Journal of Organometallic Chemistry, 327 (1987) 365–377
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STRUCTURE AND ELECTRON COUNTING OF TETRAHEDRAL AND BUTTERFLY M_2E_2 CLUSTERS: AN MO ANALYSIS OF $(L_nM)_2(\mu\text{-}X_2)$ $(X = P, PR, PM'L_5)$ COMPLEXES

J.-F. HALET and J.-Y. SAILLARD

Laboratoire de Cristallochimie, U.A. au C.N.R.S. no. 254, Campus de Beaulieu,
35042 Rennes Cedex (France)

(Received December 30th, 1986)

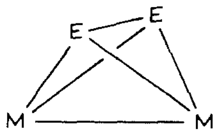
Summary

M_2E_2 clusters where both M and E are in a local conical coordination adopt a tetrahedral structure if they have six skeletal electron pairs (SEP). For a 5 SEP count, two different geometries are observed: a "contracted" tetrahedron such as $Fe_2(CO)_6(\mu\text{-}C_2\text{-t-Bu})_2$ or a butterfly structure such as $Fe_2(CO)_6[\mu\text{-PMnCp(CO)}_2]_2$. By means of extended Hückel calculations on $Co_2(CO)_6E_2$ (E = P, PH, $PCr(CO)_5$, CH, CO) complexes, the criteria determining the choice of one of these two geometries are analysed. In particular, the role of the energy of the π-type frontier orbitals of E is emphasized. The possibility of existence of tetrahedral and butterfly-like M_2E_2 clusters is examined for 5, 6, and 7 SEP counts.

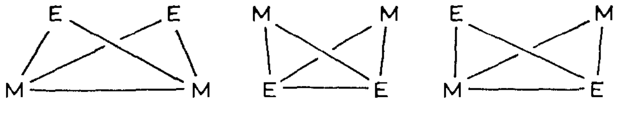
Introduction

It is well known that the transition-metal dimer complexes of the type M_2E_2, where M is a transition metal in local conical environment and E a main-group linear fragment or bare atom, commonly exhibit two types of structure, depending on their electron count. The tetrahedral structure **1** is adopted by electron-precise clusters having six skeletal electron pairs (SEPs) which are organometallic analogs of the well-known tetrahedrane C_4H_4. Numerous examples of six SEP tetrahedral compounds of the type M_2E_2 can be found in the class of dinuclear transition metal complexes with bridging acetylene, of which a typical example is $Co_2(CO)_6(\mu\text{-}C_2\text{-t-Bu}_2)$ [1]. Other representative examples are $Co_2(CO)_5(PPh_3)(\mu\text{-}P_2)$ [2] and its arsenic homologue [2] or $Fe_2(CO)_6(\mu\text{-}S_2)$ and its selenium analog [3]. Within the framework of the Polyhedral Skeletal Electron Pair (PSEP) theory [4], these compounds can be viewed as *nido*-type clusters derived from the trigonal bipyramid with one unoccupied vertex. This theory predicts for a seven SEP count a more open butterfly structure **2**, which can be obtained from **1** by the breaking of one of the six bonds. Structures **2** are of the *arachno*-type, derived from an octahedron with two

0022-328X/87/$03.50



(1)



a b c

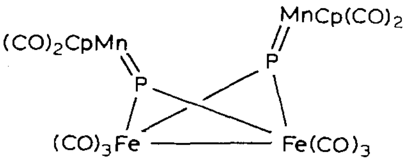
(2)

vertices vacant. Species having structures **2a** and **2b** are more common [5]. Geometry **2c** is often adopted by $M_2(\mu\text{-EE}')$ complexes [6]. An alternative *arachno* structure for 4-vertex 7 SEP clusters is the square geometry that is sometimes observed [7].

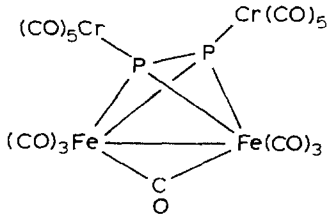
The preference for one of the **2a** and **2b** isomers depends on the respective electronegativities of the M and E groups. For example the dianion $Fe_2(CO)_6Se_2{}^{2-}$, obtained by reduction of $Fe_2(CO)_6(\mu\text{-}Se_2)$, adopts the structure **2a** [8], whereas the replacement of the two $Fe(CO)_3$ groups by two isolobal but more electropositive $Cp(CO)_2Cr$ fragments leads to the structure **2b** [2c].

M_2E_2 clusters with two electrons less than those depicted in **1**, i.e. having five SEPs, exist. Some of these complexes, such as $Fe_2(CO)_6(\mu\text{-}C_2\text{-t-Bu}_2)$ [1] are tetrahedral. This can be derived from their six SEP homologues by the removal of two electrons, creating an electron deficiency at the metal centers, which will, according to the EAN rule, be compensated by the creation of a M=M double bond. A rather short Fe–Fe bond distance is, in fact, observed in $Fe_2(CO)_6(\mu\text{-}C_2\text{-t-Bu}_2)$ (2.32 Å), together with a reorientation of the carbonyl ligands. According to theoretical calculations by Hoffman et al. [9] these structural features favour the Fe–Fe π-bonding.

The butterfly structure **2a** is also observed for compounds bearing 5 SEPs. These compounds satisfy the EAN formalism but are in disagreement with the PSEP rules. Among them is the well-known electron-precise complex $Co_2(CO)_8$ [10] the electronic structure of which has been analysed by Pinhas and Hoffmann [11]. More recently, several $M_2(\mu\text{-EML}_n)_2$ compounds like $Fe_2(CO)_6[\mu\text{-PMnCp(CO)}_2]_2$ (**3**) have been synthesized and characterized by Lang et al. [12].



(3)



(4)

On the basis of comparison of the P–ML_n bond distances in these *arachno*

TABLE 1

SKELETAL INTERATOMIC DISTANCES (Å) IN SELECTED $M_2(EM'L_n)_2$ COMPOUNDS

Compound	M–M	E–E	E–M′	Reference
$Co_2(CO)_6P_2[Cr(CO)_5]_2$	2.565(3)	2.060(5)	2.278	12
$Co_2(CO)_6P_2[Cr(CO)_5][W(CO)_5]$	2.573(1)	2.061(3)	2.361	14
$Fe_2(CO)_7P_2[Cr(CO)_5]_2$	2.605(3)	2.087(6)	2.307	13
$Mo_2Cp_2(CO)_4P_2[Re_2(CO)_6(\mu\text{-}Br)_2]$	3.077(2)	2.093(8)	2.490(4)	15
$[Mo_2Cp_2(CO)_4P_2]_2[Re(CO)_3Br]_2$	3.034(2)	2.071(9)	2.483	15
$Co_2(CO)_4[P(OMe)_3]_2As_2[W(CO)_5]_2$	2.59(2)	2.28(1)	2.60(1)	16
$Mo_2Cp_2(CO)_4As_2[Cr(CO)_5]_2$	3.064(3)	2.310(3)	2.471(3)	17
$Fe_2(CO)_6P_2[MnCp(CO)_2]_2$	2.675(3)	2.523	2.100	12
$Mn_2Cp_2(CO)_2As_2[MnCp(CO)_2]_2$	2.875		2.24	18
$Co(triphos)[\mu\text{-}(\eta^3\text{-}P_3)][Cr_2(CO)_{10}]$		2.124(4)	2.426	19

complexes with those of the related six SEP *nido* tetrahedral molecules [5] such as $Fe_2(CO)_7[\mu\text{-}P_2(Cr(CO)_5)_2]$ [13] (**4**) the authors suggested the presence of $P{=}ML_n$ double bond. Some selected structural data for complexes having an $M_2(E)_2(M'L_n)_2$ framework are shown in Table 1. Our objective in this contribution is to analyse the electronic factors favouring the five versus seven SEP count in the butterfly structure **2a**, and also those favouring structure **1** versus structure **2a** for the five SEP compounds.

Results and discussion

Let us first consider the electronic structure of $Co_2(CO)_6(\mu\text{-}P_2)$ in both tetrahedral (**1**) and butterfly (**2a**) geometries. The corresponding MO interaction diagrams are shown in Fig. 1. The orbital scheme shown on the left for geometry **1** is qualitatively similar to those for $Co_2(CO)_6(\mu\text{-}C_2H_2)$ and $Co_2(CO)_6(\mu\text{-}N_2)$ presented by Hoffmann and co-workers [9,20]. Since each $Co(CO)_3$ or P subunit possesses three frontier orbitals (one of σ and two of π symmetry) [21], both $Co_2(CO)_6$ and P_2 moieties exhibit six frontier orbitals, three bonding and three antibonding combinations. Since in both fragments the interatomic separation corresponds to single bonds, the σ orbital interactions are strong whereas the σ antibonding combinations lie at such high energies that they can be neglected in the interaction. Thus, a set of five orbitals remains on each fragment: one of the σ-type and four (two bonding and two antibonding) of the π-type, namely two a_1, one a_2, one b_1 and one b_2 in the molecular C_{2v} symmetry. As in most of the stable molecules and clusters, the ideal electron count of $Co_2(CO)_6(\mu\text{-}P_2)$ is achieved when all but the antibonding MOs are occupied. There are four antibonding MOs, one of each symmetry, and so the favourable electron count is of 6 SEP, with the ground state configuration $(a_1)^6(a_2)^2(b_1)^2(b_2)^2$.

The interaction diagram corresponding to the butterfly structure **2a** (right side of Fig. 1) can be readily derived from that corresponding to the tetrahedral structure **1**. The only major difference is in the P_2 fragment. In this case, since the $P \cdots P$ separation is large, the b_2-$\sigma^\star$ frontier orbital of this unit falls into the range of the nonbonding orbitals. Its role can no longer be neglected in the interaction with the dimetallic fragment since it will generate a nonbonding cluster skeletal orbital. The appearance of this supplementary non-bonding MO when the P–P bond is opened

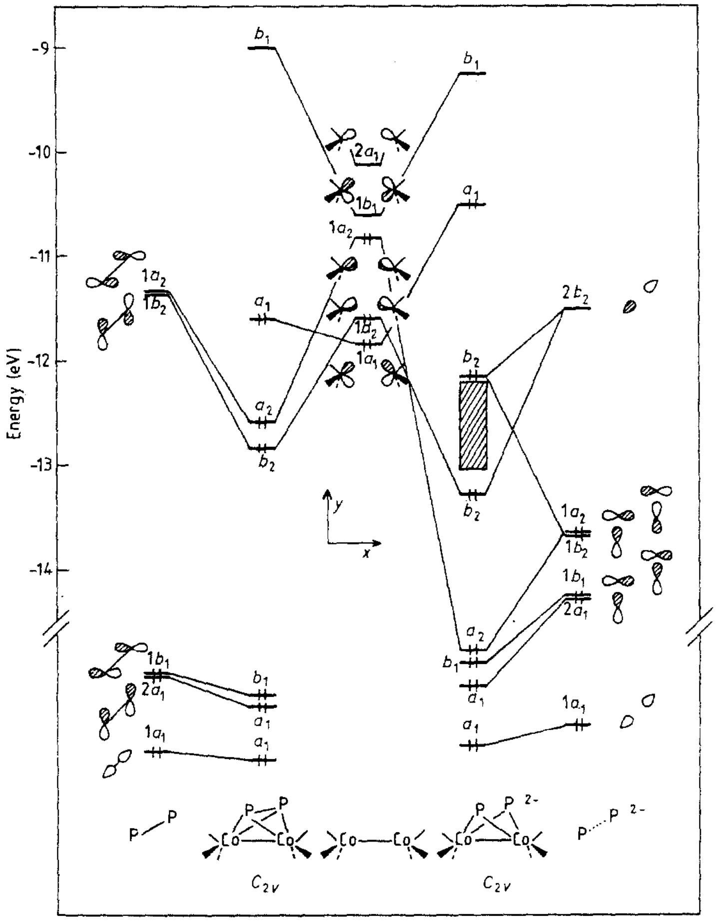


Fig. 1. Interaction diagram for $Co_2(CO)_6P_2$ in the closed and open structures.

increases the electron count to seven SEPs with the configuration $(a_1)^6(a_2)^2(b_1)^2(b_2)^4$.

The MO correlation diagram associated with the opening up of the P–P bond is shown in Fig. 2, together with the variation of the total electronic energies for the three electron counts of five, six and seven SEPs. The main feature of this diagram is the strong stabilization of the b_2 level. This is the stabilization of the $\sigma^\star$ P–P orbital already discussed. Near the end of the transit, this stabilization ceases because of an avoided crossing with a level derived from the P ··· P π-type b_2 frontier orbital.

In keeping with our previous arguments and with the observed structures of the related compounds $Fe_2(CO)_6(\mu\text{-}E)_2^{2-}$ where E = S, or Se, the minimum energy for seven SEPs is found to be that for the butterfly structure [8]. The tetrahedral structure is Jahn-Teller unstable for this electron count but the **1** → **2a** transformation is forbidden by symmetry. One can suggest that the reduction of a six SEP M_2E_2 tetrahedral cluster into a seven SEP butterfly species by cleavage of the E–E bond involves a mechanism more complex than a least motion pathway. This is

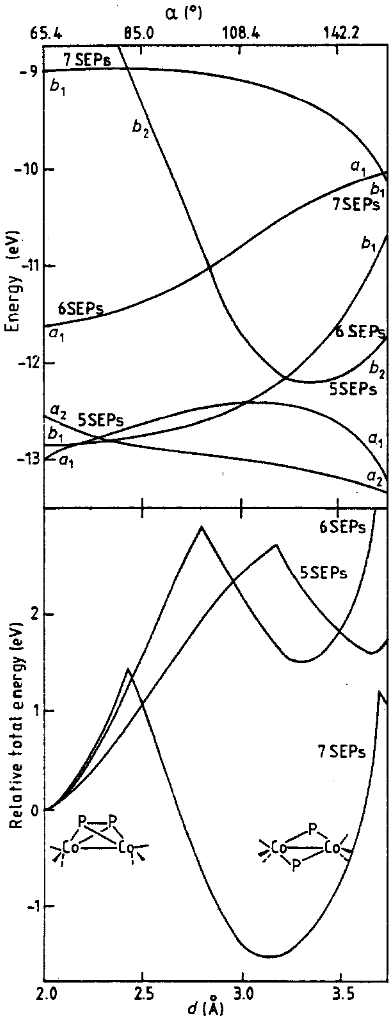
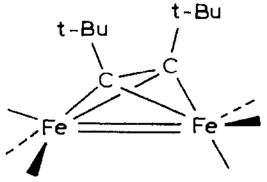


Fig. 2 Walsh diagram for the opening of the P–P vector in $Co_2(CO)_6P_2$. Only the highest occupied and the lowest vacant levels are shown. The total energy curves corresponding to the 5, 6 and 7 SEP counts are shown at the bottom.

consistent with the experimental studies of Weatherill and Rauchfuss on the $[Fe_2(CO)_6(\mu\text{-}E)_2]^x$ ($x = 0$, -2 and $E = S$ or Se) complexes [8b].

Protonation of these seven SEP anionic species gives $Fe_2(CO)_6(\mu\text{-}SH)_2$ [22], the beginning of a route for the preparation of diverse functionally substituted $Fe_2(CO)_6(\mu\text{-}SR)_2$ complexes [23]. In fact an "sp^3"-type hybridization of the sulphur atom is observed in these butterfly compounds, the R group no longer lying in the planes of the wings. $Fe_2(CO)_6(\mu\text{-}SH)_2$ has been shown to be a mixture of three isomers (*a,e*; *e,e* and *a,a*) [24,28]; the *a,e* isomer which is the more abundant in solution, is generally the one observed by X-ray diffraction [24]. Our calculations on the $Co_2(CO)_6(\mu\text{-}PH)_2$ model, where the hydrogen atoms lie in the planes of the wings, gives similar results to those obtained for $Co_2(CO)_6(\mu\text{-}P)_2^{2-}$. Rehybridization of the P atoms by bending the hydrogen atoms out of the Co_2P planes greatly stabilizes the complex. The major contribution to this stabilization comes from the HOMO which is, as in $Co_2(CO)_6P_2^{2-}$ (Fig. 1, right), an antibonding combination of the $1a_1$ orbital of the $Co_2(CO)_6$ fragment and the $2a_1$ orbital of the diphosphorus moiety. The bending of the P–H bonds decreases the overlap between these two frontier orbitals, making the HOMO of $Co_2(CO)_6(\mu\text{-PH})_2$ less antibonding between Co and P.

As expected, structure **1** is found to favour the six SEP count. For five SEPs, there is no Jahn-Teller stable minimum. However, as noticed previously, it is known from the work of Hoffman et al. [9] on $Fe_2(CO)_6(\mu\text{-}C_2R_2)$ complexes that in that case the tetrahedral geometry is stabilized by some structural rearrangements, in particular a shortening of the metal–metal vector and a reorientation of the carbonyl ligands, as observed in $Fe_2(CO)_6(\mu\text{-}C_2\text{-t-Bu}_2)$ (**5**) [1,29]. This rearrangement leads to the vacation of the a_2 skeletal orbital, which is σ M–M antibonding, the skeletal electronic configuration being $(a_1)^6(b_1)^2(b_2)^2$. In order to reconcile this SEP count with the EAN localized scheme **5**, it must be noted that in addition to the five occupied skeletal MOs, there are two other moleculer orbitals of b_2 and a_2 respective symmetry, buried within the "t_{2g} block", which participate in the cluster bonding. The magnitude of the role played by t_{2g} orbitals in the stabilization of **5** is difficult to evaluate by the means of the extended Hückel method. Their importance could be indirectly estimated by more sophisticated calculations on a main group analog of **5**, such as $B_4H_4^{2-}$ whose structure is possibly a distorted tetrahedron (both $B_4H_4^{4-}$ and B_4H_4 are tetrahedral) [30].



(5)

In the case of the 6 SEP $Co_2(CO)_6P_2$ cluster in the normal tetrahedral geometry (Fig. 1, left), the a_2 skeletal orbital lies rather far below the a_1 HOMO (1 eV). A shortening of the Co–Co vector to 2.32 Å and a reorientation of the terminal carbonyl ligands prevents this a_2 orbital going above the a_1 MO. In such a geometry the five SEP count leads to a Jahn-Teller instability, with the a_2 HOMO lying only 0.19 eV below the a_1 LUMO. The same structural reorganization for $Co_2(CO)_6(C_2H_2)$ leads to a HOMO(a_1)–LUMO(a_2) gap of 0.73 eV. Clearly a structure of the type of **5** is unfavourable for a five SEP M_2P_2 cluster.

The difference between the diphosphorus and the acetylene clusters arises mainly from the different electronegativities of P and C. The $3p$ valence AOs of phosphorous lie at lower energy than the $2p$ AOs of C, thus rendering the a_2 skeletal MO more bonding (more stabilized) in the phosphorous case.

If the ideal count is of seven SEPs, for the butterfly geometry of $Co_2(CO)_6(\mu\text{-P})_2$, why does $Co_2(CO)_8$ which has the same structure, possesses only five SEPs? The answer lies in the difference between the two isolobal P and CO groups. The π-type frontier orbitals of CO, which are its $\pi^\star$ LUMOs, lie at a much higher energy than the phosphorus $3p$ atomic orbitals. It follows that their a_1, a_2, b_1 and b_2 bonding

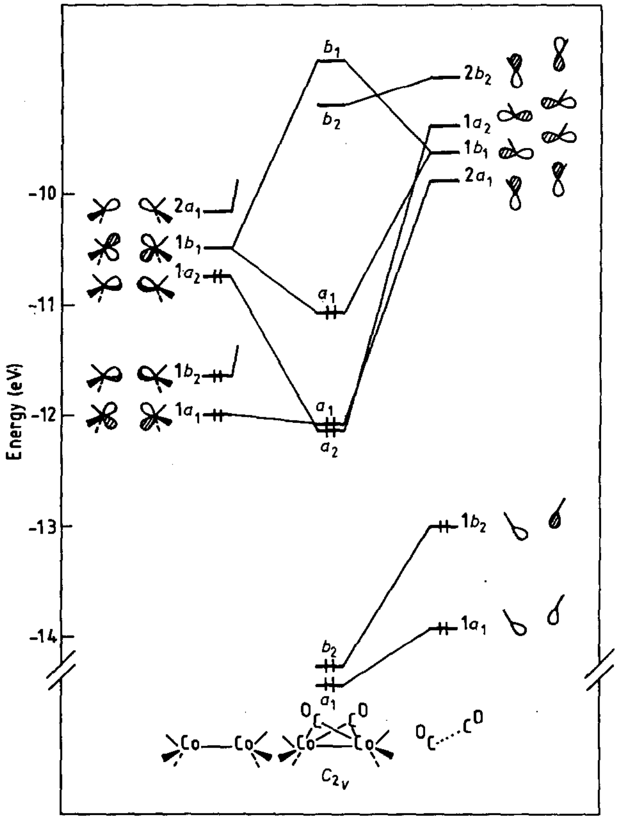


Fig. 3. Interaction diagram for $Co_2(CO)_6(\mu\text{-}CO)_2$.

and antibonding combinations in the OC ··· CO moiety also lie at a much higher energy than their P ··· P homologs. In particular, in the case of E = CO, the a_1 and b_2 components are unable to generate low-lying MOs, and consequently the number of occupied skeletal MOs of a_1 and b_2 is of one unity less than when E = P, the skeletal electronic configuration being $(a_1)^4(a_2)^2(b_1)^2(b_2)^2$ (see Fig. 3).

The MO correlation diagram corresponding to the transit **1** → **2a** for the octacarbonyldicobalt complex is represented in Fig. 4, together with the variation of the total energy for the different electron counts of five, six and seven SEPs. The main difference from Fig. 2 is the absence of the descent of the b_2 antibonding σ(C–C) level during the OC–CO cleavage. Indeed, this level still correlates with the b_2 MO derived from π-type CO frontier orbitals, which remain at high energy as we said before. In agreement with experiments and other calculations, we found $Co_2(CO)_8$ to be stable in the butterfly structure ($\alpha \sim 130°$). The tetrahedral structure favours the six SEP count while the seven SEP count leads to a Jahn-Teller instability over the whole transit. At this point of the discussion, we must mention that $Co_2Cp_2(\mu\text{-}NO)_2$ [26] an isoelectronic compound of $Co_2(CO)_8$ exhibits a planar rhombohedral structure ($\alpha \sim 180°$). Theoretical explanations have been advanced by several authors [11,27].

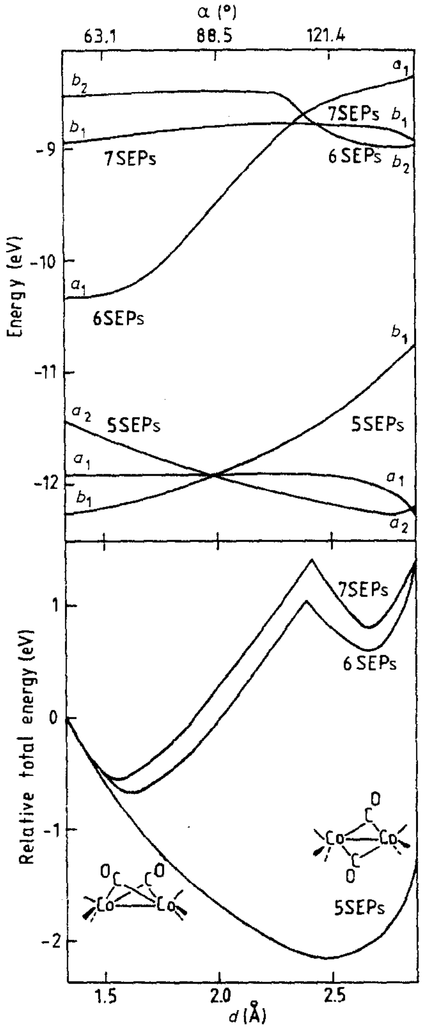


Fig. 4. Walsh diagram and total energy curves for the opening of the OC–CO vector in $Co_2(CO)_8$.

From Fig. 4 it can be seen that a planar or near planar geometry is also favoured for the four SEP count with a configuration $(a_1)^4(a_2)^2(b_2)^2$. This is, in fact, found to be the case for $Co_2Cp_2(\mu\text{-}CO)_2$ [28], which has recently been theoretically investigated [11b,27].

Before considering the transit **1** → **2a** for $Co_2(CO)_6[PCr(CO)_5]_2$, we consider the differences between the P–Cr(CO)$_5$ fragment and a phosphorus atom or a phosphinidene group. The frontier orbitals of this fragment built up with the P and the $Cr(CO)_5$ subunits are shown in Fig. 5. There is little difference between the σ-type frontier orbital of P and P–Cr(CO)$_5$. In P–Cr(CO)$_5$ this orbital is mainly composed of the phosphorus P-σ AO with some *s* character, but without any significant participation of the $Cr(CO)_5$ orbitals. This is not the case for the π-type MOs. The *e* *p*π AOs interact strongly with the *e* components of the $Cr(CO)_5$ "t_{2g}" set [21]. There is also a secondary interaction with a low lying *e* set of carbonyl levels having some

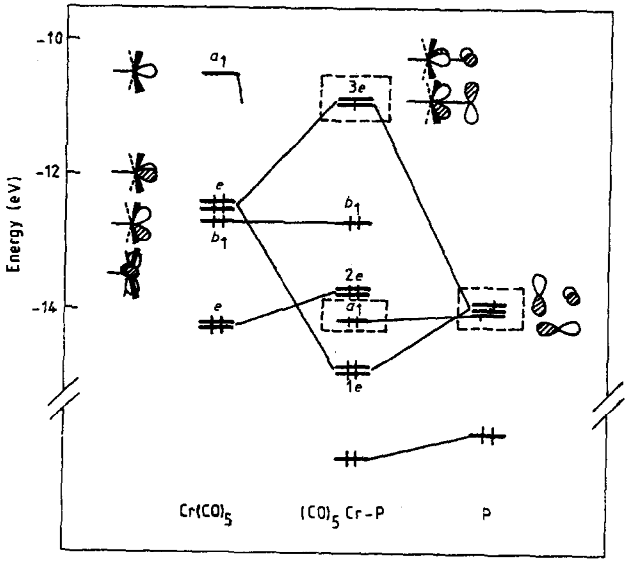


Fig. 5. Frontier orbitals for the P-Cr(CO)$_5$ fragment.

metal d_π character. Despite the fact that there is only ~ 40% phosphorus localization, the 3e level can be considered as the principal set of π-type frontier orbitals of P-Cr(CO)$_5$ because of their close proximity in energy to the Co(CO)$_3$ frontier orbital (in our calculations on the Co$_2$(CO)$_6$[P-Cr(CO)$_5$]$_2$ cluster, the 1e and 2e set

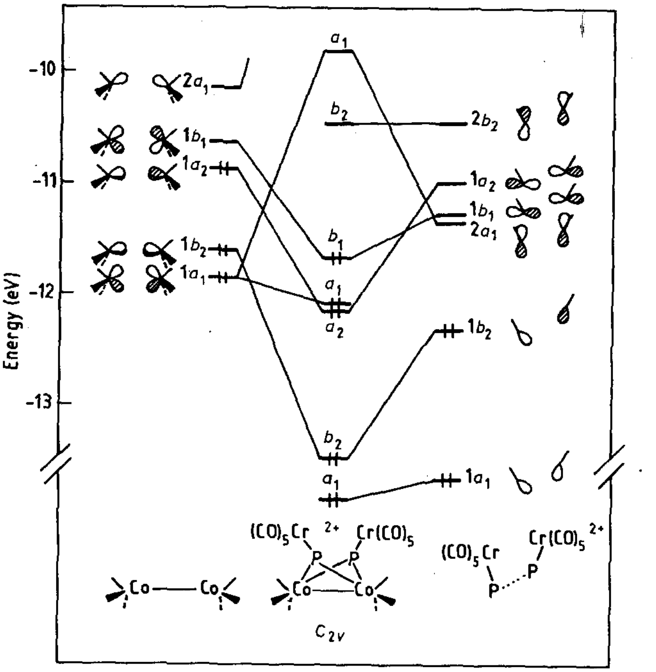


Fig. 6. Interaction diagram for Co$_2$(CO)$_6$[μ-P-Cr(CO)$_5$]$_2$.

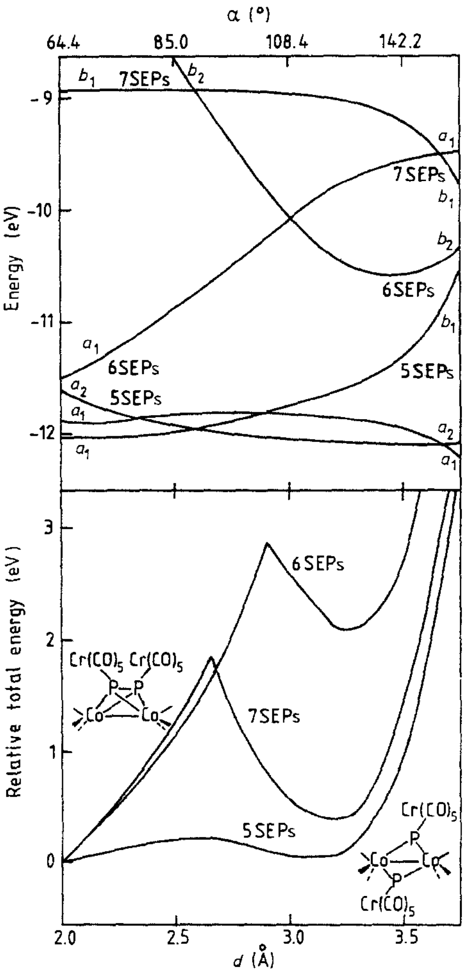


Fig. 7. Walsh diagram and total energy curves for the opening of the P–P vector in $Co_2(CO)_6[PCr(CO)_5]_2$.

of P–$Cr(CO)_5$ play a minor role by second-order mixing into 3*e*, increasing its P localization). It is important to note that the energy of the π-type frontier orbitals is intermediate between those of P and CO. Having identified the P–$Cr(CO)_5$ FMOs, it is easy to generate the six bonding and antibonding combinations of $(CO)_5Cr \cdots P\text{–}Cr(CO)_5$ and from there to analyse the interaction MO diagram of $Co_2(CO)_6[P\text{–}Cr(CO)_5]_2$ in the butterfly geometry, which is shown in Fig. 6. From this diagram it can be seen that the situation is intermediate between $Co_2(CO)_6P_2$ (Fig. 1) and $Co_2(CO)_8$ (Fig. 3). Both five and seven SEP counts seem possible for the butterfly geometry. This is clearer from Fig. 7, where the MO correlation and total energy curves during the transit **1** → **2a** of $Co_2(CO)_6[P\text{–}Cr(CO)_5]_2$ are shown. As for $Co_2(CO)_6P_2$, the σ^* P–P antibonding b_2 correlates with an MO that is mainly composed of the P–$Cr(CO)_5$ π frontier orbitals. Since these orbitals are rather high in energy (vide supra), the lowering of the b_2 level in Fig. 7 is less pronounced than in the $Co_2(CO)_6P_2$ case and there is no b_1–b_2 crossing. The conclusion is that whereas for the six and seven SEP counts the electronic behaviour of $Co_2(CO)_6[P–Cr(CO)_5]_2$ is similar to that of $Co_2(CO)_6P_2$, this is not the case for five SEPs. For this electron count, as for $Co_2(CO)_8$, the total energy curve does not show any discontinuity (the ground state configuration being $(a_1)^4(a_2)^2(b_1)^2(b_2)^2$ all over the transit). However, in contrast to that for $Co_2(CO)_8$, this curve reveals two shallow minima of almost equal energies separated by a small barrier of about 0.15 eV. At our level of calculations this energy barrier is not significant, and it is better to regard the curve as almost flat over a large range of P · · · P distances (2.00–3.20 Å). The observed experimental P · · · P distances in this kind of complex are, in fact, close to 2.52 Å, indicating some retention of the P–P bonding [25a]. The tetrahedral structure, in which the P–P separation is 2.06 Å, is Jahn-Teller unstable, as for $Co_2(CO)_6P_2^{2+}$. Also as for $Co_2(CO)_6P_2^{2+}$ and for the same reason, the a_2 skeletal MO lies significantly below the a_1 LUMO. When the structural reorganization of the type of **5** is applied (Co–Co 2.32 Å) the a_2 skeletal orbital effectively becomes the LUMO but is only 0.16 eV above the a_1 LUMO. Here again the tetrahedral geometry is disfavoured for the 5 SEP count.

Conversely, for an open structure the HOMO–LUMO gap is increased and some stabilization is achieved by shortening the P–Cr vector. Indeed, the b_2 LUMO, made up of π-type $3e$ P–Cr(CO)$_5$ frontier orbitals, is π-antibonding between P and Cr, and so is destabilized by the P–Cr shortening, whereas its low-lying occupied b_2 bonding counterpart, derived from $1e$ frontier orbitals of P–Cr(CO)$_5$, is stabilized. A similar but weaker effect of the P–Cr shortening can be traced to the a_2 MOs derived from the $3e$ and $1e$ frontier orbitals of P–Cr(CO)$_5$. Clearly, for the five SEP count, an open geometry with short P–Cr bond distance is the only possible one, stable both on the thermodynamical and the Jahn-Teller points of view.

Conclusion

The possibility of existence of 5 SEP butterfly electron precise M_2E_2 clusters requires a high energy for the $2a_1$ and $2b_1$ frontier orbitals of the E · · · E fragment. Such a situation arises when the E bare atom or conical fragment has its π-type frontier orbitals lying at high energy; this is the case, for example, when E = CO. (It should also be noted that electron precise M_2E_2 butterflies exist for non-conical E groups such as PR_2, NR_2 or $P{=}CR_2$ [31]. These planar units possess only one π-type frontier orbital, and consequently the $2a_1$ and $2b_2$ levels of the E · · · E fragment are absent in these complexes, leading to the same situation as that mentioned above.)

When the π-type frontier orbital of E are low lying, the butterfly structure is favoured for a 7 SEP count, in agreement with the PSEP theory. Nevertheless the 5 SEP count is possible, but only if E is not too electronegative. The corresponding structure is then tetrahedral, of the type of **5**. In some intermediate cases both (tetrahedral type **5** and butterfly) structures should be possible. However in the case of $Co_2(CO)_6[P–Cr(CO)_5]_2$ [27] our calculations show that a structure of the type of **5** is unlikely to exist, the more stable open geometry gaining some additional stability by conjugation with the π-type systems of the Cr(CO)$_5$ units.

Appendix

All the calculations were carried out within the extended Hückel formalism [32] using the weighted H_{ij} formula [33]. The utilized atomic parameters are summarized

TABLE 2

EXTENDED HÜCKEL PARAMETERS

Orbital		H_{ii} (eV)	Exponents [a]	
			ζ_1	ζ_2
H	1*s*	−13.60	1.30	
C	2*s*	−21.40	1.625	
	2*p*	−11.40	1.625	
O	2*s*	−32.30	2.275	
	2*p*	−14.80	2.275	
P	3*s*	−18.60	1.60	
	3*p*	−14.00	1.60	
Cr	4*s*	−8.66	1.70	
	4*p*	−5.24	1.70	
	3*d*	−11.20	4.95 (0.4876)	1.60 (0.7205)
Co	4*s*	−9.21	2.00	
	4*p*	−5.29	2.00	
	3*d*	−13.18	5.35 (0.5551)	1.90 (0.6461)

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

in Table 2. When possible, geometrical models used for calculations were based on X-ray structures (ref. 12 for $Co_2(CO)_6P_2$ and $Co_2(CO)_6[PCr(CO)_5]_2$; ref. 1 for $Co_2(CO)_6(CH)_2$; ref. 10 for $Co_2(CO)_8$). In all the calculations the following bond distances (Å) were used: P–Cr 2.20; Co–C(O) 1.80; Cr–C(O) 1.85; C–O 1.15 (terminal), 1.20 (bridging); P–H 1.41; C–H 1.09.

References

1 F.A. Cotton, J.D. Jamerson and B.R. Stults, J. Amer. Chem. Soc., 98 (1976) 1774.

2 C.F. Campana, A. Vizi-Orosz, G. Palyi, L. Markó and L.F. Dahl, Inorg. Chem., 18 (1979) 3054.

3 C.F. Campana, F. Yip-Kwai Lo and L.F. Dahl, Inorg. Chem., 18 (1979) 3060.

4 K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 1; K. Wade in B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, New-York, 1980, p. 193; D.P.M. Mingos, Acc. Chem. Res., 17 (1984) 311.

5 (a) O.J. Scherer, Angew. Chem. Int. Ed. Engl., 24 (1985) 924 and references therein; (b) D. Fenske and K. Merzweiler, Angew. Chem. Int. Ed. Engl., 25 (1986) 338; (c) L.V. Goh, C. Wei and E. Sinn, J. Chem. Soc., Chem. Commun., (1985) 462; (d) D.J. Jones, T. Makani and J. Rozière, J. Chem. Soc., Chem. Commun., (1986) 1275.

6 See for example A.J. Carty, Pure & Appl. Chem., 54 (1982) 113 and references therein.

7 (a) A.J. Carty, N.J. Taylor and W.F. Smith, J. Chem. Soc., Chem. Commun., (1978) 1017; (b) H. Patin, G. Mignani, A, Benoit, J.-Y. La Marouille and D. Grandjean, Inorg. Chem., 20 (1981) 4351.

8 (a) D. Seyferth, R.S. Henderson and L.-C. Song, Organometallics, 1 (1982) 125; (b) T.D. Weatherill, T.B. Rauchfuss and R.A. Scott, Inorg. Chem., 25 (1986) 1466.

9 D.M. Hoffman, R. Hoffmann and C.R. Fisel, J. Amer. Chem. Soc., 104 (1982) 3858.

10 G. Gardner Sumner, H.P. Klug and L.E. Alexander, Acta Cryst., 17 (1964) 732.

11 (a) D.L. Thorn and R. Hoffmann, Inorg. Chem., 17 (1978) 126; (b) A.R. Pinhas and R. Hoffmann, Inorg. Chem., 18 (1979) 654.

12 H. Lang, L. Zsolnai and G. Huttner, Angew. Chem. Int. Ed. Engl., 22 (1983) 976.

13 H. Lang, G. Huttner, L. Zsolnai, G. Mohr, B. Sigwarth, U. Weber, O. Orama and I. Jibril, J. Organomet. Chem., 304 (1986) 157.

14 A. Vizi-Orosz, G. Palyi, L. Marko, R. Boese and G. Schmid, J. Organomet. Chem., 288 (1985) 179.

15 O.J. Scherer, H. Sitzmann and G. Wolmershäuser, Angew. Chem. Int. Ed. Engl., 23 (1984) 968.

16 M. Müller and H. Vahrenkamp, J. Organomet. Chem., 252 (1983) 95.

17 G. Huttner, B. Sigwarth, O. Scheidsteger, L. Zsolnai and O. Orima, Organometallics, 4 (1985) 327.

18 G. Huttner, U. Weber, B. Sigwarth, O. Scheidsteger, H. Lang and L. Zsolnai, J. Organomet. Chem., 282 (1985) 331.

19 C.A. Ghilardi, S. Midollini, A. Orlandini and L. Sacconi, Inorg. Chem., 19 (1980) 301.

20 (a) K.I. Goldberg, D.M. Hoffmann and R. Hoffmann, Inorg. Chem., 21 (1982) 3863. (b) See also E.L. Anderson, T.P. Fehlner, A.E. Coti and D.R. Salahub, J. Amer. Chem. Soc., 102 (1980) 7122. R. Lissillour, J. Ben Naceur and H. Patin, J. Chim. Phys., 81 (1984) 225.

21 R.H. Hoffmann, Angew. Chem. Int. Ed. Engl., 21 (1982) 711.

22 D. Seyferth, R.S. Henderson and L.-C. Song, J. Organomet. Chem., 192 (1980) C1.

23 D. Seyferth, G.B. Womack and R.S. Henderson, Organometallics, 5 (1986) 1568 and references therein.

24 A. Shaver, P.J. Fitzpatrick, K. Steliou and I.S. Butler, J. Amer. Chem. Soc., 101 (1979) 1313.

25 (a) L.F. Dahl and C.H. Wei, Inorg. Chem., 2 (1963) 328, (b) N.G. Connely, G.A. Johnson, B.A. Kelly and P. Woodward, J. Chem. Soc., Chem. Commun., (1977) 436; (c) For a theoretical work see B.K. Teo, M.B. Hall, R.F. Fenske and L.F. Dahl, Inorg. Chem., 14 (1975) 3103.

26 I. Bernal, J.D. Korp, G.M. Reisner and W.A. Herrmann, J. Organomet. Chem., 139 (1977), 321.

27 K.A. Schugart and R.F. Fenske, J. Amer. Chem. Soc., 108 (1986) 5094, 5100.

28 L.M. Cirjak, R.E. Ginsburg and L.F. Dahl, Inorg. Chem., 21 (1982) 940.

29 Other organometallic clusters with a tetrahedral core, having 5 SEPs are known: see for example $Fe_2W(\mu\text{-}CC_6H_4Me)(\mu\text{-}PPh_2)(CO)_6Cp$ in J.C. Jeffrey and J.G. Lawrence-Smith, J. Chem. Soc., Chem. Commun., (1986) 17.

30 See for example: J.K. Kennedy, Prog. Inorg. Chem., 101 (1984) 6550; R.L. Johnston and D.M.P. Mingos, J. Organomet. Chem., 280 (1985) 407; A.J. Stone, Polyhedron, 3 (1984) 1299.

31 a See for example: J.M. Coleman and L.F. Dahl, J. Amer. Chem. Soc., 89 (1967) 542; b M.B. Hall and L.F. Dahl, Inorg. Chem., 140 (1975) 3103; c A.H. Arif, A.H. Cowley and S. Quashie, J. Chem. Soc., Chem. Commun., (1985) 428.

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

33 J.M. Ammeter, H.B. Bürgi, J.C. Thibeault and R. Hoffmann, J. Amer. Chem. Soc., 100 (1978) 3686.