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Electronic structure study of the reactivity centres in Ti_8C_{12} clusters

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Abstract. The reactivity centres of Ti_8C_{12}, for the three structures suggested in conformity with experimental observations, are studied by extended Huckel theory, The C_2 unit can complex with transition metal fragments such as $Pt(PH_3)_2$ with the unusual net result of transferring two electrons to Ti_8C_{12}. The metal centre, Ti can accommodate extra two-electron donors like CO. Model systems are used to explain the carbon and metal environment in Ti_8C_{12}.

Keywords. Reactivity centres; Ti_8C_{12} clusters; extended Huckel theory; transition metal fragments.

1. Introduction

The recent discovery of metallocarbohedrenes (Met-Car) has opened a new branch of chemistry in clusters (Guo *et al* 1992; Wei *et al* 1992; Cartier *et al* 1993). Castleman has suggested a structure (1) with T_h symmetry based on an icosahedron. Many theoretical studies have been directed to establish the structure of the first Met-Car, a Ti_8C_{12} cluster (Grimes and Gale 1992, 1993; Lin and Hall 1992; Reddy *et al* 1992; Hay 1993; Methfessel *et al* 1993; Reddy and Khanna 1993). Geometry optimization with T_h symmetry (1) (figure 1) has shown Ti_8C_{12} to have a triplet state. The Jahn–Teller distorted structure with D_{2h} symmetry (2) (figure 1) is calculated to be a singlet and lies lower in energy (Marie-Madeleine *et al* 1992). In another study a Ti_8 skeleton based on a face-bridged tetrahedron was considered (Dance 1992). This structure, 3, (figure 1) was optimized to be a minimum in the quintet state, lower in energy than both 1 and 2 (Marie-Madeleine *et al* 1993). These three structures are consistent with the experimental observations. Titration with NH_3 and CH_3OH produces $Ti_8C_{12}(NH_3)_8$ and $Ti_8C_{12}(CH_3OH)_8$, detected in mass spectral analysis (Guo *et al* 1992). Guo has reported recently that the reaction of Ti_8C_{12} towards any ligand is associative (Guo *et al* 1993).

There are several interesting features in these structures. The C_2 units in 1 and 2 are similar to those in tetrametallated ethylene, with pyramidalization at carbon centres and is reminiscent of the structure of a metal–ethylene π-complex with all the substituents of the ethylene bent away from the metal (Hoffmann *et al* 1979). This might provide an ideal bonding arrangement for an incoming metal fragment to interact with C_2 in M_8C_{12}. While isomer 2 has three different sets of C_2 units

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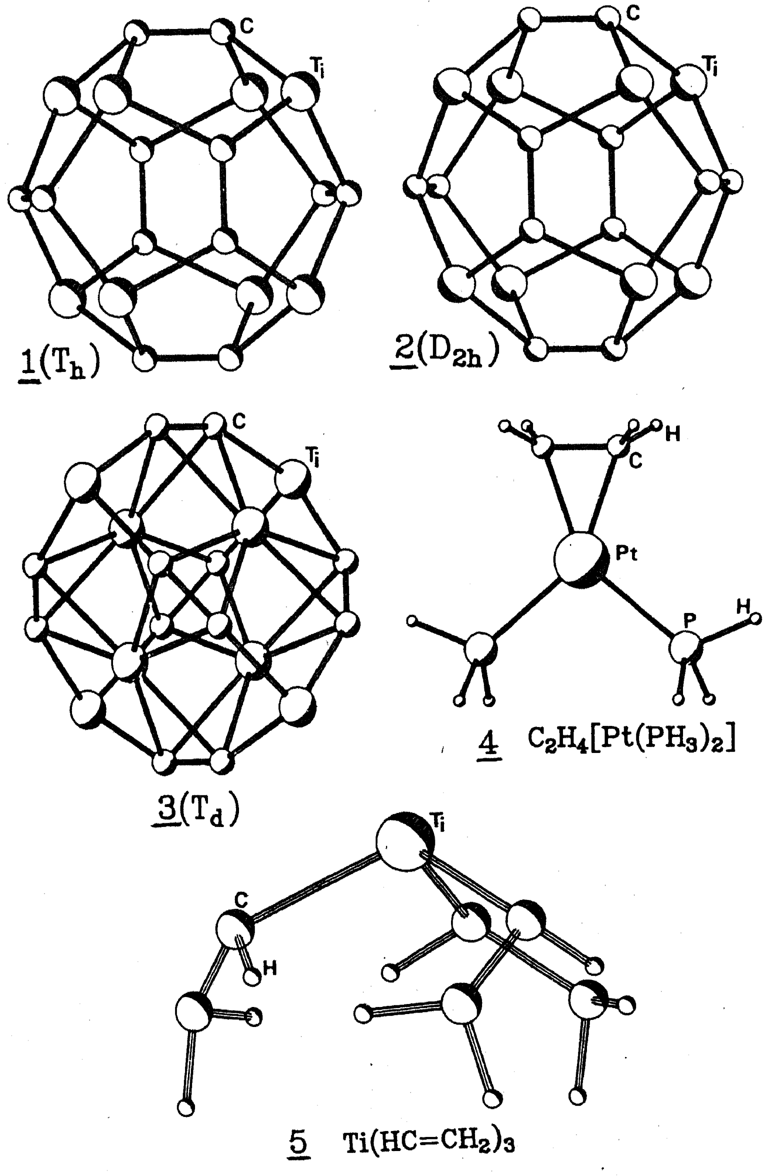

Figure 1. Ti_8C_{12} in T_h(1), D_{2h}(2) and T_d(3) symmetries, $C_2H_4[Pt(PH_3)_2]$ (4) and the model system $Ti(HC{=}CH_2)_3$ (5).

(the C–C distances are 1·299, 1·392 and 1·478 Å), the basic framework in 1 and 2 is the same. Structure 3, a tetracapped tetrahedron, also presents interesting analogies. The C_2 unit is different from those in 1 and 2, but is similar to one of the minima calculated for tetralithioethylene with two terminal lithiums and two bridging lithiums in the two π-planes (Schleyer *et al* 1992).

The metal in 1 and 2 can be viewed as a trivinyl derivative, with the three ligands arranged in a pyramidal fashion. Therefore it can accommodate extra ligands for complexation. There are two types of metal environments in 3. Four metal atoms form an inner tetrahedron and the other four cap the faces of this inner tetrahedron. Four Ti atoms around one C_2 unit form a butterfly arrangement with the two inner titanium atoms as the hinge. This leads to an outer metal with three σ bonds with three C_2 units and an inner metal having π-interaction with three C_2 units.

Keeping these structural possibilities in view, this paper discusses the interaction of fragments such as $Pt(PH_3)_2$ and carbon monoxide at various sites in the Ti_8C_{12} skeleton. The electronic structure calculations were performed using the fragment molecular orbital approach within the extended Huckel theory with the parameters given in tables 1 and 2.

Table 1. Extended Huckel parameters.

Atom	Orbital	H_{ii}	ζ_1	ζ_2
Ti	4*s*	−8·97	1·075[a]	
	4*p*	−5·44	0·675	
	3*d*	−10·81	4·500 (0·4206)[c]	1·400 (0·7839)
Pt	6*s*	−9·08	2·550[b]	
	6*p*	−5·48	2·550	
	5*d*	−12·59	6·010 (0·6334)	2·700 (0·5513)
C	2*s*	−21·40	1·625[b]	
	2*p*	−11·40	1·625	
P	3*s*	−18·60	1·600[b]	
	3*p*	−14·00	1·600	
H	1*s*	−13·60	1·300[b]	
O	2*s*	−32·30	2·275[b]	
	2*p*	−14·80	2·275	

[a]Joseph and Hoffman (1976); [b]Hoffman *et al* (1979)

Table 2. Important bond lengths of various isomers.

Structure	Bond type	Bond length (Å)
1	M–M	3·06
	M–C	1·98
	C–C	1·40
2	M–M	3·03
	M–M	3·19
	M–M	3·27
	M–C	2·14
	M–C	2·06
	C–C	1·29
	C–C	1·47
3	M–M	2·86
	M–M	2·90
	C–C	1·34
	M–C	2·19
	M–C	2·93

2. Results and discussion

Since the electronic structure description of 1 and 2 in our study agrees well with the previous *ab initio* MO and density functional theory calculations, only a brief description is given here (Methfessel *et al* 1993; Grimes and Gale 1992). The electronic structure of 3 is discussed in detail because there is no such discussion in literature except the report of the optimized structure. Our emphasis will be on assessing the reactivity centres in the molecule.

2.1 *Electronic structure of 1 and 2*

The electronic structure of 1 is constructed by the interaction of Ti_8 and C_{12} (figure 2). Only the important interactions are shown. The π bonding combinations between carbon π orbitals and Ti_8 fragments are lower in energy than the sigma combination. The π-bonding MOs resulting from carbon π^* orbitals lie above the σ levels in energy. This interaction diagram clearly shows that at the frontier range there is a greater contribution from carbon π^* levels. Below this one finds the carbon σ contribution.

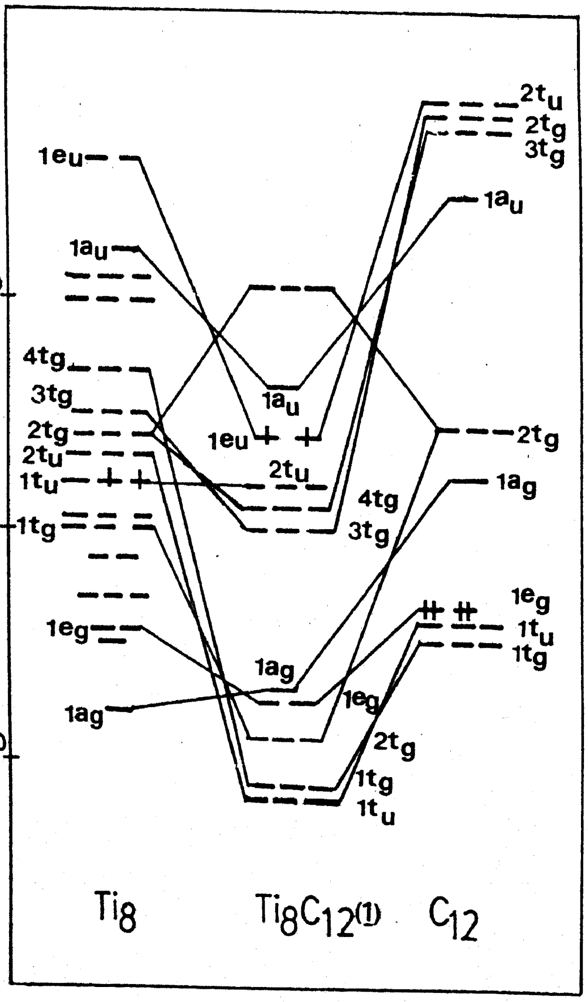

Figure 2. Interaction diagram between Ti_8 and C_{12} to give the energy levels of Ti_8C_{12}(1). T_h symmetry labels are used.

The HOMO is a doubly degenerate $1e_u$ set with only two electrons and leads to a triplet ground state.

The electronic structure of 2 is not very different from 1. There are three groups of orbitals in 2. The group at HOMO is rich in metal *d*-orbitals with carbon π^* participation. The second group below this has predominantly carbon *p*-orbitals of the C–C bond direction along with some contribution from the metal *d*-orbitals. The third group which is below the second one is mainly contributed by the carbon *s*-orbitals. In general these descriptions of the electronic structure of 1 and 2 agree well with the previous theoretical calculations.

2.2 *Electronic structure of 3*

The coordination around carbon in 3 is different from 1 and 2. To understand this new geometry at the C_2 unit, we have taken a smaller fragment Ti_4C_2 of Ti_8C_{12} (3). The molecular orbitals of Ti_4C_2 are constructed from the fragments Ti_4 (in butterfly geometry) and C_2 (figure 3a). The symmetric combination of σ and the π^* orbitals of C_2 are empty, whereas the C–C σ, the *anti*symmetric combination of lone pairs and π orbitals are filled in C_2. The molecular orbitals of M_4 are similar to those of the butterfly clusters (Lauher 1978). The long metal–metal distance restricts the energy spread to be small. The π orbitals of C_2 interact with $1b_1$ and $4b_1$ of the Ti_4 unit leading to $1b_1$ and $2b_1$ of Ti_4C_2. The non-bonding σ-orbitals of C_2 (a_1) and $1a_1$ of Ti_4 leads to $1a_1$ of Ti_4C_2. These $1b_1$, $2b_1$ and $1a_1$ MOs in Ti_4C_2 are responsible for σ-bonding between the outer Ti and C_2. MOs $1b_2$ and $2b_2$ of Ti_4C_2 arise from b_2 of C_2 and $1b_2$ and $3b_2$ of Ti_4. These interactions mainly lead to π-bonding between the inner Ti atoms in the Ti_4 and the C_2 units. The HOMO of Ti_4C_2 is purely metal based arising from $1a_2$, which has π antibonding interactions between the inner and outer titanium atoms. The LUMO is mainly based on outer titanium atoms and is π-type. The interesting feature of this diagram is the HOMO-1 ($4b_2$) of Ti_4C_2, a bonding MO between π^* orbitals of C_2 and z^2 orbitals on outer Ti atoms.

With this understanding of Ti_4C_2, we proceed to form Ti_8C_4 by taking two Ti_4C_2 units. The important developments during dimerization are formation of MOs $1e$, $2a_2$, $2a_1$, $1b_2$ and $3a_1$ corresponding to metal–metal bonds. The $1e$ and $2a_2$ MOs are responsible for bonding between inner titanium atoms. The MOs $1a_1$, $2a_1$ and $1b_2$ are responsible for bonding between inner and outer titanium atoms. The MOs $3a_1$ and $4a_1$ are mainly outer titanium metal-based orbitals. In short, dimerization of Ti_4C_2 brings in metal–metal interactions between inner–inner and inner–outer titanium metals.

Ti_8C_{12} (3) can now be obtained by adding the remaining C_2 units to Ti_8C_4. Some of the important interactions in the formation of 3 are shown in figure 3b. The MOs of $4C_2$ units are given on the right hand side of the diagram. MOs $1a_1$ and $2a_1$ are symmetric combination of π-orbitals of C_2 units. $4a_1$ of Ti_8C_4 interacts with $2a_1$ leading to σ-bonding between the outer titanium atoms and the C_2 units and π interactions between the inner titanium atoms and C_2. $1e$ and $2e$ of the $4C_2$ units are π orbitals, which interact with inner titanium atoms in a σ-fashion and with outer metals in a π-fashion. The non-bonded σ-orbitals $4a_1$, $3e$ and $5a_1$ of the C_2 units form mainly σ-bonds with outer metals. The π^* MOs $1b_1$, $4e$ and $5e$ of the C_2 units are mainly responsible for σ-bonding with inner metals and antibonding π-interactions with outer metals. The HOMO of 3 is triply degenerate with two electrons, which makes the system susceptible to Jahn–Teller distortion. One way of stabilizing the system is by exciting one electron from $2a_u$ to HOMO, which gives a spin multiplicity of 5 (Marie-Madeleine *et al* 1993).

2.3 *Oxidation state of metal atoms in* Ti_8C_{12}

Each metal atom in 1 may be viewed as a trivinyl derivative. This leads to a $+3$ oxidation state at the metal with a d^1 configuration. Similarly each C_2 unit can be viewed as tetrametallated ethylene, that is C_2's exist as C_2^{4-}. The Mulliken charge on the metal atom is $+0{\cdot}41$ and on C is $-0{\cdot}27$. Isomer 2 can also be viewed in the same way as 1, since the structural features of them are similar. In 2 also the Mulliken charge on metal is approximately $+0{\cdot}41$. But the C's have $-0{\cdot}21$, $-0{\cdot}26$ and $-0{\cdot}34$ for the three different carbons.

The oxidation state of the two types of metals in isomer 3 is different. Since each metal in the outer tetrahedron is bonded to three C_2 units, the outer metal may have a $+3$ oxidation state. There are four outer titanium metals, which leads to each C_2 having a -2 charge. This electron counting leaves the linner titanium atoms in a zero oxidation state as the interactions with C_2 units may be treated as π-type. But this is not in tune with the calculations, which show that the inner titanium atoms have more charge than the outer ones (0·54 vs 0·11).

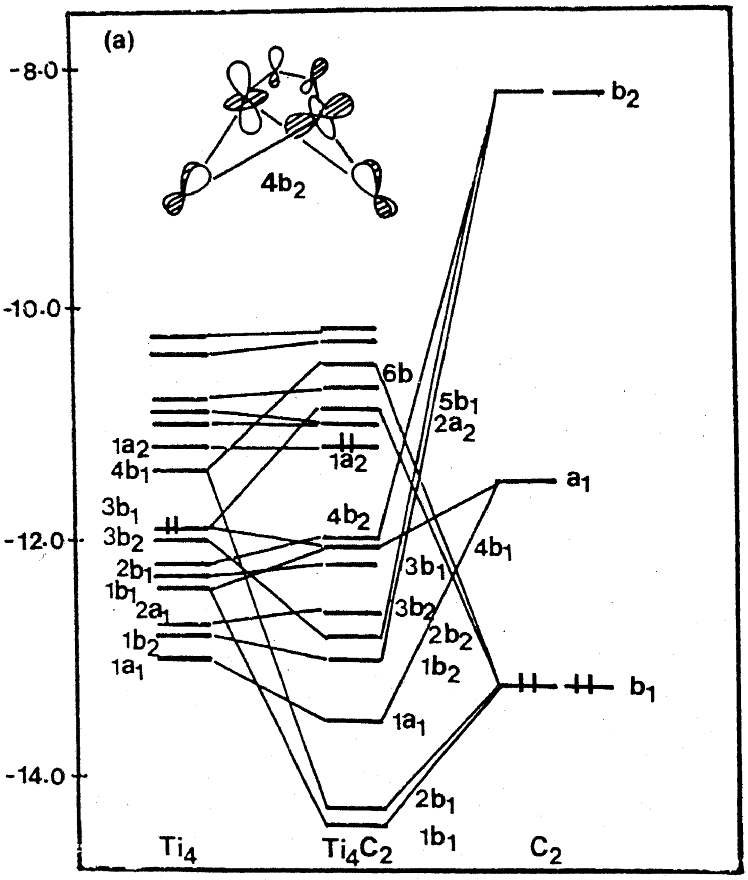

Figure 3(a). Interaction diagram between Ti_4 and C_2 to give the energy levels of Ti_4C_2 with C_{2v} geometry.

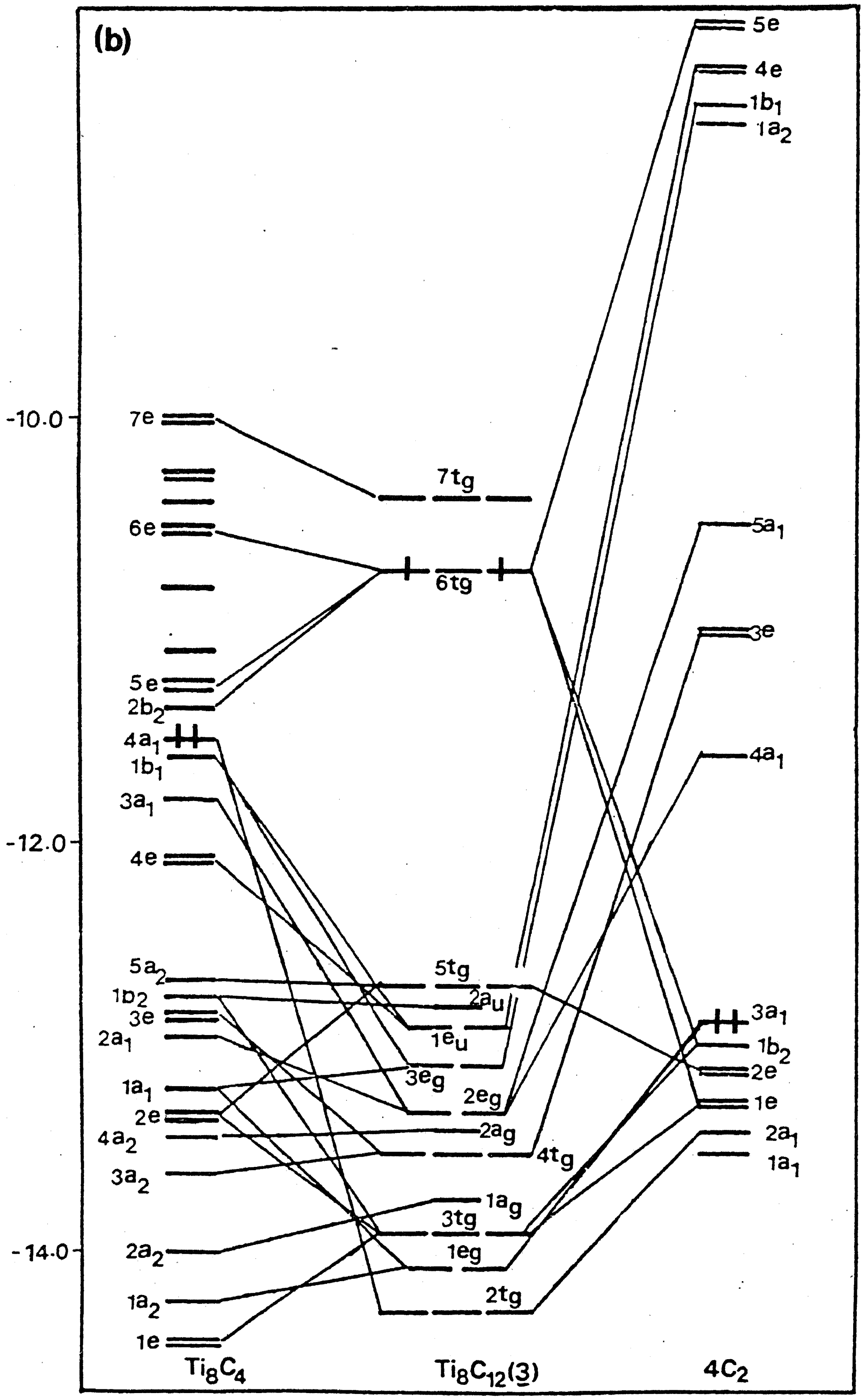

Figure 3(b). Construction of energy levels of Ti_8C_{12}(3) from Ti_8C_4 and $4C_2$ units. For Ti_8C_4 and $4C_2$'s the D_{2d} symmetry labels are used, and T_d symmetry labels are used for Ti_8C_{12}.

Another way of counting electrons leads to the following. Each inner titanium interacts with $3C_2$ units. The inner metal–carbon distance (2·2 Å) is very close to that of a σ bond between them (in Ti–vinyl systems the Ti–C single distance is 2·2 Å, Orpen *et al* 1989). Thus each inner metal is connected to six carbons, whereas each outer one is connected to three carbons only. Formal oxidation state counting would have led to four outer metals with + 3 and each inner metal with + 6. But the latter is impossible in an early transition metal. This would also leave each C_2 formally as C_2^{-6} with a C–C single bond. The truth is somehwere in between these extremes. All that can be said safely is that the inner titanium metal is at a higher oxidation state than the outer one. The overlap population between inner Ti–C is 0·26. But between the outer Ti–C it is 0·76 due to the extra π-bonding. The C–C overlap population (1·23) shows C–C to be close to a double bond (the C–C bond distance is 1·34 Å).

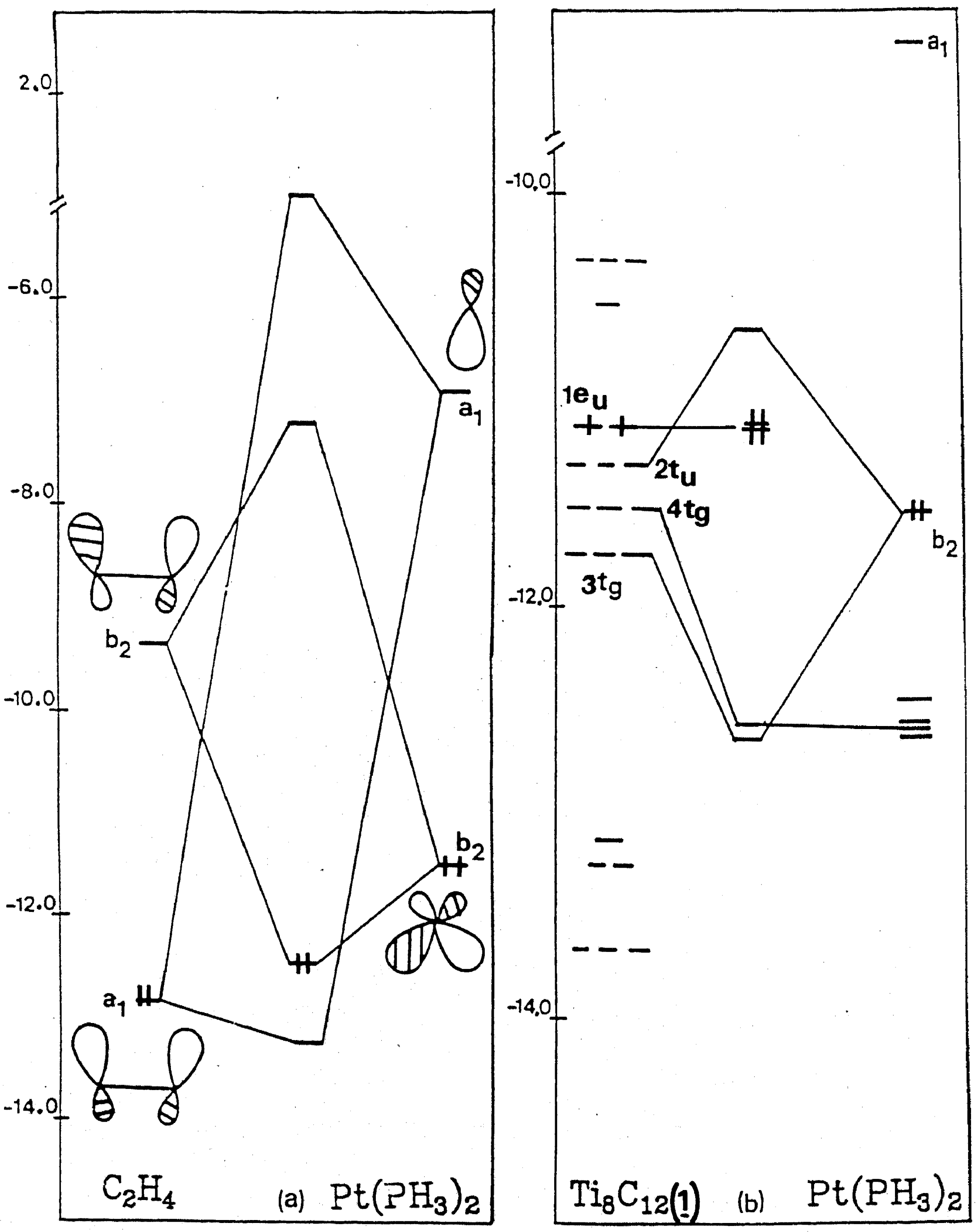

Figure 4. (a) & (b) (Caption on facing page.)

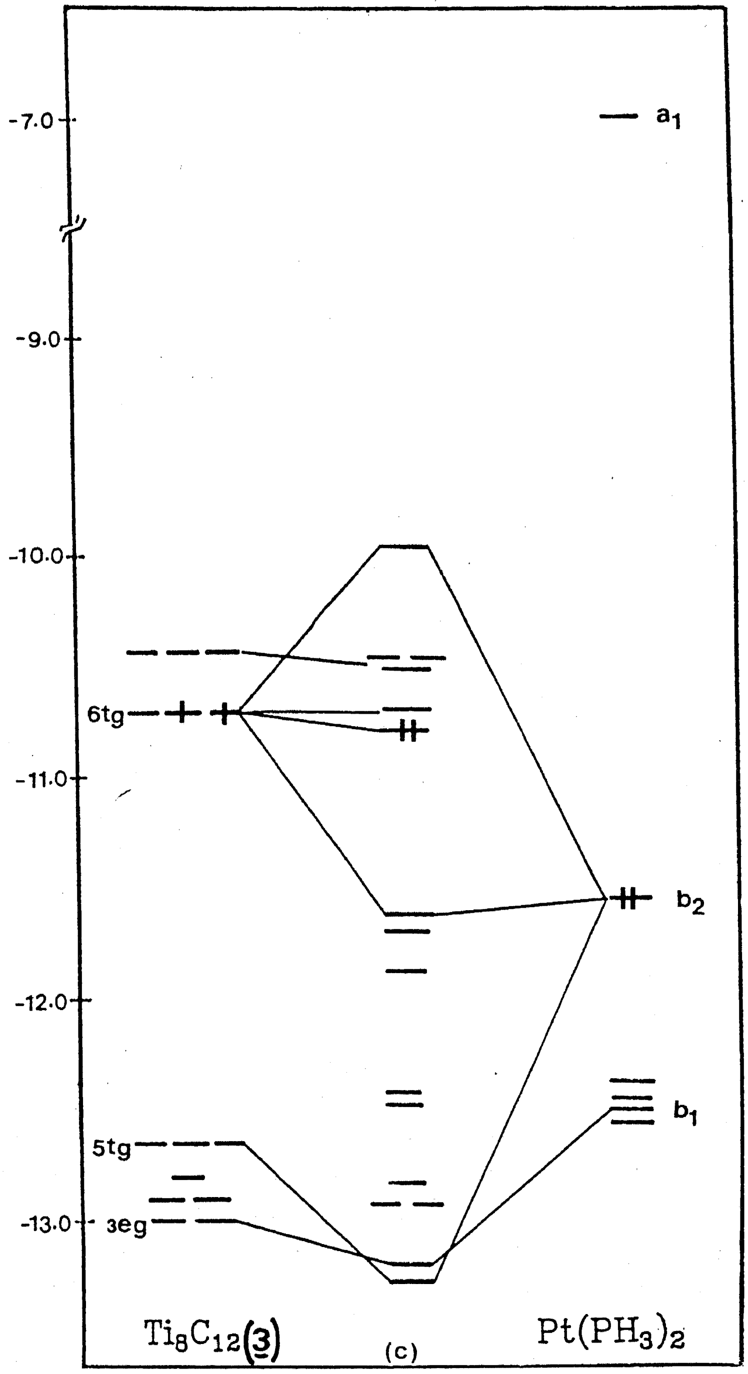

Figure 4. Interaction diagram between (**a**) C_2H_2 and $Pt(PH_3)_2$, (**b**) Ti_8C_{12}(1) and $Pt(PH_3)_2$ and (**c**) Ti_8C_{12}(3) and $Pt(PH_3)_2$.

2.4 *Carbon environment in Ti_8C_{12}. Interaction of C_2 with $Pt(PH_3)_2$*

The carbons in a transition metal ethylene complex are pyramidalized towards the metal. The C_2 unit in 1 and 2 is pyramidalized in the same way. Even though the C_2 unit in 3 is of a different type it is also pyramidalized. Thus the C_2 units in Ti_8C_{12} should act as ethylenes towards transition metal fragments. To study this type of bonding in detail we have considered the interaction of $Pt(PH_3)_2$ with Ti_8C_{12}. $Pt(PH_3)_2C_2H_4$ is a well known π-complex where the Pt–C bond occurs mainly from the interaction of the π^* (b_2) MO of ethylene with the hybridized d-orbital (b_2) of $Pt(PH_3)_2$. Figure 4 gives the interaction diagram between $Pt(PH_3)_2$ (with standard geometry, Orpen *et al* 1989) and isomers 1 and 3. Isomer 2 was left out due to its close resemblance to 1. The equivalent orbital of ethylenic b_2 in 1 is $3t_g$ and $2t_u$. Since $3t_g$ is an occupied orbital unlike b_2 in C_2H_4, the interaction between $3t_g$ and b_2 of $Pt(PH_3)_2$ should have caused destabilization. However the two electrons instead of going to an antibonding orbital, fill the degenerate HOMO fully. Thus $Pt(PH_3)_2$ may be treated as a two-electron donor to Ti_8C_{12} (1).

Structure 2, also has pyramidalized C_2 units. Out of three types of C_2 units, the C_2 unit which has a short C–C bond gives maximum stabilization with $Pt(PH_3)_2$. The interactions between $Pt(PH_3)_2$ and 2 are not very different from 1. The result is donation of electrons from the metal fragment to 2.

Though the geometry around C_2 unit in 3 is different from the other two, it is possible to trace pyramidalized π^* orbitals. In 3 the MO $6t_g$ is similar to π^* of C_2H_4 which interacts with the b_2 orbital of $Pt(PH_3)_2$. HOMO-1 of 3 is also of appropriate energy to mix with b_2 of $Pt(PH_3)_2$. Another stabilization in this complex is from the $3e_g$ orbitals of 3 mixing with b_1 of the metal fragment. $Pt(PH_3)_2$ donates two electrons on complexing with 1, 2 or 3. The two electrons from $Pt(PH_3)_2$ fill the LUMO of 2, whereas in 1 and 3 they stabilize the half-filled HOMOs. Therefore the C–C overlap population values 1·10, 1·28 and 1·23 are changed to 0·94, 1·10 and 1·08 in 1, 2 and 3 respectively after complexing with $Pt(PH_3)_2$.

2.5 *Metal environment. Interaction with carbonyls*

Our calculations on model system $Ti(HC=CH_2)_3$ (5) has shown that the metal in the non-planar geometry of this complex represents the metal in Ti_8C_{12}. Since we are interested in extra ligand complexation on metal in Ti_8C_{12}, we have studied the complexation of carbon monoxide on 5. Figure 5a gives the interaction diagram between 5 and $(CO)_3$ fragments with standard titanium carbonyl distances (Orpen *et al* 1989). The angle 80·0° was fixed between carbonyl–titanium–carbonyl. The staggered form which gives pseudo-octahedral geometry is found to be more stable. The hybridized metal orbitals in 5 are $4e$, $3a$ and $5e$. The major interactions are between $3e$, $4e$ and $5e$ set of 5 and $1e$ and $2e$ set of $(CO)_3$ (figure 5a). The σ interactions occur between $1e$ and $2e$ of 5 and $1e$ of $(CO)_3$. The symmetric combination of the π^* orbitals of $(CO)_3$, (that is $3a$ and $3e$) do not have orbitals of right symmetry to mix with 5. There is a stabilization of 10 eV in the formation of the carbon monoxide complex as judged by the change in the sum of one electron energies.

The metal contribution in $3t_g$ and $2t_g$ orbitals of 1 and $5t_g$ and $2e_g$ orbitals of 3 (which are based on the outer tetrahedron of titaniums) are similar to $5e$, $4e$ and $3e$ orbitals of 5. Figure 5 shows the interaction between Ti_8C_{12} (in structures 1 and 3) and $(CO)_3$, which is more or less similar to that between 5 and $(CO)_3$. Isomer 2 also shows an interaction similar to 1. All the titanium metals in 1, 2 and outer titanium metals in 3 have shown enough capability of complexing with carbonyls. There is an enormous stabilization of 10·20, 10·19 and 11·40 eV for 1, 2 and 3 respectively as calculated from change in the sum of one-electron energies in complexation with $(CO)_3$.

The Mulliken charge on the metal changes drastically on complexation with carbon monoxide. The changes are from +0·41, +0·40 and +0·11 on 1, 2 and 3, to −0·08, −0·33 and −0·68 respectively after complexing with carbon monoxide. These changes also indicate the electrophilic nature of the metal in the cluster. The outer titanium metal in 3 is most electrophilic in nature, next is the metal in 2 followed by 1. There are changes in overlap population also. The M–M overlap population of 0·10, 0·11 and 0·18 in 1, 2 and 3 is decreased to 0·03, 0·05, and 0·09 respectively after complexing with carbon monoxide. The M–C overlap population 0·66 and 0·75 in 1 and 3, and 0·53, 0·61 and 0·72 for short, medium and long C_2 units in 2 also decreased to 0·45 and 0·59 in 1 and 3, and 0·35, 0·41 and 0·48 for the three C_2 units in 2. In general this may be considered as a result of donation of electrons from carbonyl to the cluster, where predominantly M–C and M–M antibonding MOs are at the receiving end.

We conclude that, despite the structural differences, all the titanium metals in 1, 2 and outer titanium metals in 3 show the capability of complexing with carbonyls. It may be possible that by allowing three CO's at each metal the macro complex $Ti_8C_{12}(CO)_{24}$ may be obtained. Since we get a high stabilization for each $(CO)_3$ unit on one metal, Ti_8C_{12} may be used as a carbon monoxide absorber.

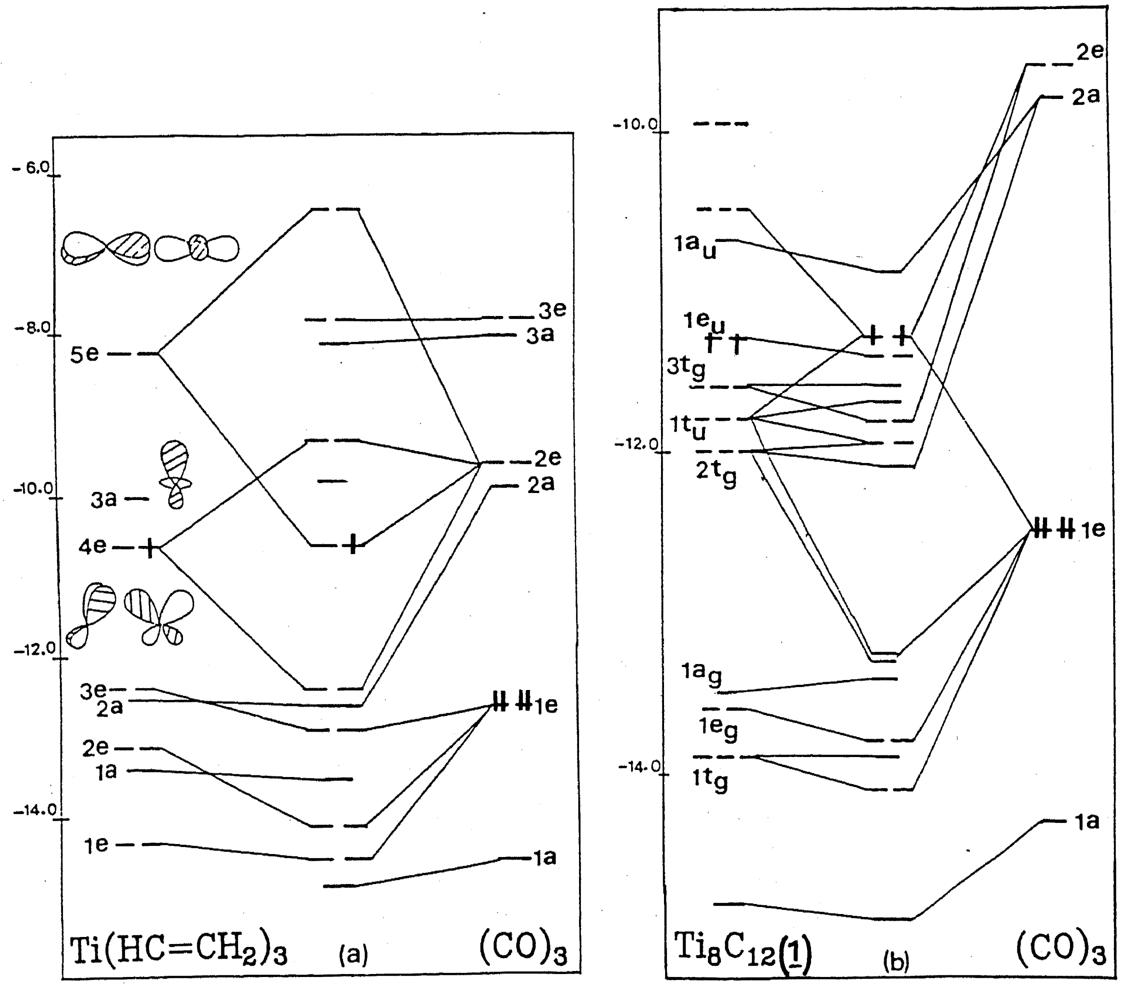

Figure 5. **(a)** & **(b)** (Caption on next page.)

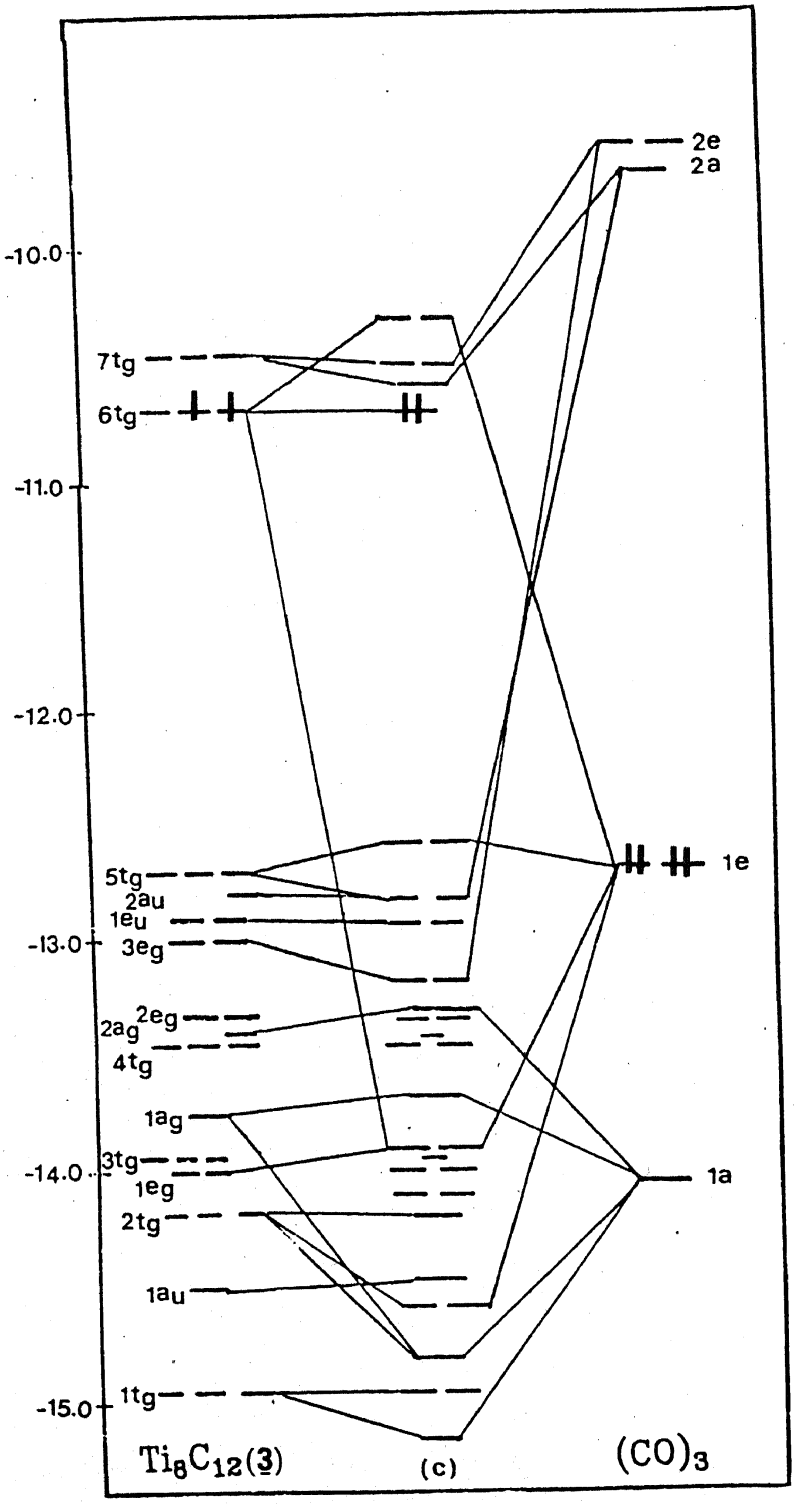

Figure 5. Interaction diagram between (**a**) $Ti(HC{=}CH_2)_3$ and $(CO)_3$, (**b**) Ti_8C_{12}(1) and $(CO)_3$ and (**c**) Ti_8C_{12}(3) and $(CO)_3$.

3. Conclusions

The Ti_8C_{12} cluster is a highly electron-deficient species. The cluster is ready to accept electrons from traditional ligands such as carbon monoxide and also from transition metal fragments. In soot obtained in the experiments of Castleman, Ti_8C_{12} may exist as associated clusters with the interaction of Ti metal in one cluster with C_2 units in the other. Metallocarbahedrenes should also be good ligands for forming large clusters.

Acknowledgements

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