of this type, however, but the e.a.n. rule would predict an M=M double bond. The present calculations suggest a M–M non-bonding situation with occupation equally of M–M bonding and antibonding orbitals. (*ii*) With 14 *d* electrons (34 valence electrons), two electrons will occupy the M–M bonding orbital (a_1). The vast majority of the molecules in Table 1 fall into this category as does our model compound $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$ and the analogue $[Co_2(C_5H_5)_2(\mu\text{-}PPh_2)_2]$. On electron counting, an M–M single bond is predicted and indeed Figure 1 shows double occupation of an M–M (π-type) bonding orbital. (*iii*) With 16 electrons (36 valence electrons), two electrons will occupy the M–M antibonding orbital (b_2). No formal M–M bond exists. Structural data are only available for one example of this class, $[Ni_2(C_5H_5)_2(\mu\text{-}PPh_2)_2]$ (Table 1), although electrochemical reduction of $[M_2(CO)_6(\mu\text{-}PR_2)_2]$ species indicates that similar phosphido-bridged carbonyl analogues exist.[15]

One interesting point is that the orbitals comprising the HOMO and LUMO of the 34-electron series are mainly metal located. Dessy *et al.*[16] initially concluded from experimental evidence that these orbitals were mainly bridging-ligand based, a claim not substantiated by this or other theoretical work. The variation in energy of the valence orbitals as the angle θ is adjusted is shown in Figure 3, where the behaviour of all the *d* orbitals of Figure 1(*c*) is shown. We may readily see that the 36-electron system should strongly favour $\theta = 180°$ due to the overwhelming energy change on distortion associated with the higher-energy b_2 orbital. This is antibonding both between M and P and between M and M, (6). The rapid stabilisation for $\theta \longrightarrow 180°$ can be traced to (*i*) reduced M–M repulsion arising from the out-of-phase overlap of $d_{x^2-y^2}$ and (*ii*) reduced out-of-phase overlap (becoming zero at $\theta = 180$) between M d_{yz} and P p_y orbitals. The $\theta = 180°$ situation is that found for $[Ni_2(C_5H_5)_2(\mu\text{-}PPh_2)_2]$. Previous rationalisations of this geometry have generally only emphasised the effect of metal–metal interaction in this orbital. The effect of the metal–phosphorus interaction is in the same direction. The energy change associated with the next lowest (a_1) orbital is smaller and in the opposite direction to this b_2 orbital. This arises from the fact that whilst it is M–P antibonding it is M–M bonding. Thus increasing θ decreases M–P repulsions, but also reduces M–M overlap, (7).



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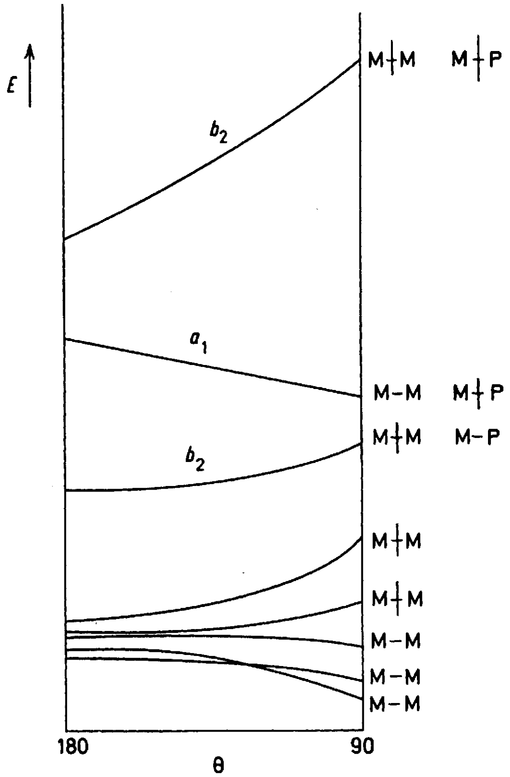
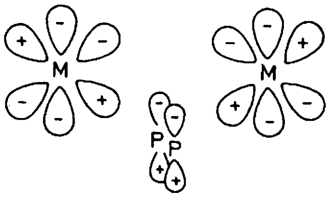


FIGURE 3 Energy behaviour with θ, the hinge angle of the (predominantly) metal *d* oribtals in Figure 1(*c*). A–B and A + B represent respectively bonding and antibonding between the atoms A and B



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Hence M–P and M–M interactions operate energetically in opposite directions in this orbital. As we shall see below, this balance is important in determining the actual geometry adopted in these systems.

For molecules with 34 electrons we therefore expect to see a value of θ much less than 180°. For all of the systems in Table 1 we see values ranging from 88 to 124°. The e.a.n. rule requires an M–M single bond for this configuration and indeed the orbital depicted in (7) is the one responsible for the M–M 'bent' bond shown in (4). The m.o. description of this orbital is close to that described by Teo *et al.*[8] and consists mainly of d_{z^2} (-0.22), $d_{x^2-y^2}$ (0.19), and d_{yz} (0.40). This combination leads to a build-up of electron density in the region opposite the P_2F_4 unit and thus a bonding interaction between the two Fe atoms as in (4).

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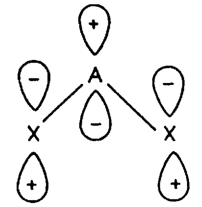
[15] R. E. Dessy and L. A. Bares, *Accounts Chem. Res.*, 1972, **5**, 415.

[16] R. E. Dessy, A. L. Rheingold, and G. D. Howard, *J. Amer. Chem. Soc.*, 1972, **94**, 746.

For the 32-electron systems the calculated energy changes on distortion are modest compared to those for the 34- and 36-electron systems. The minimum in this rather softer potential surface lies somewhere between the small values of θ found for the 34-electron molecules and 180°. Figure 3 indicates that the M–M bond order for this configuration is close to zero. The requirements of the e.a.n. rule might have led us to demand a M=M double bond, however, with a short M–M distance and to expect a much harder potential surface.

We return to the rather interesting case of the 34-electron molecules where we have seen that the equilibrium Fe–Fe distance and θ are set by the mutual balance of Fe–Fe attractive and Fe–P repulsive forces in the HOMO. How then do we expect the equilibrium value of θ to change with the nature of the ligands attached to the phosphorus atoms, particularly between the CF_3 and Me, H, or Ph substituted molecules? Steric factors do not seem to be important in determining the M–M and M–P distances. With a variety of hydrocarbon ligands of differing steric requirements attached to the phosphorus atom, only rather small changes are observed in θ and the Fe–Fe distance. In the recent m.o. study by Teo *et al.*[8] the energy levels and orbital characters were also found to be relatively insensitive as to whether the phosphorus substituents were Me, H, or Ph. The well known high electronegativity of CF_3 compared to Me, H, Ph, and all the other non-fluorine containing substituents suggests that the reason for the dramatic structural change on fluorine substitution may lie here. The C–P–C angle of 86° in the CF_3-substituted species compared to the just less than tetrahedral angle in $[Fe_2(CO)_6\{(\mu\text{-}OH)(\mu\text{-}P[C_6H_4Me\text{-}p]_2)\}]$ and related species[17,18] underlines this point and indicates rather significant structural substituent effects at P. The only major difference between the CF_3-substituted species and those containing Me, H, or Ph is that the M–M distance and flap angle θ are increased in the former *via* the hinging distortion (5) which we have specifically examined above.

We first make use of a series of experimental results on the AX_2 systems (A = N or P; X = F or Cl) in order to obtain some idea of the m.o. structure of these fragments. The e.s.r. spectra of these 19-electron radicals have been studied[19,20] in inert-gas matrices and the spin distribution of the odd electron has been calculated from nuclear hyperfine splittings. The out-of-plane orbital containing this electron is given in (8) and it was found that the amount of spin density on the A atom was very sensitive to the electronegativity difference between A and X. For PF_2 the orbital containing the odd electron was almost pure P 3*p* in character (91% P, 4.5% F), whereas for NCl_2 with a much smaller electronegativity difference the molecular orbital contained much less N 2*p* character (57% N, 21.5% Cl). We expect similar m.o. descriptions to apply to the AX antibonding in-plane orbitals as a function of electronegativity difference. (*i.e.* Whereas the AX bonding orbitals contain a larger amount of character from the electronegative substituent orbitals, the opposite is true for the AX antibonding orbitals. Also the antibonding orbitals contain more character from the less electronegative atom the larger the electronegativity difference.) These simple m.o. ideas are probably obvious but it is very gratifying to have in these cases firm experimental support of them. It is one of these in-plane P_2F_4 orbitals which is involved in the balance shown schematically in (7). As the electronegativity of X increases the amount of P 3*p* character in this orbital increases leading to larger Fe(*d*)–P(*p*) repulsions (a larger negative overlap population in m.o. terms). A larger value of θ and hence a longer Fe–Fe distance in the CF_3 complex compared to the Me or Ph analogues of Table 1 is the result.



(8)

At the quantitative level the calculated hinge angle as a function of electronegativity of the ligand X is shown in Table 2. The observed trend is reproduced numerically; smaller angles than observed are however found for the situation with no 3*d* orbitals on phosphorus, and larger angles than observed when these 3*d* orbitals are included. [Of course one does not know how good the P 3*d* parametrisation is. Using these particular values (see Appendix) the *g* tensor components of PF_2 were also overestimated whereas when *d* orbitals were ignored the values were underestimated.[20]] The effect of including 3*d* orbitals on the phosphorus atom is to increase the contribution of the P 3*p* orbital in the HOMO, thus increasing Fe–P repulsions and increasing the Fe–Fe distance and hinge angle (see above).

TABLE 2

Calculated hinge angles in model calculations[a] in $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$

Fluorine ionization energy/eV	F–P–F angle/°	Hinge angle/°	
		With P 3*d*	Without P 3*d*
17.42	95[b]	125[c]	108[c]
15.42	103	118	105
13.42	110	111	102

[a] The results give an idea of the trends to be expected as the structural characteristics of the system are changed. [b] These parameters correspond to a real F atom and an F–P–F angle close to the C–P–C angle observed (97°) in $[Fe_2(CO)_6(\mu\text{-}CF_3)_2]$. [c] Observed hinge angle in $[Fe_2(CO)_6(\mu\text{-}CF_3)_2]$ is 118°.

This should be accompanied by a decrease in the Fe–P distance on fluorine substitution since the increase of P 3*p* character in the relevant orbitals should lead to an overall increased Fe–P overlap population *via* the Fe–P bonding orbitals. The observed contraction from 2.217(1) (X = Me or Ph) to 2.194(1) Å (X = CF_3) is thus significant [Δ = 0.023(2) Å]. Similar contractions occur between the X = CF_3 and other X = H, Me, or Ph molecules. This Fe–P contraction on fluorine substitution should, taken on its own, result in a more compact structure with a concomitant shortening of the Fe–Fe distance. (Alternatively, if the M–M distance is kept fixed, θ should open up to compensate for this change in M–P length.) If the geometry were primarily determined by M–M bonding effects as most previous studies have indicated then, on the basis of the e.a.n. rule, only small changes in θ should be the result

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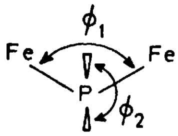
in this 34-electron series when the bridging substituents are changed. The dramatic change in geometry when an H atom three bonds away from the M–M region is replaced by an F atom is very striking. In a similar argument the angle θ *should* decrease as the electronegativity of the bridging atom A increases. Interestingly, we find in the Group 5 series that θ decreases in the order As (125) > P (100—119) > N (88—104°), which is also the order of increasing electronegativity.

Finally, it is interesting to note that use of the tangent-sphere ideas of Bent [21] or Mulliken's isovalent hybridisation concept [22] leads to a predicted substituent effect in the correct direction.* Within the PX_2 unit the more electronegative substituent has a higher demand for P 3*p* character. This leaves more phosphorus 3*s* character for bonding to the Fe atoms for $X = CF_3$ compared to X = Me, H, *etc.* A smaller angle ϕ_1 [(9)] and larger ϕ_2 is the result. The observed C–P–C (ϕ_2) angle of 96° for $X = CF_3$ compared to the near-tetrahedral angle [18] for X = Me or Ph meshes nicely with the opening up of ϕ_1 on fluorine substitution. Such an argument would also support shorter Fe–P bond lengths for $X = CF_3$ (more *s* character) than for X = Me, Ph, *etc.* as is observed.



(9)

DISCUSSION

The results presented above indicate that at least two factors contribute to the gross structural features of these complexes. Both metal–metal and metal–A interactions are present and the overall geometry is a balance between the two. The recent crystal structure determination of $[Fe_2(CO)_6\{\mu\text{-}P(CF_3)_2\}_2]$ with a much longer Fe–Fe distance compared to that in non-fluorine-containing analogues has brought to our attention the fact that M–P and in general M–A interactions may be much more important in determining geometries than previously thought. Our m.o. results bear this out in several ways. First, the changes in energy of the accessible molecular orbitals on forming $Fe_2(CO)_6$ from two $Fe(CO)_3$ units are much smaller than the energy changes when P_2F_4 is introduced into the latter structure. Secondly, the size of the M–P overlap population is generally an order of magnitude larger than that of the M–M population in these systems. For example, with a hinge angle of 118° and an M–M distance of 2.8 Å the bond-overlap population for each Fe–P link is 0.26 and for the Fe–Fe link is 0.049. Both of these observations should not be too surprising given the geometrical location of the M and A atoms. However, thirdly, the changes in M–A overlap population on distortion are larger than those associated with M–M interactions. Thus the two iron atoms are more strongly held together *via* the Fe–P linkages than through direct interaction. Lastly, the minimum-energy geometry of the A_2M_2 ring is particularly sensitive to the electronegativity of the A atom substituents and the geometry around the A atom.

APPENDIX

The Extended Hückel calculations were performed, using the methods developed by Hoffmann,[10,11] on the University of Newcastle-upon-Tyne's IBM 360/67 and 370/169 computers. Orbital exponents and diagonal matrix elements are shown in the Table. The same values for the transition-metal centre were used irrespective of the nature of the metal. Interatomic distances were as follows: Fe–C 1.80; C–O 1.13; P–F 1.6; and Fe–P 2.19 Å.

		Exponent	Diagonal matrix element (eV)
Fe	3*d*	2.600	−11.67
	3*s*	0.970	−9.75
	3*p*	0.970	−5.89
C	2*s*	1.625	−21.40
	2*p*	1.625	−11.40
O	2*s*	2.275	−32.30
	2*p*	2.275	−14.80
P	3*s*	1.600	−18.60
	3*p*	1.600	−14.00
	3*d*	1.100	−2.50
F	2*s*	2.600	−42.51
	2*p*	2.600	−17.42

The C–M–C angles were set at 90° with all the M–CO units linear. The actual deviations from regularity are in fact small. The F–P–F angle was initially set at 100° but was later varied (see below). The P–Fe–P angles were fixed at 83.4° (the observed value in $[Fe_2(CO)_6\{\mu\text{-}P(CF_3)_2\}_2]$). The dihedral angle θ in (5) was systematically varied. The electronegativity variation in the phosphorus substituents was simulated by increasing or decreasing the F-atom diagonal matrix element by 2 eV.† In addition the F–P–F angle was also varied to simulate the observed behaviour on moving from the Me compound (C–P–C just less than tetrahedral) to the CF_3 analogue (C–P–C 96.8°). Decreasing the F–P–F angle or increasing the F 2*p* diagonal matrix element led to energy minima at larger values of θ (*i.e* longer M–M distances). The angle θ was more sensitive to variations in the bond angle than to variations in the substituent electronegativity. Both factors will, of course, change the hybridisation demands around the P atom.

We have not quoted values of orbital energies and detailed m.o. descriptions in this paper but have used the Extended Hückel Method as a vehicle with which to view the bonding situation in more detail than provided by symmetry arguments alone. We take to heart Mason and Mingos' comment [23] that ' the prospect of carrying out realistic molecular-orbital calculations designed to comment upon the extent of involvement of individual ligand orbitals in the various bridge orbitals ' is poor, but simply point out that the experimental changes in θ on variation of the electronegativity of the bridging atom substituents is matched qualitatively by the theory.

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* This has also been suggested in a personal communication to R. C. Dobbie from L. F. Dahl (July 1974).

† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

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