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Extended Polymetallic Sandwich Compounds

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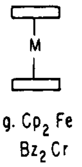
The electronic requirements for stability of a new class of polymetallic sandwich compounds, $M_n$bis(fused arene), are presented. For the n-acene case a good HOMO–LUMO gap is predicted for $8 - (2/n)$ electrons per atom. This gives rise to stable complexes for M_2 = Mn_2bis(naphthalene), M_3 = Mn–Fe–Mnbis(anthracene), and M_n = Fe_nbis(polyacene), but intermediate oligomers will have small gaps. The polymer $^{1}_{\infty}$[M(naphthalene)] has an interesting band structure with two band gaps predicted (M = Cr, Fe). Polymeric $^{1}_{\infty}$[M(cyclopentadienyl)] and $^{1}_{\infty}$[M(benzene)] exhibit band gaps at M = Mn and Cr, respectively. M_2bis(pentalene) complexes are found to have significant HOMO–LUMO gaps for M = Co and Ni, but not for M = Fe, in accord with the stability of the former two compounds but the nonexistence of the latter. An analogy between pentalene and naphthalene as ligands is made, and a series of isoelectronic molecules containing two different organic ligands is suggested.

Introduction

Since the discovery of ferrocene, metal sandwich compounds **1** have become the symbol of modern organometallic chemistry. These compounds present both a rich chemistry and structural diversity. For instance, the ferrocene motif cannot only be found in ferrocene itself[1] but in dimers such as 1,1′-biferrocenylene,[2] **2**, cyclic oligomers such as [1^n]ferrocenophanes,[3] polymers such as polyferrocenylene, **3**,[4] and helical ferrocene[5] or as a part of more complex clusters.[6] The possibility of having a triple-decker sandwich, first pointed out by Wilkinson,[7] was realized in 1972 when Salzer and Werner[8] prepared the tris(η-cyclopentadienyl)dinickel cation, $[Ni_2(C_5H_5)_3]^+$. Since then, different triple-decker,[9] tetra-decker[10] and penta-decker[11] compounds have been made. It is thus surprising that an alternative series of polymetallic sandwich compounds, that in which several metal atoms are sandwiched between two fused polycyclic systems, e.g., **4**, has been little explored. The pioneering work of Katz and co-workers[12–15] has led to the only examples of this type



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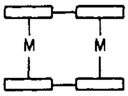

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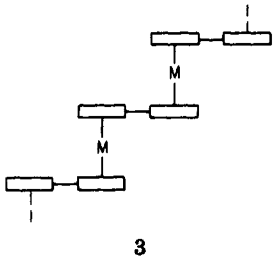

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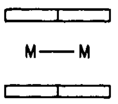

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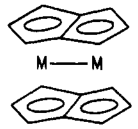

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[1] Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125. Fischer, E. O.; Pfab, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem. Biophys. Biol.* **1952**, *78*, 377.

[2] Rausch, M. D.; Kovar, R. F.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1969**, *91*, 1259. Hedberg, F. L.; Rosenberg, H. *J. Am. Chem. Soc.* **1969**, *91*, 1258. Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1969**, *8*, 1970.

[3] Katz, T. J.; Acton, N.; Martin, G. *J. Am. Chem. Soc.* **1969**, *91*, 2804; **1973**, *95*, 2934.

[4] Cowan, D. O.; Park, J.; Pittman, C. U.; Sasaki, Y.; Mukherjee, T. K.; Diamond, N. A. *J. Am. Chem. Soc.* **1972**, *94*, 5110. Lorkowski, H. J. *Top. Curr. Chem.* **1967**, *9*, 207.

[5] Katz, T. J.; Pesti, J. *J. Am. Chem. Soc.* **1982**, *104*, 347.

[6] Nesmeyarov, A.; Strutchov, Yu. T.; Sedova, N. N.; Andrianov, V. G.; Volgin, Yu. V.; Sazonova, V. A. *J. Organomet. Chem.* **1977**, *137*, 217. Nesmeyarov, A. N.; Sedova, N. N.; Struchkov, Yu. T.; Andrianov, V. G.; Stackheeva, E. N.; Sazonova, V. A. *J. Organomet. Chem.* **1978**, *153*, 115.

[7] Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 209.

[8] Salzer, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 930.

[9] Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 1 and references therein.

[10] Siebert, W.; Rothermel, W.; Böhle, C.; Kruger, C.; Brauer, D. J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 949. Siebert, W.; Böhle, C.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 746. Siebert, W.; Edwin, J.; Wadepohl, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 149. Edwin, J.; Bochmann, M.; Böhm, M. C.; Brennan, D. E.; Geiger, W. E.; Krüger, C.; Pebler, J.; Pritzkow, H.; Siebert, W.; Swiridoff, W.; Wadepohl, H.; Weiss, J.; Zenneck, U. *J. Am. Chem. Soc.* **1983**, *105*, 2582.

[11] Whiteley, M. W.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 452.

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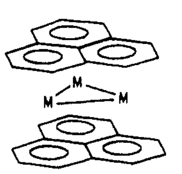
of which we are aware **5**. Both Ni_2bis(pentalene) and Co_2bis(pentalene) where a close metal–metal contact has apparently been created are known,[13] but interestingly the analogous iron compound could not be synthesized. No other sandwich compounds where metal atoms are forced into juxtaposition by fused organic networks are known. It is the possibility of generating extended metal–metal arrays through sandwiching that makes this series of compounds interesting. Additionally, just as bis(cyclopentadienyl)metal systems opened the way to the chemistry of bis(cyclopentadienyl)ML_n compounds, these polymetallic sandwiches could lead to some interesting new chemistry too. In the light of this comment the remarkably small number of characterized systems of this type is most surprising when one recalls the many M_2L_6(polyolefin) complexes known.[16] In principle, the substitution of the several L groups by another polyolefin should be possible to give compounds of the type shown in **4**. How will the stability of such species be controlled by the level structure of the organic unit? From a different point of view, the fact that may transition-metal diborides adopt the AlB_2 crystal structure,[17] where layers of metal atoms are sandwiched between layers of electron-rich "graphite-like" boron atoms, raises the possibility of the existence of discrete sandwich systems with several interacting metal atoms leading eventually to species such as the polymetallic sandwich structure **6**. Polymeric systems such



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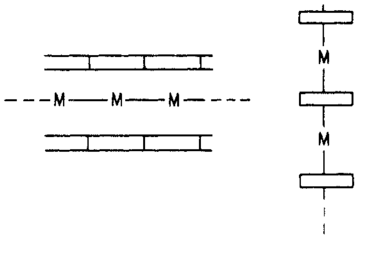

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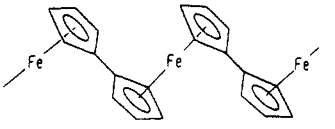
as those shown in **7** have yet to be made but for which metal M should they be stable? Polyferrocenylene, **8**, is an example of **3**. It is just a series of linked 18-electron ferrocene units but what are the electronic requirements for the fused analogues **9**? These species represent a new class of one-dimensional systems, an area currently of great interest.



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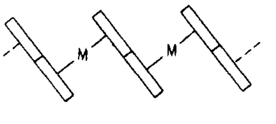

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In this paper we explore some of these possibilities and try to delineate the electronic requirements for stabilization of this type of compound. Our arguments are supported by calculations of the extended Hückel type both for molecules and solids with parameters given in the Appendix.

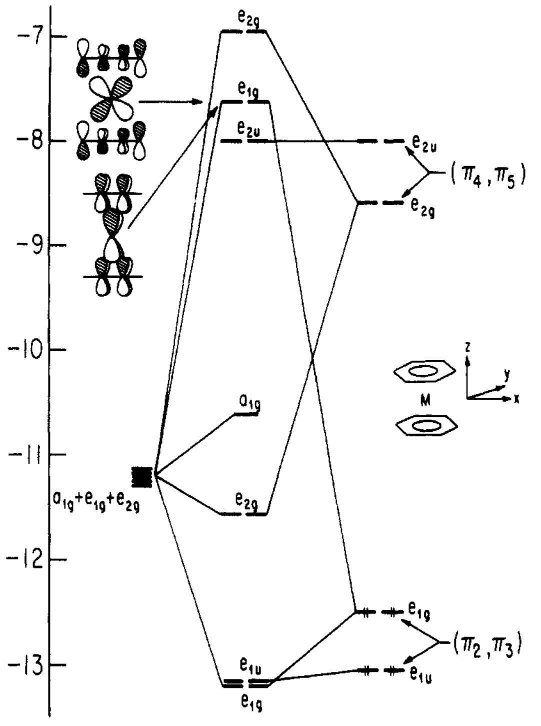

Figure 1. Interaction diagram for bis(benzene) chromium. Only the degenerate pairs of π orbitals of benzene and the d orbitals of chromium are shown. The benzene orbital occupancy shown is that appropriate for two neutral ligands.

Double-Decker Polymetal Sandwich Compounds

The simplest series of polymetallic sandwiches are those containing the polyacenes. Due to the large number of orbitals, even in M_2bis(naphthalene) the interaction diagrams will be quite complex, but we will be able to present a simplified picture by focusing on metal d–ligand π interactions. We begin by considering the case of chromium bis(benzene), MBz_2 (Figure 1). The metal z^2 orbital (a_{1g}) remains almost nonbonding even if it has the right symmetry to interact with one of the proper combinations of the benzene orbitals. This is due to the fact that its conical nodal surface points directly toward the π system of the benzene moieties. The two in-plane $x^2 - y^2$ and xy orbitals (e_{2g}) are somewhat stabilized by the symmetrical combination of the benzene LUMO's and, as a result, remain in the low-energy region, but the two xz and yz orbitals have good overlap with the antisymmetric combination of the HOMO's and are strongly destabilized. (Parenthetically we point out that even if the destabilization of xz and yz orbitals appears from our diagram to be dominated by the interaction with the π orbitals, there is also a substantial contribution of the occupied σ orbitals of benzene. This fact has also been noticed in the case of triple-decker compounds.)[18]

Two metal orbitals are destabilized, leaving three behind, and with a HOMO–LUMO gap which we calculate to be 2.56 eV, a stable d^6 chromium bis(benzene) species is found. So, for electron-counting purposes when studying higher members of this series we can disregard the effect of the three z^2, xy, and $x^2 - y^2$ orbitals on each metal and

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(12) Katz, T. J.; Schulman, J. *J. Am. Chem. Soc.* **1964**, *86*, 3169. Katz, T. J.; Balogh, V.; Schulman, J. *J. Am. Chem. Soc.* **1968**, *90*, 734. Gitany, R.; Paul, I. C.; Acton, N.; Katz, T. J. *Tetrahedron Lett.* **1970**, 2723.

(13) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1972**, *94*, 3281. Katz, T. J.; Acton, N.; McGinnis, J. *J. Am. Chem. Soc.* **1972**, *94*, 6205.

(14) Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1980**, *102*, 1058.

(15) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. C.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181. Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788. Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 956. Koller, F. H.; Doll, K. H.; Prossdorf, W.; Muller, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 151. Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009, 3663. Elschenbroich, C.; Heck, J. *J. Am. Chem. Soc.* **1979**, *101*, 6773.

(16) For an extensive review see: Deganello, C. "Transition Metal Complexes of Cyclic Polyolefins"; Academic Press: New York, 1979.

(17) E.g., Wells, A. F. "Structural Inorganic Chemistry"; Oxford University Press: London, 1975; p 841.

(18) Lauher, J.; Elian, M.; Summerville, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

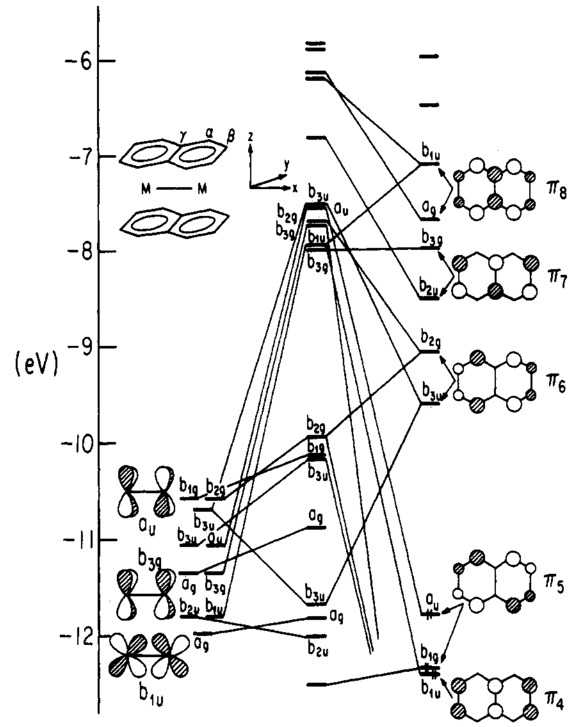
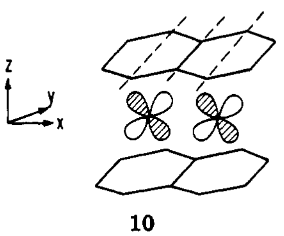


Figure 2. Interaction diagram for M_2bis(naphthalene). Only the π orbitals of naphthalene and the d orbitals of the metals are shown. The orbital occupancy shown is that appropriate for two neutral ligands.

establish how many combinations of the *xz* and *yz* orbitals are strongly destabilized on coordination of the ligands. The detailed interaction diagram for M_2bis(naphthalene) is shown in Figure 2. There are some clear similarities to the case of MBz_2. There is a good HOMO–LUMO gap for 14 metal electrons (numerically calculated to be 2.05 eV). There is a significant difference, however, since not all the *xz* and *yz* orbitals are destabilized. With the axis system shown the four combinations of the *xz* and *yz* orbitals have symmetries a_u, b_{3g}, b_{1u}, and b_{2g}. As can be seen in Figure 2 only three of these combinations are strongly destabilized. These are the two *yz* combinations and the *xz* M–M bonding combination. The *xz* M–M antibonding combination, b_{2g}, remains at low energy. With only three metal orbitals destabilized on coordination the appropriate metal atom to stabilize this structure is manganese. Interestingly although there are reports of metal vapor/arene cocondensation experiments with earlier transition metals,[19] the experiment with manganese and naphthalene does not appear to have been attempted. Two facts contribute to the different behavior of the *xz* orbitals in the sandwich complexes of benzene and naphthalene. The b_{2g} orbital interacts with the in-phase combination of the π_2 orbitals of naphthalene. This interaction is less effective than it was in the benzene sandwich: first, because of the larger difference in energy between the orbitals (calculated to be 3.0 vs. 1.48 eV) and, second, due to the three nodal planes shown in **10**, only the β-carbons can contribute to the overlap. In addition, interaction with the appropriate combination of the naphthalene LUMO's (now of the appropriate symmetry and with a good energy match for interaction) cooperates in keeping the xz^+ (b_{2g}) orbital at low energy. (We use + and − superscripts to label in- and out-of-phase combinations of relevant d orbitals.) In contrast, the bonding combination



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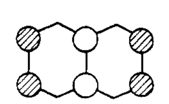

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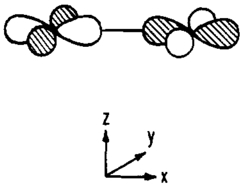
xz^- (b_{1u}) finds a naphthalene orbital with an excellent energy match (calculated to be 0.59 eV) and with exactly the same nodal characteristics, **11**. Consequently, the orbital is strongly destabilized. The empty ligand orbital of the correct symmetry to relieve this interaction is too high in energy to have any significant effect.

The *yz* combinations have excellent overlap with occupied ligand π levels. The empty orbitals of the correct symmetry are now too high in energy (a_u) or have a very good overlap (b_{3g}) to play any important role. Note that the appropriate combination of π_7, even if it is of the correct symmetry to interact with yz^+ (b_{3g}), has nodal planes precisely in the planes of the *yz* orbitals. The result is that both *yz* combinations are destabilized. The only other important interaction is the one between the $x^2 - y^{2-}$ combination, b_{3u}, **12**, and the out-of-phase combination of the two naphthalene LUMOS, **13**, which is the equivalent of the e_{2g} interaction in the benzene case.



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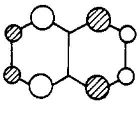

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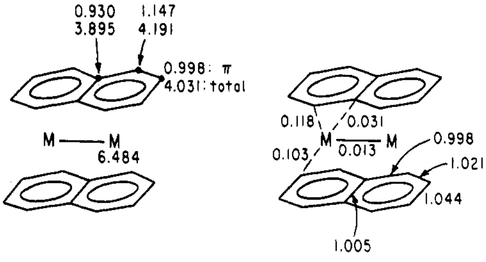
The electron densities and overlap populations are shown in **14** for the case of 14 metal electrons (M = Mn).



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There is a net transfer of 0.52 electrons to each naphthalene which has its origin in the mixing of the naphthalene LUMO into the occupied b_{2g} and b_{31} orbitals which we have just described. The overlap populations can be readily understood on the basis of the interaction diagram of Figure 2. The metal–metal overlap population is almost zero. Only the metal $x^2 - y^2$ and *xz* orbitals can contribute to this parameter since in all other cases the in-phase and out-of-phase metal combinations are either both occupied or both empty. The $x^2 - y^{2+}$ combination is occupied and does not interact appreciably with the ligand orbitals. The $x^2 - y^{2-}$ combination interacts strongly with the ligands, and there is an important electron transfer from metal to ligands. Overall the contribution of the $x^2 - y^2$ orbitals is thus positive. The xz^+ combination, being the middle member of a three-orbital set, contributes almost two electrons to metal–metal antibonding. The strong interaction of xz^- with the ligands has, as a result, the partial occupation of this orbital with one electron. The overall

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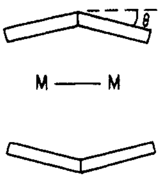
[19] Chromium bis(naphthalene) is known: Kündig, E. P.; Timms, P. L. *J. Chem. Soc. Dalton Trans.* **1980**, 991; *Chem. Comm* **1977**, 912. Elschenbroich, C.; Mockel, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 870.

contribution of the xz orbitals thus turns out to be negative and the same size as the positive contribution from the $x^2 - y^2$ orbitals. The overall M–M population is then close to zero.

Another result worthy of mention is the small bonding interaction between the metal and the γ-carbon atoms compared with the interactions with the α- and β-carbons. (The calculated M–C overlap populations for $(C_6H_6)_2Cr$ are 0.0965.) Five metal–ligand interactions can contribute appreciably to these overlap populations, namely, the bonding interactions between the a_u, b_{3g}, b_{1u}, b_{2g}, and b_{3u} orbitals. Three of them implicate ligand orbitals without any contribution from the γ-carbons (b_{3u}, b_{2g}, and a_u). Those of b_{3g} and a_1 symmetry involve the yz orbitals of the metal and will not be effective. Only one of the interactions can thus contribute to the M–C_γ overlap population. For the α- and β-carbons three of the interactions are effective. It then follows that a structural change which increases the bonding interactions between the α- and β-carbons with the metal atoms without changing very much the metal–γ-carbon interactions will be stabilizing. Our calculations show that the system is stabilized by bending the naphthalene units by 5° (15) which results in movement of the α- and β-carbon atoms toward the metals. The details of the charge distribution in 14 suggest that heterocyclic molecules, in which the α-carbon atoms have been replaced by more electronegative atoms, would be stabilized even better than naphthalene itself. (An example of such a ligand would be perhaps 1,8-naphthyridine, which contains two nitrogen atoms, or the relevant tetraazanaphthalene.)



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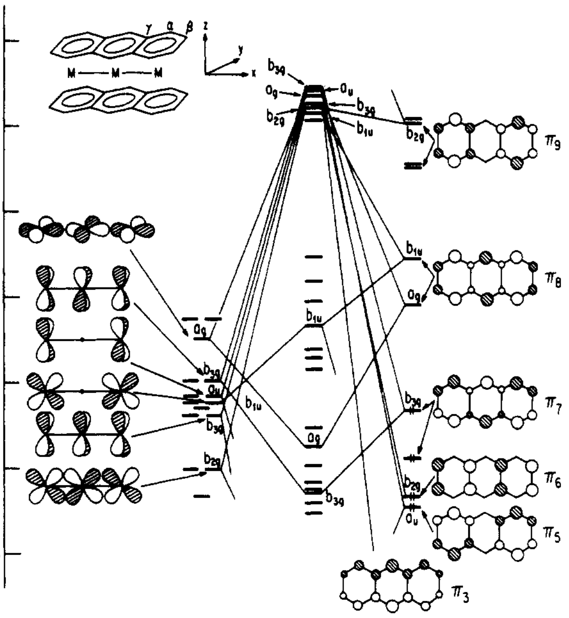
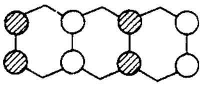


Figure 3. Interaction diagram for M_3bis(anthracene). Only the π orbitals of anthracene and the metal d orbitals are shown. The orbital occupancy shown is that appropriate for two neutral ligands.



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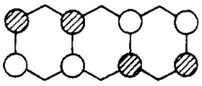

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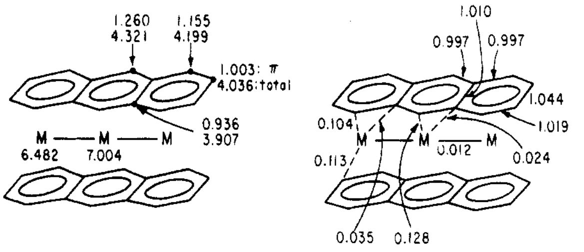
A simplified interaction diagram for M_3bis(anthracene) is shown in Figure 3. There is a sizeable gap (calculated to be 1.60 eV) for 22 metal electrons. Now only four of the six xz and yz orbital combinations are destabilized, and again, these are the three combinations of the yz orbitals and the all-bonding combination of the xz orbitals. The all-bonding xz combination finds a perfect match in energy and overlap with the orbital 16 and is again strongly destabilized. The repulsion is relieved to a small extent by interaction with π_9 because of both overlap and energy reasons. The second xz combination (b_{1u}) is destabilized by interaction with an occupied π orbital (π_4) but also finds an interaction with the LUMO of the anthracene. The result is that the b_{1u} orbital is kept at low energy. As both overlap and energy match are good, the interaction results in a strong transfer of xz character to the empty orbital. The all-antibonding xz combination does not have a very good overlap with π_6 because of the two additional nodal planes. The next occupied orbital which can interact with it is the very low energy π_2 orbital, and the mixing with π_9 is somewhat more efficient than it was in the case of the other b_{2g} combination. The orbital is kept at low energy. In contrast, the three yz combinations find three occupied ligand orbitals which overlap well with them. In all cases the larger coefficients are at the α-carbons and the match in energy is also good. Additionally, there is virtually no interaction with empty orbitals because these lie high in energy (cf. π_{11} and π_{14} of naphthalene). The π_{10} orbital 17 which by symmetry could interact with the a_1 combination has a very small overlap because it is concentrated exclusively on the β-carbons. Note the parallelism with the b_{3g} interactions in the naphthalene sandwich. In consequence, a total of four orbitals are destabilized and we are left with a total of 22 electrons per three metal atoms for stability. Clearly two different types of metals have to be used if a neutral system is to result. The electron densities and overlap populations for a 22-electron sandwich are shown in 18. There is a transfer of one electron to each anthracene. According to these results the more electronegative metal should preferentially lie at the central position, and so Cr–Ni–Cr or Mn–Fe–Mn are likely candidates to stabilize this structure. The somewhat unexpected result that the more electronegative atom perfers the position with the higher coordination number is a consequence of the strong depopulation of the xz combination of 19 through the interaction with π_8 and π_4 as noted above. The overlap populations show the same



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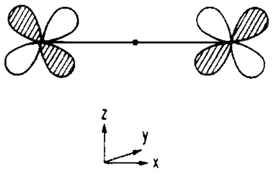

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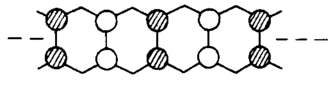
trends noted for M_2bis(naphthalene) and similar arguments can be used to understand them. These results suggest too that heterocyclic molecules, where electronegative atoms replace those carbon atoms with the largest charge density will be even better than anthracene as a ligand. One could imagine complexes with phenoxazine or phenothiazine with an 18-electron metal count (e.g., $M_3 = Cr_3$).

The detailed analysis of the naphthalene and anthracene compounds has shown many similarities in the form of the metal–ligand interactions. The analysis of the higher members of the series allows an easy generalization of the major electronic features for this type of complex. We do not need to draw explicit interaction diagrams to proceed to the analysis of the tetracene or pentacene compounds. A qualitative study, only considering the interaction between the different combinations of the xz and yz orbitals and the ligand π orbitals, suffices. The main results of this analysis for $M_n$bis(n-acene) are as follows: (a) The all-bonding xz combination always finds a very good match in overlap and energy with the orbital **20** (which in Hückel theory remains at $\alpha + \beta$ for any polyacene) and is destabilized. (We will qualify this remark for the infinite polymer later.) (b) The second xz combination always has the appropriate symmetry to interact with the LUMO and will remain at low energy. (c) Because the xz orbitals can only overlap with π orbitals through the β- and γ-carbons and because the overlap becomes smaller as the number of nodal planes increases, the interaction of the orther xz combinations with the ligands will be small and in any case will be counterbalanced by interactions of the same order with empty orbitals. (d) The n combinations of the yz orbitals interact very well with the n occupied orbitals of the proper symmetry (b_{3g} and a_u) of the polyacene. These orbitals have the proper nodal pattern and concentrate in the β- and γ-carbons as required. The result is that $n + 1$ orbitals are destabilized in energy and $2(5n - (n + 1)) = 8n - 2$ electrons are needed to fill up all the bonding and nonbonding orbitals (i.e., $8 - (2/n)$ electrons per metal atom.) One way of looking at this which preserves an 18-electron count at each metal center is to include 2 electrons for each metal–metal contact. This leads to the same result as our scheme above concerning the best metallic candidate for a good HOMO–LUMO gap. That the overlap populations of **14** and **18** show negligible metal–metal bonding should not worry us. A similar result would be found in $Fe_2(CO)_9$, for example, where a metal–metal bond is formally required if an 18-electron count at the metal is demanded. Thus our complex is neither a $\eta^4\eta^4\eta^6\eta^6$ complex with an Mn–Mn single bond nor a diradical $\eta^6\eta^6\eta^6\eta^6$ complex. Very strong through-bond coupling via the naphthalene π orbitals is at work here.



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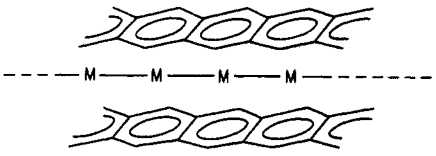
Could the infinite limit of this series, namely, **21**, be stable? The band structure of this polymer is shown in Figure 4. A band gap calculated to be 1.2 eV occurs for an occupation of 44 electrons per C_8H_4M repeat unit of the chain (M = Fe) and suggests that this polymer should be a semiconductor. The electron densities and overlap populations **22** show the same characteristics described above for the naphthalene and anthracene sandwiches. Why is there a band gap for this electron count? It is of course the value predicted using the formula just presented for the discrete molecular case but, as we will show, occurs in a somewhat different way. We need to look at the band structure. The repeat unit of the polymer is a bis(butadienyl)metal fragment. At the zone center and edges the symmetry is D_{2h} but only C_{2v} at all other k points. As a result, at $k = 0$ the xz orbitals may not mix with the π orbitals and remain at low energy (somewhat destabilized by intermetal interactions). At all other points the xz and π orbitals can mix. As xz is symmetric with respect to the vertical mirror plane, it will interact with the two symmetric orbitals of the butadienyl fragment. The two corresponding crystal orbitals of the isolated polyacene[20,21] at $k = 0$ and $k = \pi/a$ are shown in **23**–**26**. If the interaction between the metal and polyacene chains is ignored the three bands will behave as shown in **27**. When the interaction is switched on, there will be no major changes at $k = 0$ but the xz crystal orbital at $k = \pi/a$ (**28**) will interact strongly with **26** (as happened in the molecular sandwiches). **24** will not mix with **28**, and the simplified band structure **27** will be modified as shown by the arrows



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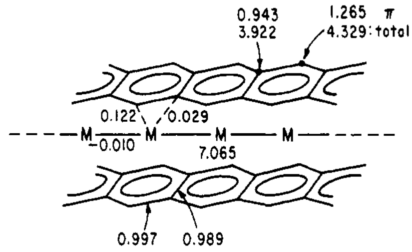

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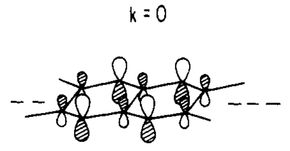

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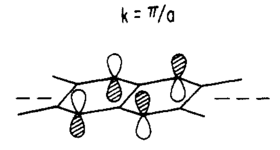

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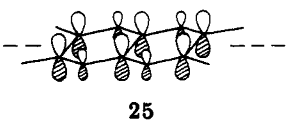

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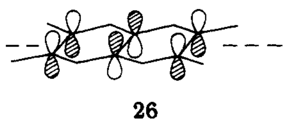

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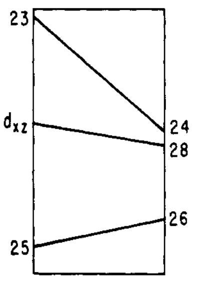

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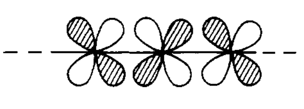

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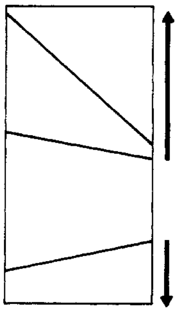
(20) For a discussion of the band structure of polyacene see: Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc.* **1979**, *A366*, 23. Yamabe, T.; Tonaka, K.; Ohzeki, K.; Yata, S. *Solid State Commun.* **1982**, *44*, 823. Kertesz, M.; Hoffmann, R. *Solid State Commun.* **1983**, *47*, 97.

(21) Burdett, J. K. *Prog. Solid State Chem.* **1984**, *15*, 173.

in **29**. As the three bands have the same symmetry at all other points, they will mix and we can expect a band structure similar to that of **30**, an argument substantiated by the actual calculation. In other words, the valence band (AS) is always maintained at low energy. The conduction band (AA) which reflects the antibonding interaction between *yz* and the orbitals of the polyacenes remains flat all along the Brillouin zone and a band gap results.



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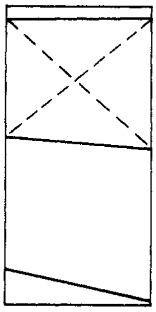

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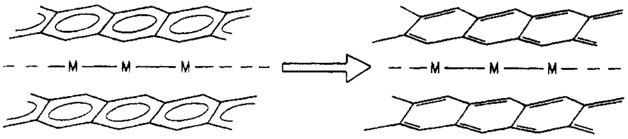
There is another simple explanation for these results. If we come back to Figure 2, we can see that the b_{1u} orbital is destabilized by **11** but the destabilization is somewhat attenuated by one empty orbital. The orbital **11** remains almost constant in energy all along the series (at $\alpha + \beta$) but the empty orbital of the appropriate symmetry drops sharply as the chain length increases ($\alpha - 1.303\beta$ in naphthalene, $\alpha - \beta$ in anthracene, $\alpha - 0.77\beta$ in tetracene, etc.). At a certain point therefore the effect of the empty orbital outweighs the effect of **20** and all the xz orbitals will remain at low energy. This suggests that only the first few members of the series and the infinite polymer will be stable, since an oligomer of intermediate size will have small HOMO–LUMO gap.

An additional point to be considered for the $M_n$bis(polyacene) system is the effect of the metal on the distortion (**31**) to the alternating system (analogous to the Peierls distortion of polyacetylene itself). For the isolated polyacene system we calculate an energy lowering of 0.29 eV for such a distortion. (The electronic details of such distortions in the organic materials are discussed in ref 20 and 21.) In the metal sandwich system the distortion is also stabilizing (0.43 eV) although there are only minor modifications to the band structure. Why is the distortion stabilizing? A brief comment is in order. The only differences in the band structures of the distorted and undistorted systems occur near the zone center for the AS (*xz*) and SA (*xy*) bands. As we have already commented, the *xz* orbital cannot mix with the π orbitals of the ligand at $k = 0$. A similar situation applies to the *xy* orbital. This orbital is antisymmetric with respect to the *xz* plane and can only mix with the crystal orbitals built from the π_2 and π_4 orbitals of the butadiene fragment. The corresponding crystal orbitals are shown in **32**, **33**, and **34**. Due to the additional symmetry planes (see **32**) present at $k = 0$ these orbitals cannot interact with each other. Since these extra symmetry planes disappear under the distortion, there are additional mixings at the zone center and both bands, AS (*xz*) and AA (*xy*), are stabilized. One could regard this as a second-order effect equivalent to the one occurring in the isolated polyacene.



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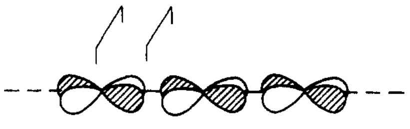

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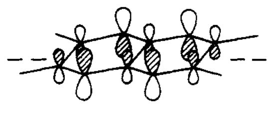

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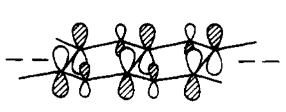
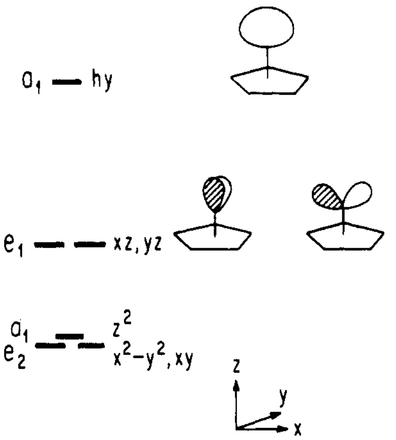


34

Multi-Decker Sandwich Compounds without Metal–Metal Contacts

Several compounds with this topology are known. For instance the triple-, tetra-, and penta-decker sandwiches[9-11] pertain to this class. Some polymeric cyclopentadienyl systems are also known although the M–Cp–M skeleton forms a zigzag chain.[22] The band structures for polymeric $M(C_5H_5)$ (M = Fe) and $M(C_6H_6)$ (M = Cr) are shown in parts a and b of Figure 5. They are very similar as could be expected from the isolated character[23] of the two fragments. The major difference lies in the *xz*, *yz* (e_1) band, a fact we will discuss later.

It is useful to describe in some detail the band structure of these polymers. The orbitals of a CpM fragment are well-known[18,24] (**35**). They are also included for comparison in Figure 5c. Two further orbital paris, mainly ligand in character, which we will call $\pi(e_1)$ and $\pi(e_2)$, lie below the *xy*, $x^2 - y^2$ pair and above the hybrid (hy) orbital, respectively. The CpM fragment can interact with a further Cp to form a Cp_2M molecule or with another CpM group to give CpMCpM. In both cases the important interactions are those of the a_1 and e_1 frontier orbitals. Both the hy (a_1) and *xz*, *yz* (e_1) orbitals are destabilized by interaction with a π(Cp) orbital (or mainly π(CpM) orbital in the case of reaction with CpM) of the same



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[22] (a) CpIn and CpTl: Frasson, E.; Menegeus, F.; Panattoni, C. *Nature (London)* **1963**, *199*, 1087. (b) Thallium tricyanovinylcyclopentadienide: Freeman, M. B.; Sneddon, L.; Huffmann, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5194. (c) Cp_2Pb: Panattoni, C.; Bombieri, G.; Croatto, U. *Acta Crystallogr.* **1966**, *21*, 823. (d) $CpZnCH_3$: Aoyagi, T.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Organomet. Chem.* **1978**, *146*, C29. (e) Cp_2Mn: Bunder, M.; E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1235.

[23] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[24] Chen, M. M. L.; Mingos, D. M. P.; Elian, M.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

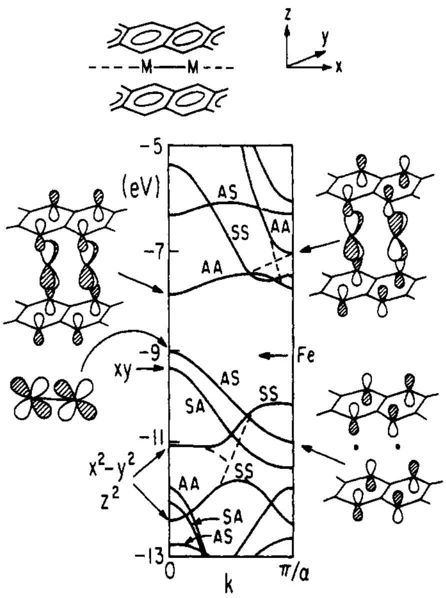

Figure 4. The band structure of **21**. The bands are labeled according to their symmetric (S) or antisymmetric (A) behavior with respect to the *xy* and *xz* planes.

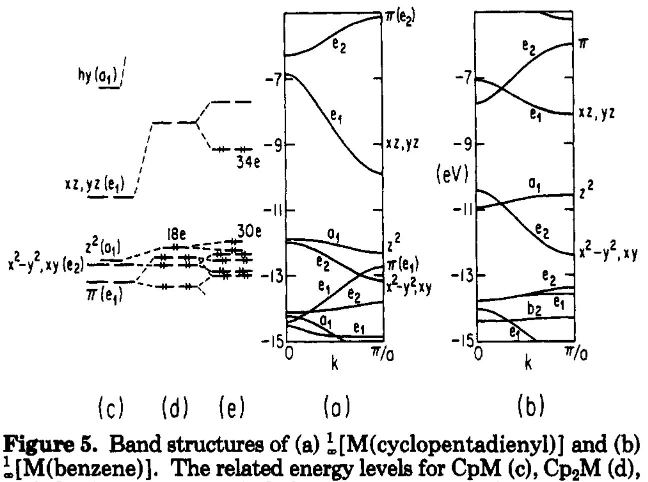

Figure 5. Band structures of (a) $^{1}_{\infty}[\mathrm{M(cyclopentadienyl)}]$ and (b) $^{1}_{\infty}[\mathrm{M(benzene)}]$. The related energy levels for CpM (c), Cp_2M (d), and Cp_3M_2 (e) are included for comparison. Some relevant electron occupancies are shown in d and e.

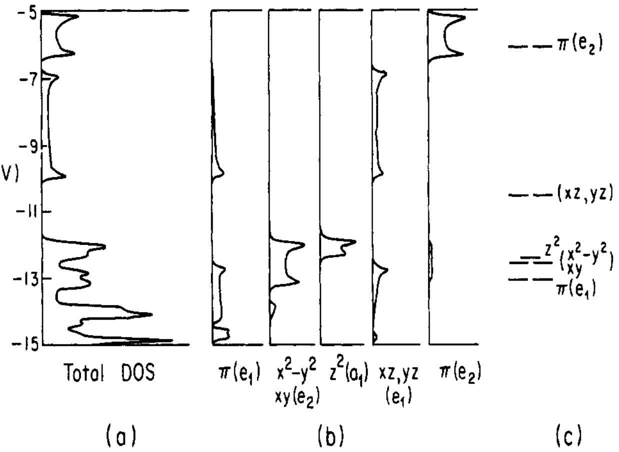

Figure 6. (a) Total density of states for $^{1}_{\infty}[\mathrm{M(cyclopentadienyl)}]$. (b) Projected densities of states for the orbitals $\pi(e_1)$, $(x^2 - y^2, xy)$, z^2, (xz, yz), and $\pi(e_2)$. (c) Energy levels of an MCp unit for comparison.

symmetry. The effect is stronger for the a_1 orbital because of a larger σ contribution to the overlap. The other orbitals are almost unchanged because of poor overlap. The pertinent energy levels of Cp_2M are included in Figure 5d. For the case of the CpM–CpM interaction, when the two units interact, the occupied orbitals destabilize the *xz* and *yz* orbitals on the left-hand unit but leave a set of low-lying *xz* and *yz* orbitals on the terminal M. These are then the frontier orbitals which interact with those of another CpM fragment. Clearly, what we are describing is the formation of the *xz*, *yz* (e_1) band of Figure 5a. At any stage of this process the growing of the chain can be stopped by interaction with the π (e_1) set of a Cp fragment to "seal off" the end of the (MCp) chain. Figure 5d shows the levels for a triple decker. The bands derived from the other orbitals, with the exception of the hy and π_1(Cp) orbitals (not shown in Figure 5) will be narrow because of the poor interaction between these orbitals when the polymer is built up.

An alternative way to analyze the band structures (and the most convenient one when proceeding to two- and three-dimensional systems) focuses directly on the density of states. An important trick here is the projection out of the contribution of selected atomic or fragment orbitals from the total density of states. This method of analysis is then the solid-state equivalent of the usual fragment orbital analysis.[26] The result of this analysis for the CpFe polymer is presented in Figure 6 where the total density of states and the contributions of the $\pi(e_1)$, $\pi(e_2)$, $(x^2 - y^2, xy)$, z^2, and (*xz*, yz) are depicted. Notice how the contributions of the interacting e_1 orbitals, π and (*xz*, *yz*), are split into two regions. This is the equivalent of our understanding of the interaction of two nondegenerate orbitals in molecules. The lower energy orbital ($\pi(e_1)$) is most heavily weighted in the lower energy band and the higher energy orbital (*xz*, *yz*) most heavily represented in the upper band. The contribution of these interacting orbitals extends over a considerable energy range (large dispersion) while the poorly interacting z^2 and $(x^2 - y^2, xy)$ contributions span a more reduced energy range (smaller dispersion). This analysis nicely complements the "polymerization" approach presented above. Notice that a band gap is predicted for M = Mn (or a d^7 metal).[21,27,28] Exactly the same analysis can be performed for the benzene–metal polymer. Here the appropriate metal for a band gap is chromium. The main difference between the two band structures lies in the *xz*, *yz* (e_1) band which is about twice as dispersive in the cyclopentadienyl compared to the benzene polymer. It is clear from the above discussion that the width of this band is a measure of the strength of the interactions between the xz, yz metal orbitals and the cyclic polyene $\pi(e_1)$ orbital. The size of this interaction also determines the gap between the two mainly *xz*, *yz* orbitals in the corresponding triple-decker molecule[18] (Figure 5e). It follows from HOMO–LUMO gap arguments that it is then unlikely that benzene-based triple-decker compounds with a 34-electron count, similar to those known for cyclopentadienyl-based systems, would be stable. The electronic requirements for stabilization of these structures are the same, but because the cyclopentadienyl unit is formally included as an anion, the

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[25] See: Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150 where such a projection occurs in a chemical context for the first time.

[26] Hoffmann, R.; Fujimoto, H.; Swenson, J. R.; Wan, C. C. *J. Am. Chem. Soc.* **1973**, *95*, 7644.

[27] Although the CpMn polymer is not known, Cp_2Mn is known both as a monomer (Haaland, A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 257) and polymer (ref 22e).

[28] For the theoretical analysis of other cyclopentadienyl polymers see: (a) Canadell, E.; Eisenstein, O.; Rubio, J. *Organometallics* **1984**, *3*, 759. (b) Canadell, E.; Eisenstein, O.; Hughbanks, T. *Inorg. Chem.* **1984**, *23*, 2435. (c) Böhm, M. C. *Z. Naturforsch., A* **1984**, *39A*, 223.

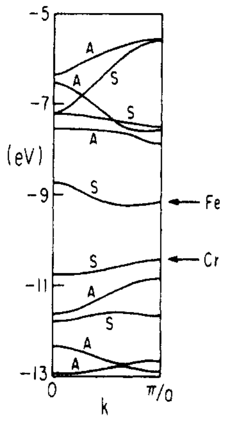
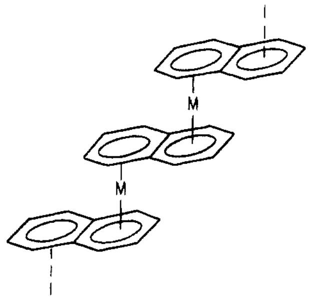


Figure 7. Band structure of **36**, showing two band gaps appropriate to the metals chromium and iron.

metal atoms used in the cyclopentadienyl systems are usually more electronegative and, as a result, the energy difference between the interacting orbitals is smaller and the interaction is more effective. Nevertheless it should be pointed out that on energy gap arguments the 30-electron $Cr_2(C_6H_6)_3$ triple decker could be perfectly stable. Similar arguments may be used to view systems containing substitution by boron of the carbon atoms of the rings (see ref 28c). Analogous electron-counting rules are found here.

As we have shown, naphthalene should form a dimetal sawndwich with manganese. There is an alternative polymetallic structure (**36**) which has the same stoichiometry.[29] This polymer is similar to polyferrocenylene (**8**),[2] but since the organic rings are fused, a greater electronic delocalization is possible. Katz and co-workers have made different attempts to synthesize polymers with this topology.[14] The band structure for this polymer is shown in Figure 7. Interestingly, there are two different electron counts associated with a band gap corresponding to iron and chromium polymers. This contrasts with the recent results on the band structure of polyferrocenylene[30] where only one band gap (for M = Fe) was found in this region. The reasons for this difference are interesting ones and draw on our previous discussion.



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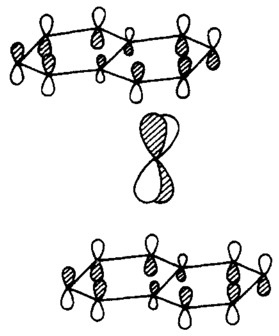
The *yz* orbital, as in all other cases, is destabilized and becomes therefore the conduction band of the iron polymer at $k = 0$ (**37**). The valence band for the chromium polymer is mainly z^2 in character all across the Brillouin zone. But there is a band in between these two bands and well separated from both. Because of the inversion center on the metal, the *xz* orbital cannot interact with the orbital **12** at $k = 0$ (**38**). Interaction with other π orbitals can occur but is less favorable, and the *xz* orbital remains between the nonbonding and antibonding metal–ligand regions at $k = 0$. Obviously, the reasoning is reversed at $k = \pi/a$, and the orbital is there strongly repelled. At the same time the LUMO of naphthalene, which interacts with $x^2 - y^2$ at $k = 0$, cannot interact efficiently with any d orbital at $k = \pi/a$ (**39**), and, in consequence, at the zone edge the corresponding crystal orbital is almost purely made of this orbital and appears at ~−9 eV, the energy of the LUMO of naphthalene. As the two bands have the same symmetry, they mix strongly along the Brillouin zone and the result is the flat band at −9 eV, well separated from the others. What we have just described is in fact nothing more than a three-orbital interaction between the orbital **12**, *xz*, and the LUMO of naphthalene. To these three orbitals correspond three bands in the band structure: the flat band at −9 eV, the dispersive one between −7 and −6 eV, and another one not shown in the Figure which appears just below −13 eV.



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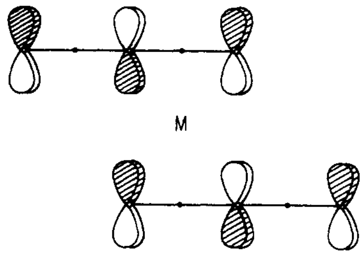

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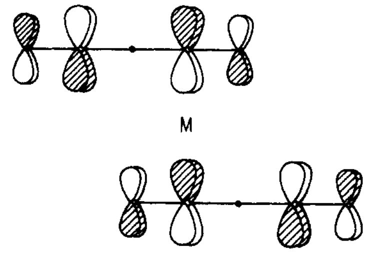

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The essential difference between this system and poly((benzene)chromium) is thus clear. In this case the *xz* orbital can only interact with the HOMO of benzene and does not find any empty π orbital of the same symmetry. In the naphthalene case the *xz* orbital can interact with both the high-lying orbital **12** and the LUMO. The orbital remains between the occupied and the empty levels. Let us note that the argument depends only on the nature of the ligand but not on the details of the polymer topology. The same argument should apply to **40**. As can be easily verified from our previous arguments, the nature of the band structure for this polymer is the same as that for **36**. The only difference is that the interactions we have described at $k = 0$ for **36** occur at $k = \pi/a$ for **40** and vice-

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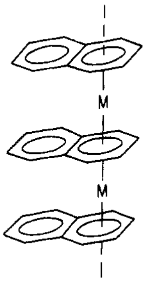
(29) For some oligomers presumably with this topology see: Elschenbroich, C.; Heck, J. *J. Am. Chem. Soc.* **1979**, *101*, 6773. Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1. Elschenbroich, C.; Heck, J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 479.

(30) Böhm, M. C. *J. Chem. Phys.* **1984**, *80*, 2704.



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versa. Nevertheless the arrangement **36** will be preferred because of smaller π-type two-orbital–four-electron repulsions between the organic units. The Mulliken population analysis for **36** shows a small positive charge on naphthalene (+0.120) for M = Cr. In agreement with our discussion of the nature of the center band the charge on naphthalene for M = Fe is −1.13. Due to the nature of the band structure it would be interesting to study the electrical properties of these polymers and especially of doped polymers in which this central band is only partially occupied.

Double-Decker Sandwich Compounds with Zigzag Metal Chains and Planar Metal Clusters

Naphthalene is an interesting ligand which may be stabilized by different metal atoms in different types of sandwiches. As a variant on the systems described above, with fused three-ring systems we can change the terminal metal–metal distances in the metal cluster. Figure 8 shows how the HOMO–LUMO energy gaps change for the trimetal sandwiches of anthracene, phenanthrene, and the phenalenyl radical. The gaps are very similar for the anthracene and phenanthrene cases, suggesting that the electronic requirements for the linear and zigzag chain sandwiches are similar. The situation however is very different for the case of M$_3$bis(phenalenyl) where there are two gaps of only 0.8 eV corresponding to electron counts of 18 and 22 for the metal atoms. HOMO–LUMO gap arguments suggest therefore that isolation of this sandwich is unlikely for any electron count. The interaction diagram for this system is shown in Figure 9. As in the M$_3$bis(anthracene) compound four of the six combinations of the xz and yz orbitals are strongly destabilized. However the two remaining combinations, **41**, which are equivalent by symmetry and interact with a pair of occupied orbitals **42**, do not find a very low-lying empty orbital of the ligand to relieve this interaction (in anthracene the LUMO plays this role) and appear higher in energy than in the corresponding anthracene case. More importantly, the antibonding combination of the in-plane orbital **43** which interacts with the out-of-phase combination of the radical orbital of the ligands **44**, appears at a lower energy than the corresponding orbital in the anthracene compound (see Figure 8). The analysis of this interaction shows that the overlap integrals are similar in both cases (0.214 vs 0.195) but the energy difference is now greater (0.88 vs 0.39 eV). An increase of 0.5 eV in a small energy difference has a very sizeable effect on the interaction and the antibonding combination appears 0.8 eV lower in energy than in the anthracene containing molecule. A calculation for M$_4$bis(pyrene)8 **45**, gives a still smaller gap of 0.6 eV for an electron count corresponding to iron, and there is no gap at all for the two-dimensional limit of the series. This leads to the conclusion that polymetallic sandwiches are metallic conductors for the two-dimensional solids but using HOMO–LUMO arguments will not be stable as molecules containing planar clusters of metal atoms.

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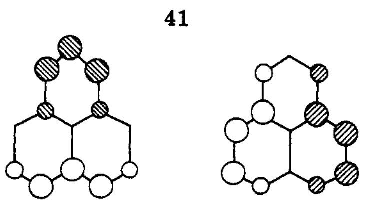

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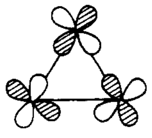

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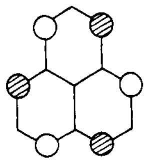

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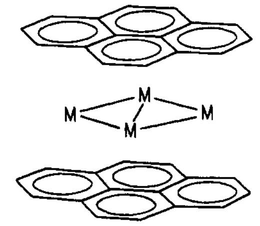

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M$_2$bis(pentalene) Compounds

After having explored several hypothetical sandwiches it is time to return to those which are actually known. A D_{2h} sandwich structure was assigned to the pentalene complexes Co$_2$(C$_8$H$_6$)$_2$ and Ni$_2$(C$_8$H$_6$)$_2$ (**5**) on the basis of NMR data[13] but as a single-crystal X-ray study has not proven possible the details of the structure are uncertain. Do these molecules have a sizeable energy gap? An interesting experimental observation concerning the free neutral ligand is that it is unknown, but salts of the dianion are well characterized.[31] (Derivatives of neutral pentalene, such as the perphenyl, are known.) Calculations with two planar pentalenes and a Co–pentalene distance of 1.66 Å gave an an energy minimum for a Co–Co distance of 2.6 Å. The interaction diagram is shown in Figure 10. Given this observation concerning the ligand and its dianion, the situation is remarkably similar to the case of Mn$_2$bis(naphthalene) if naphthalene is replaced by pentalene dianion. The two yz combinations (b_{3g}, a_u) are destabilized as is the bonding xz combination (b_{1u}). The antibonding xz combination remains at low energy. With three combinations pushed up and the pentalene now formally entering the complex as a 10-electron donor the appropriate metal is cobalt. The HOMO–LUMO gap is calculated to be 1.42 eV. Additionally, there is a second energy gap of 1.0 eV calculated for the electron count corresponding to nickel but only one of 0.45 eV for iron. When, in addition to the Co–Co distance, both the metal–pentalene distance and the bending of pentalene were allowed to vary, it was found that the pentalenes bent 5° toward the metal atoms. This bending motion, very similar indeed to the one cal-

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[31] Knox, S. A. R.; Stone, F. G. A. *Acc. Chem. Res.* **1974**, *7*, 311.

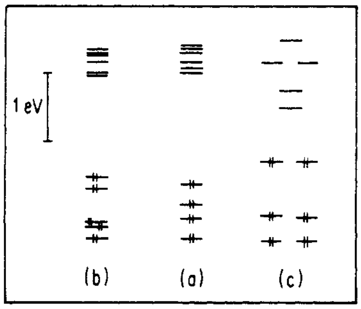


Figure 8. Energy levels for the trimetal sandwiches of (a) anthracene, (b) phenanthrene, and (c) phenalenyl. The level occupations correspond to 22 metal electrons.

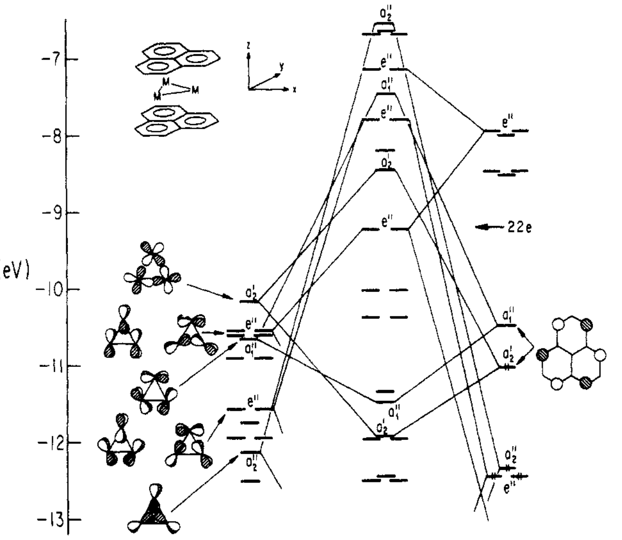


Figure 9. Interaction diagram for M_3bis(phenalenyl). Only the π orbitals of phenalenyl and the metal d orbitals are shown. The orbital occupancy shown is for a pair of neutral ligands.

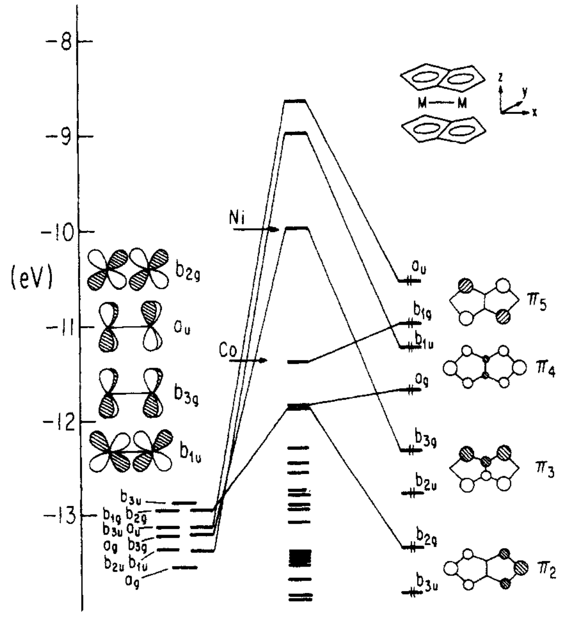
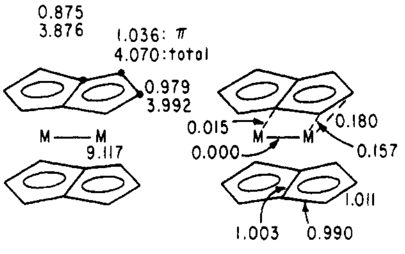


Figure 10. Interaction diagram for M_2bis(pentalene). Only the metal d orbitals and the ligand π orbitals are shown. The ligand orbital occupancy corresponds to a pair of dianions.

culated for naphthalene, is accompanied by a decrease in the metal–metal distance to 2.5 Å. With this geometry the energy gaps are calculated as 2.2, 1.05, and 0.2 eV for the electron counts corresponding to Co, Ni, and Fe, respectively. This is in nice agreement with the observations of Katz,[13] which we mentioned in the Introduction, if we once again identify a significant HOMO–LUMO gap with kinetic and structural stability.

Another point to consider is the possibility of a bending motion such that the angle between the normals to the pentalene planes is less than 180°. Such a distortion is analogous to the "bent" MCp_2 configuration. Some model calculations show that this bending is only energetically favorable when the metal is titanium or vanadium. However pentalene is probably too small a ligand to accommodate either of these metals. Sandwich compounds of this type are more likely to be found with larger ligands such as fulvalene. Indeed such species are known.[32]

The electron densities and overlap populations for the Co and Ni electron counts are shown in **46** and **47**, respectively.



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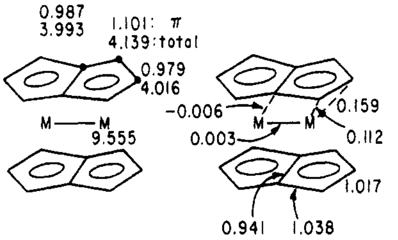

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In the second case there is a transfer of 0.45 electrons to each pentalene. As noted for the naphthalene sandwiches the overlap population of the metal atom with the central atom of the pentalene is very small while the values for the more exterior atoms is considerable. This result lies behind the tendency of pentalenes to bend with the α- and β-carbons moving toward the metal atoms. As a consequence of the populations shown in **47**, we might be tempted to describe the nickel compound as essentially two bis(allyl)metal units, linked by two pairs of carbon atoms. However a similar situation appears for the cobalt case in **46**, and such a description camouflages the fact that the two "allyl" units are intimately linked electronically.

The good match in symmetry between the first five π orbitals[33] of pentalene, azulene, naphthalene, and cyclooctatetraene suggests that different sandwich compounds could be obtained by replacing pentalene by one of these ligands and adjusting the electron count at the metals. So, compounds **48**–**52** are electronically equivalent to Co_2bis(pentalene). The azulene sandwiches are interesting because of the possibility of the 5–7/5–7 and 5–7/7–5 isomers. We feel less confident that a similar series of compounds can be made for the Ni_2bis(pentalene) case. The

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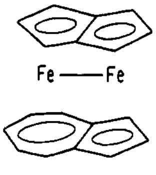
[32] V_2(fulvalene)$_2$ and V_2(fulvalene)$_2$(CO)$_2$ as well as [V_2(fulvalene)$_2$(CH_3CN)$_2^{2+}$](PF_6^-)$_2$ are known. (Smart, J. C.; Pinsky, B. L.; Fredrich, M. F.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 4371. Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009, 3663.) The pair of fulvalene molecules in the last cation are bent.

[33] Streitweiser, A., Jr.; Coulson, C. A.; Brauman, J. I. "Supplemental Tables of Molecular Orbital Calculations"; Pergamon Press: Elmsford, N.Y., 1965; Vol. 2.



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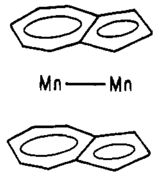

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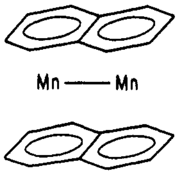

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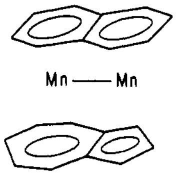

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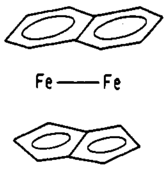

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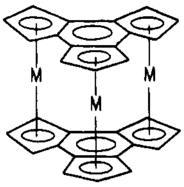
gap is not too great, and our exploratory calculations show it is quite sensitive to small changes in the actual energy levels of the ligands. In fact, Ni_2bis(pentalene) could well be a high-spin system.[34] There are clearly several distortions of this series of molecules which we have not examined. One is the slippage of the polymetal unit off the organic moieties. Such a distortion appears for example in the complex $Fe_2(CO)_5$azulene where one iron atom is η^5 (the five ring) and one iron is η^3 (three atoms of the seven ring). In this molecule both iron atoms have 18-electron counts. It is quite possible that distortions of this type in our $M_n$bis(fused arene) systems can stabilize molecules with small HOMO–LUMO gaps at the geometries we have examined.



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The results described in this paper show a very interesting dependence of the level structures of these molecules on the geometry of the organic ligands. Importantly the fusion of the organic rings creates new electronic possibilities. The 1,1′-biferrocenylene molecule[2] has a good HOMO–LUMO gap for M = Fe and behaves just as two coupled ferrocene moieties. (Similarly our calculations show that the "gazebo" structure **53** behaves as three coupled ferrocene units and M = Fe is the metal of choice for a good energy gap.[14]) However $M_n$bis(fused arene) molecules are very different and may lead either to good HOMO–LUMO gaps for a specific electron count (linear or zigzag metal chains), implying structural stability or small gaps which may not be sufficient for stability (planar metal clusters). In the former case the electron count at the metal is not the one which would have been anticipated from previous experience.

Table I

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	c_1[a]	c_2
Cr[38]	4s	−8.66	1.70			
	4p	−5.24	1.70			
	3d	−11.20	4.95	1.80	0.5058	0.6747
Fe[39]	4s	−9.22	1.90			
	4p	−5.37	1.90			
	3d	−12.70	5.35	1.80	0.5366	0.6678
Co[38]	4s	−9.21	2.0			
	4p	−5.29	2.0			
	3d	−13.18	5.55	2.10	0.5679	0.6059
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
H	1s	−13.60	1.30			

[a] Contraction coefficients used in the double-ζ expansion.

Acknowledgment. This research was supported by a grant from the Exxon Foundation and by the National Science Foundation via DMR 8019741. We would like to thank Professor T. A. Albright for some useful comments.

Appendix

The calculations are of the extended Hückel type[35] with the parameters and exponents of Table I. The modified weighted Wolfsberg–Helmholz formula was used.[36] Except when specifically stated the calculations have been performed with chromium as the metal atom. The metal atoms were placed over the centers of the rings at 1.616 Å. The C–C distances were taken to be 1.40 Å. For calculations on the Co_2bis(pentalene) complex, a regular pentalene with C–C = 1.40 Å and C–C–C = 108° was used. Fe–C distances of 2.12 Å were used for the $FeCp^+$ polymer. The tight binding method[37] was used to generate band structures for the one- and two-dimensional systems. A set of 6k points was used in the calculation of charges and overlap populations for the one-dimensional systems. A set of 50k points was used to generate the DOS curves of Figure 6. The curves were smoothed by using Gaussian functions with a standard deviation of 0.08 eV.

Registry No. **1** (M = Cr), 1271-54-1; **5** (M = Ni), 95464-97-4; **5** (M = Co), 37337-88-5; **5** (M = Fe), 95464-99-6; **18** (M–M–M = Cr–Ni–Cr), 95512-40-6; **18** (M–M–M = Mn–Fe–Mn), 95531-26-3; **36** (M = Fe), 95465-02-4; **36** (M = Cr), 95465-04-6; **48**, 95464-98-5; **49**, 95512-37-1; **50**, 95512-36-0; **51**, 95512-38-2; **52**, 95512-39-3; **53**, 95465-00-2; $[Fe(C_5H_5)]_x$, 95465-05-7; $[Cr(C_6H_6)]_x$, 95465-06-8; tetracene, 92-24-0; pyrene, 129-00-0; anthracene, 120-12-7; phenanthrene, 85-01-8; phenylenyl, 3924-44-5; pentalene, 250-25-9; naphthalene, 91-20-3.

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(34) The existence of a HOMO–LUMO gap for Co_2bis(pentalene) is a parameter independent result. The gap for Ni_2bis(pentalene) is more sensitive to the actual parameters of the calculation. A similar result was found when exploring the electronic structures of hypothetical polymetallic sandwich compounds of the radialenes. For instance, it was found that the M_3bis(trimethylenecyclopropane) structure could be stable for both 26 and 30 metal electron counts. (For 30 electrons the structure may be regarded as three independent 14-electron $M(olefin)_2$ units.) This result is related to the interaction of the e′ combination of metal z^2 orbitals with the e′ combination of the π_{C-C} orbitals. This result was obtained with the nickel parameters of: Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. When the nickel levels are decreased in energy, only the energy gap corresponding to the 30-electron count survives. Nevertheless, the possibility raised by this calculation is intriguing and merits further attention.

(35) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(36) Ammeter, J. H.; Bürgi, H. B.; Thibeault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(37) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

(38) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(39) Albright, T.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.