

structure of polycyclobutadiene.

The most intriguing feature of these band structures is the existence of a crossing (avoided in **6a**, but allowed in the higher symmetry **6c**) between the valence and conduction bands. Such crossings are rare^{25b,29} and, when seen, typically occur very near the zone edge. We are unaware of any system with a crossing at $\pi/2a$, as in **6c**, or even nearly as far back toward the center of the Brillouin zone. In the present system this produces a very high density of states at the Fermi level. Formally, **6b** and **6c** are true metals, while **6a** has a small band gap and a low ionization potential compared to other conducting polymers. While one might expect that the parent polycyclobutadiene would be a very reactive substance, suitably substituted derivatives could have truly remarkable properties.

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Conclusions

Unlike the analogous polyphenyls, which are essentially a chain of benzene rings, the homologous structures based on cyclobutadiene exhibit structural and electronic properties quite unlike the monomer. Bi(cyclobutadienyl) is best considered as two allyls plus ethylene, tri(cyclobutadienyl) as two allyls plus dimethylene-cyclobutanediyl,²⁸ and tetra(cyclobutadienyl) as two bi(cyclobutadienyl) units. The band structure of the infinite polymer is quite intriguing, suggesting a very small (or zero) band gap and a high density of states near the Fermi level.

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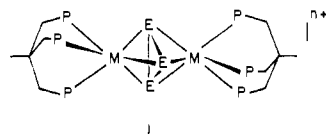
Inorganic Rings, Intact and Cleaved, between Two Metal Fragments

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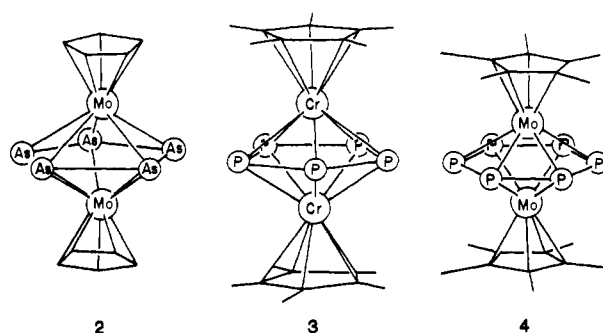
Contribution from the Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster, FRG, Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301, and Department of Chemistry, Georgetown University, Washington, D.C. 20057. Received April 8, 1988

Abstract: The electronic structure of CpME_nMCp ($M = \text{Cr}, \text{Mo}; E = \text{P}, \text{As}$) triple-decker complexes is explored, where the middle deck contains a five- or six-membered ring of group 15 E atoms. From another point of view, the metal and group 15 atoms form a polynuclear cluster. All hitherto known compounds possess short metal-metal distances across the central ring, are electron deficient, and do not follow the triple-decker 30 electron or Wade-Mingos skeletal electron counting rules. In addition, the complex $\text{CpMoAs}_3\text{MoCp}$ exhibits a substantial distortion from idealized 5-fold symmetry; the middle deck shows a partitioning into As_2 and As_3 fragments. By making use of the frontier orbitals of the CpMo and E_n fragments the electronic structure of these "inorganic" triple-decker compounds is analyzed. The short metal-metal distances in these systems are responsible for their apparent electron deficiency. The distortion of the central As_3 ring in $\text{CpMoAs}_3\text{MoCp}$ is traced to the simultaneous working of first- and second-order Jahn-Teller effects.

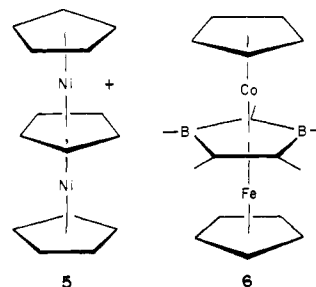
Some remarkable compounds containing homoatomic rings of main group elements stabilized by coordination to transition-metal fragments have been synthesized.¹ Sacconi and co-workers described a number of "double sandwich" compounds [(triphos)- $M'-(\mu-(\eta^3-E_3)M''(\text{triphos}))^{n+}$ (**1**) containing cyclo-triphosphorus $\eta^3\text{-P}_3$ or cyclo-triarsenic $\eta^3\text{-As}_3$ groups sandwiched between two ML_3 fragments.² Rheingold, Scherer, and their co-workers added



variety to this class of compounds when they reported the synthesis and structure of $\text{CpMoAs}_3\text{MoCp}$ (**2**),³ $\text{Cp}^*\text{CrP}_5\text{CrCp}^*$ (**3**),⁴ and $\text{Cp}^*\text{MoP}_6\text{MoCp}^*$ (**4**).⁵ Although these complexes clearly look like triple-deckers,^{1c} they also differ from the classic examples such as Cp_3Ni_2^+ (**5**),^{6a} $\text{CpCo}(1,3\text{-C}_3\text{B}_2\text{H}_5)\text{FeCp}$ (**6**),^{6b} $\text{CpRuCp}^*\text{RuCp}^{+6c}$ or Sacconi compounds **1**, both structurally and electronically. First, in contrast to all known and hypothesized triple-decker sandwiches, there are relatively short metal-metal



contacts across the central ring. The metal-metal distance in **2**,



which contains a cyclo- As_3 ring, is 2.764 Å. This is intermediate

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between bond distances typically assumed for Mo–Mo single bonds (2.9–3.2 Å) and Mo–Mo double bonds (~2.6 Å). In **3** and **4** containing (undistorted) cyclo-P₅ and cyclo-P₆ as the middle deck of the triple-decker complex, we find metal–metal separations of 2.727 and 2.647 Å, respectively. Furthermore, these compounds are electron deficient: **2** and **3** are 27-electron compounds. As usual, the electron counting can be accomplished in a number of ways. Here is one: in **2** and **3** we have two 6-electron-donating Cp[−] ligands and one 6-electron-donating E₅[−] (E = P, As) ligand

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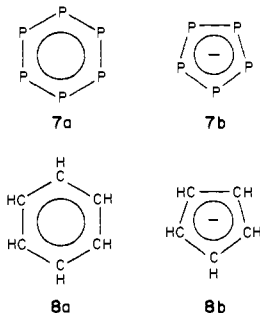
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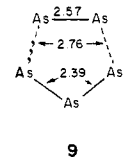
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isoelectronic to Cp[−]. In addition there are nine electrons left on two metal atoms, giving a total of 27 electrons. **4** is a 28-electron species. All of these compounds violate the 30/34 electron rule put forward by Elian et al.⁷ for triple-decker sandwiches.

The structure of the middle deck is of special interest. Cyclic P₆ (hexaphosphabenzene) (**7a**) or cyclic P₅[−] (pentaphosphacyclopentadienyl anion) (**7b**) could have the aromatic structure of their organic counterparts (**8a,b**), all CH units being replaced by



isoelectronic phosphorus atoms. No evidence for free P₅, P₅[−], or P₆ has been reported in the literature. Isolated planar P₆ rings (formally P₆^{4−}) have been observed in the binary phosphides Rb₄P₆^{8a} and K₄P₆^{8b} and planar Ge₅^{6−8c} and Si₅^{6−8c} rings have been observed in solid-state compounds as well. In **3** and **4**, which are central in this paper, we find undistorted cyclo-P₅ and P₆ units. The average P–P distances are 2.18 and 2.17 Å, slightly shorter than a typical single bond distance of 2.21 Å in P₄.⁹ The As₅ group in **2**, however, is severely distorted. All the As–As distances deviate significantly from a “normal” single bond length of 2.42–2.44 Å.¹⁰ The shortest As–As distances are 2.397 and 2.389 Å, and the longer distances vary between 2.563 and 2.762 Å, suggesting fractional bond orders and allowing a partitioning of the As₅ ring in As₂ and As₃ fragments as shown in **9**.



That the E–E separations in these compounds are in the range of normal single bond distances (with the exception of the last compound, **2**) is significant in the following context: One might have imagined that the metal centers in these compounds, electron deficient as they are, could move toward saturation by using the E–E σ-bonding electrons. But that would have weakening of the E–E bond as a consequence, and that does not seem to occur.

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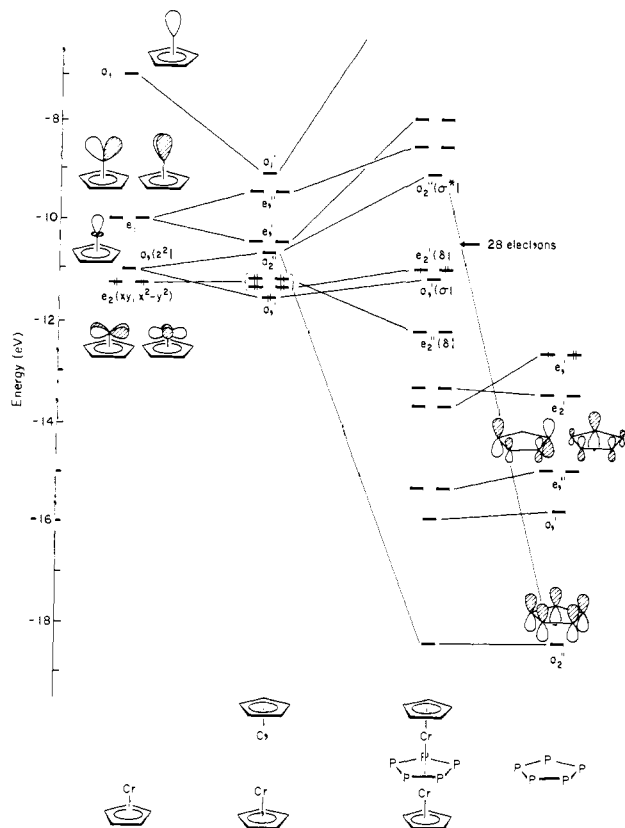


Figure 1. Interaction diagram for the frontier orbitals of $\text{CpCrP}_3\text{CrCp}$ (D_{5h}). On the left two CpCr fragments are combined to a moderately interacting $\text{CpCr}\cdots\text{CrCp}$ unit, which in the following step is allowed to react with the central P_3 .

We can approach these compounds from the cluster point of view as well. Let us consider **3** to be a polyhedral cluster containing a main group P_3 building block, which is capped by two CpM transition-metal fragments. Now one should be able to apply the Wade-Mingos skeletal electron counting rules,¹¹ which allow the association of a total cluster electron count with a given cluster geometry. For a closo-deltahedron of main group elements the magic cluster electron count is $4n + 2$ (n = number of vertices), which is 30 in the present case. Substituting two transition-metal fragments for two main-group atoms gives a cluster electron number of 50. **2** and **3** possess 47 electrons and come out to be electron deficient species, just as we figured before based on the 30/34 electron rule.⁷ For **4** the magic electron count is 54, to be contrasted with an actual electron count of 52. Thus **4** is an electron-deficient species as well. From still another point of view these molecules can be regarded as interesting borderline cases or possibly as hybrids between classic organometallic species and inorganic Zintl-type compounds, some recent example here being $[\text{Ti}_6\text{Fe}_{10}(\text{CO})_{36}]^{6-12}$ and $[\text{Bi}_4\text{Fe}_4(\text{CO})_{13}]^{2-13}$.

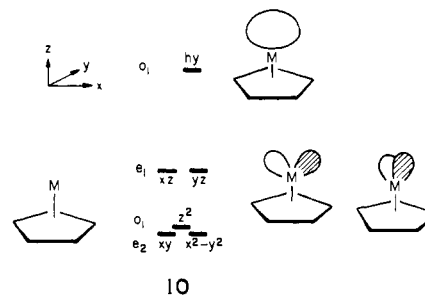
We would like to understand the bonding in these and some related compounds. In particular, we are interested in the unusual electron count and the distortion observed in **2**. Our conclusions are mainly based on symmetry and overlap arguments supple-

mented by extended Hückel calculations.¹⁴ The technical details relevant to the calculations may be found in the Appendix. We note here some important work done by Burdett and Pourian,¹⁵ who analyzed the bonding in complexes having polyhydrogen units and investigated possible modes of distortion for some of these species. One early contribution on hydrogen bridged complexes came from this group.¹⁶

We will proceed in this paper by first building up the electronic structure of the P_3 and As_3 bridged complexes and then looking at the distortion observed in the latter example. The bonding in related compounds containing a planar polygon of cyclically bound group 15 atoms is analyzed subsequently. In a separate paper these structures will be linked geometrically and electronically to a class of sulfur-bridged Mo-transition-metal clusters.

Bonding in the CpME_nMCp Complexes

We start our analysis with a fragment analysis based on a $\text{CpM-E}_n\text{-MCp}$ partitioning of the molecule. The orbitals of the isolated CpM fragments are well known¹⁷ and the assembly of the molecule is aided considerably by symmetry. The characteristic features of the CpM fragment are given in **10**. There are relatively low lying orbitals, a_1 and e_2 , originating primarily from metal z^2 , $x^2 - y^2$, and xy , which are partially filled for a d^4/d^5



system. At higher energy we find an e_1 set, mainly metal xz and yz , hybridized with x and y , which makes these orbitals extend away from the Cp ligand. At still higher energy is a a_1 hybrid of metal z^2 and s pointing away from the ligand as well. The interaction with other fragments is carried mainly by these a_1 and e_1 hybrids.

The interaction diagram in Figure 1 was constructed from an extended Hückel¹⁴ calculation in an idealized D_{5h} symmetry with distances given in the Appendix. On the extreme left we give the levels of the CpCr fragment (the actual calculations were done on $\text{CpCrP}_3\text{CrCp}$ instead of $\text{Cp}^*\text{CrP}_3\text{CrCp}^*$, see Appendix), whose level sequence is basically explained in **10**. At a $\text{Cr}\cdots\text{Cr}$ distance of 2.727 Å we find only moderate level splittings except for the a_1' and a_2'' levels derived from the a_1 hybrid orbitals of the CpCr fragment. On the right side of Figure 1 are given the levels of the bridging P_3 fragment. It is isoelectronic to a Cp fragment and we expect to see the same orbitals. Lowest in energy (not shown) are five σ bonding levels. Next comes the a_2'' and e_1'' π set interspersed with the lone pair levels a_1' , e_1' , and e_2' . Some 7 eV higher in energy come the e_2'' (π) levels followed by the σ^* levels far up in energy. In the last step the $[\text{CpCr}\cdots\text{CrCp}]$ and P_3 levels are allowed to interact. The a_2'' and e_1'' donor orbitals of the P_3 unit strongly interact with the corresponding symmetry combinations derived from the CpM a_1 hybrid and the xz , yz orbitals. The nonbonding set derived from the $x^2 - y^2$ and xy

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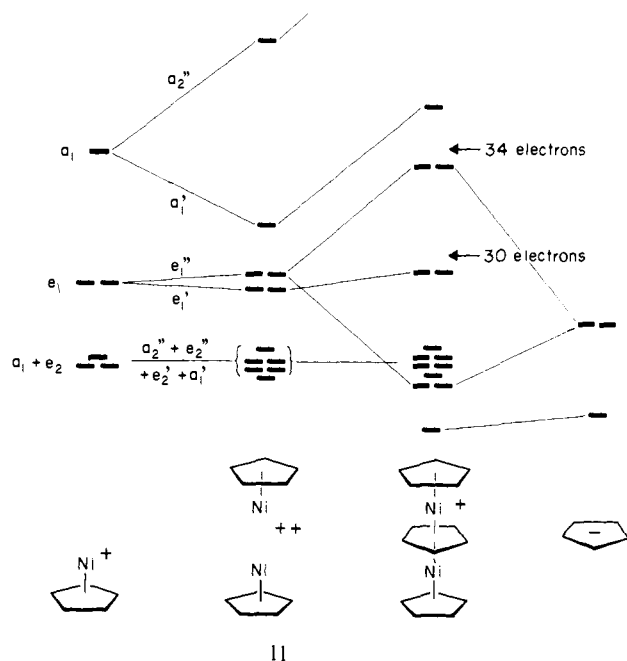
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orbitals is much less perturbed. It is doubled and stays approximately at the same energy. Note that the levels derived from the z^2 orbitals are split by ~ 2.2 eV. The effect on the π orbitals and lone pairs is less pronounced.

The emerging orbital pattern is contrasted with the level pattern found for the classic triple-decker compounds, which is constructed for **5** in **11**. The overall orbital sequence is similar. There is some difference in the separation of the e_2' and e_2'' levels in **11**. The most important feature, however, is the enhanced separation of the a_1' and a_2'' levels in **3**. The a_2'' level is moved above the " t_{2g} " block creating a HOMO-LUMO gap of approximately 2 eV in the compounds under study in this work.



For the P_5 complex **3**, if one fills all orbitals up to the large gap one obtains a 28-electron species corresponding to a $[\text{CpCrP}_3\text{CrCp}]^-$ monoanion. In fact, **3** can be oxidized and reduced reversibly to give a 26-electron monocation or 28-electron monoanion.^{4a} From ESR data Scherer et al.^{4a} find a nondegenerate 2A_1 ground state for the neutral compound. This requires the ordering of the a_1' and e_2' levels in our calculations to be reversed. The computed energy difference between these levels is 0.16 eV, which is not a serious discrepancy considering the approximate nature of our calculations.

One way then to bring the observed orbital pattern into concordance with polyhedral skeletal electron pair counting rules or the triple-decker formalism is to include an explicit metal-metal σ bond. This removes one orbital (σ^* or a_2'') from the valence set, leaving 48 (skeletal electron pair counting rule) or 28 (triple-decker count) as the magic or stable electron count.

Let us turn now to **2**, the As counterpart of **3**. In Figure 2 we show an interaction diagram for the undistorted (hypothetical) $\text{CpMoAs}_3\text{MoCp}$. On the left are the orbitals of the CpMo fragments combined to form a $[\text{CpMo}\cdots\text{MoCp}]$ unit. On the right are given the levels of the As_3 fragment. The overall picture is quite similar to that for **2** in Figure 1. Note, however, the energy range covered by the levels of the P_5 and As_3 fragments. Whereas the energy range covered by the levels of the P_5 unit spreads out over 60 eV (not the whole range is shown in Figure 1), all the levels for the As_3 fragment are contained within a 15 eV energy interval. The reason is the interatomic overlap. For the diffuse As orbitals the interatomic overlap $\langle \text{As}|\text{As} \rangle = 0.45$ is smaller than for the more contracted P orbitals, where the computed overlap $\langle \text{P}|\text{P} \rangle = 0.79$. The result is a reduced level splitting.

From the interaction diagram in Figure 2 we see that there is a better energy match and more mixing between the metal-based fragment orbitals (FMO's) and the π^* and σ^* orbitals of the central As_3 ring. Whereas there is a significant contribution of π^* and σ^* orbitals of the As_3 fragment for **2** (undistorted), we

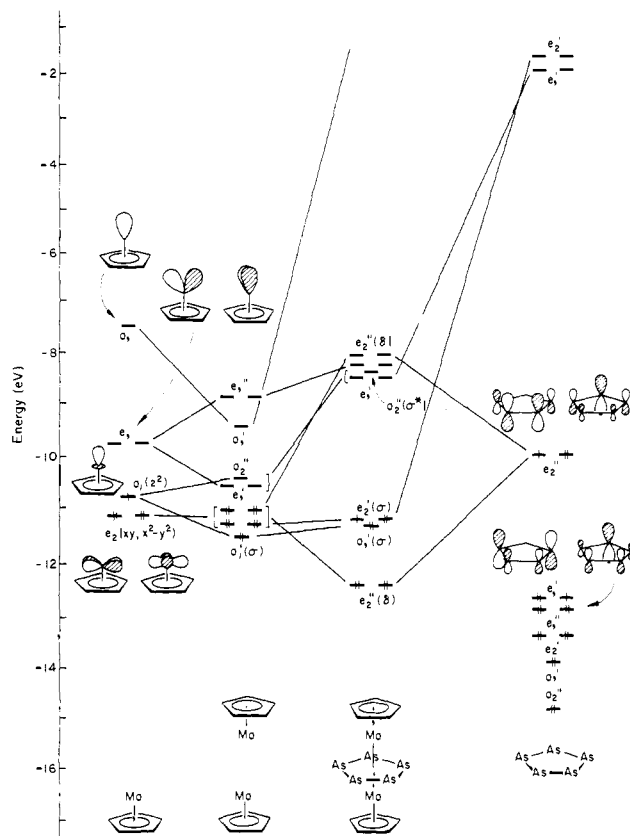


Figure 2. Interaction diagram for the frontier orbitals of $\text{CpMoAs}_3\text{MoCp}$ (D_{3h}). On the left two CpMo fragments are combined to form a $\text{CpMo}\cdots\text{MoCp}$ unit. The composite is then mixed with the central As_3 unit at right.

do not find any contribution from the corresponding levels of the P_5^- group in **3**, since the π^* and σ^* levels are about 20 eV higher in energy now. In fact, as we will see in a moment, the contribution of these levels to the HOMO and LUMO is responsible for the observed distortion in **2**.

In the previous section we have seen that the new magic electron count results from the a_2'' orbital being pushed up above the metal " t_{2g} " block. There are two possible reasons for this: (1) metal-metal bonding and (2) overlap between the central ring and metal d-orbitals. We should mention here that the metal-metal bond is subject to a number of geometrical constraints. The combined limitations imposed by the given M-P and P-P distances leave only a narrow range for metal-metal bonds. Only for some ring sizes, namely five-, six-, and seven-membered central rings, do these combined restrictions allow a situation where short metal-metal contacts are possible. For three-membered rings, e.g., in the Sacconi compounds,² only long metal-metal bonds have been observed. Four- and seven-membered rings are not yet known,¹⁸ and for five- and six-membered rings—the systems we focus on here—short metal-metal distances are found.

From the interaction diagram in Figure 1 it is impossible to decide what factors are responsible for the a_2'' level being moved above the " t_{2g} " block. One way to clarify this point is to vary the metal-ligand distance as well. The underlying reason is, of course, that if metal-metal bonding is the dominant factor, the $a_1' - a_2''$ ($z^2 - z^2$) splitting should decrease for longer metal-metal separations.

The development of the frontier orbitals as a function of the metal-metal distance is shown in Figure 3a. The splitting between the (metal-metal bonding) a_1' level and the (metal-metal antibonding) a_2'' level increases substantially for smaller metal-metal

(18) A complex $\text{Cp}^*\text{CoP}_4\text{CoCp}^*$ has been synthesized which possibly contains cyclo- P_4 as the middle deck (32 electron triple-decker complex). A possible alternative structure is $\text{Cp}^*\text{Co}(\mu-\eta^2-P_2)_2\text{CoCp}^*$ with 36 electrons. Bach, I.; Scherer, O. J. Unpublished research, cited in ref 1a.

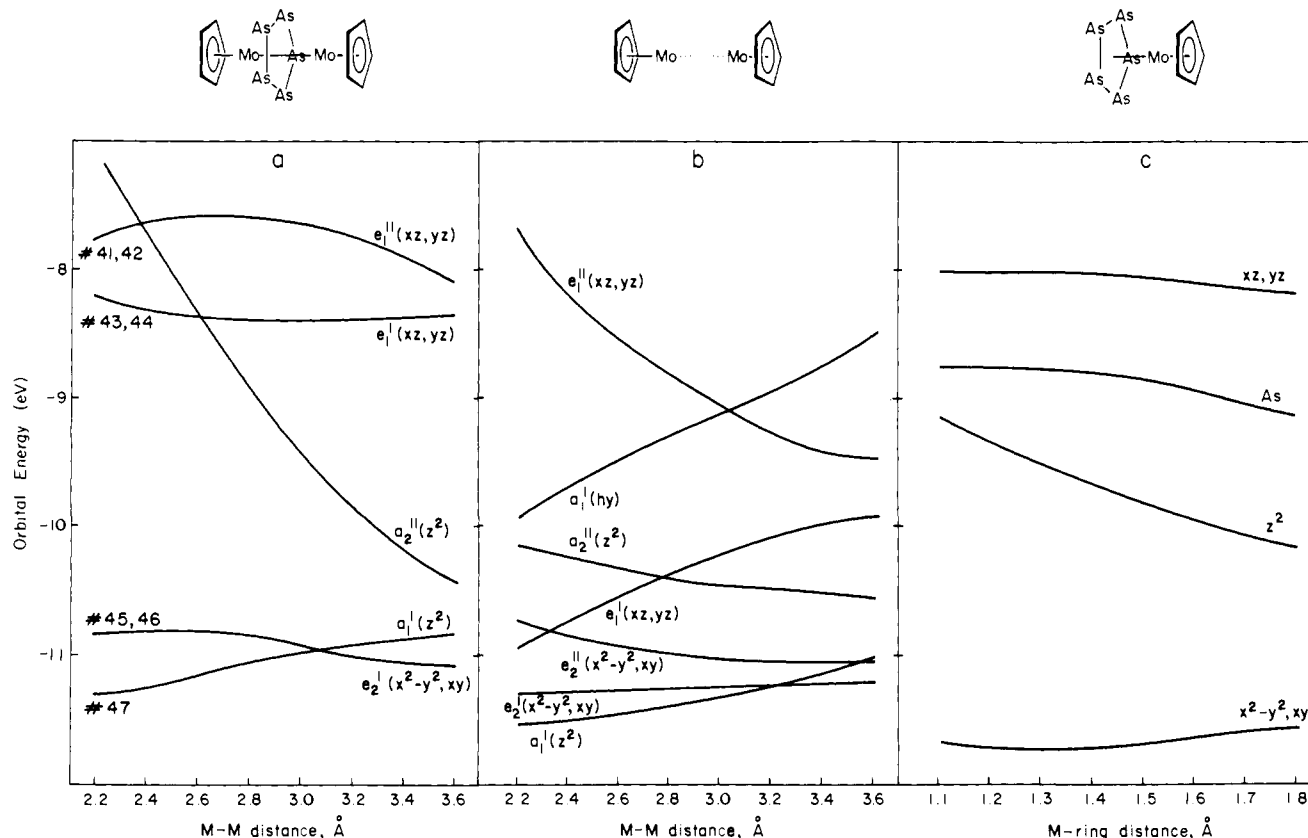


Figure 3. Frontier orbitals of CpMoAs₅MoCp (a), CpMo...MoCp (b), and As₅MoCp (c) as a function of the metal-metal distance or the distance between the metal and the center of the As₅ ring, respectively.

separations. Further consideration of fragment overlaps indicates that over almost the whole range of metal-metal distances the $\langle z^2|z^2 \rangle$ overlap nicely parallels the splitting of the a_1' and a_2'' levels. Metal-metal and metal-ligand bonding, however, are not easily decoupled, and the $\langle z^2|a_2''(\pi) \rangle$ overlap increases over the whole range of distances as well. A separation of M-M and M-L bonding can be achieved by comparing the orbital energies of **2** with those of CpMo...MoCp and As₅MoCp. If metal-metal bonding were most important for the new magic electron count in **2** and **3**, the a_1' and a_2'' orbital energies in CpMo...MoCp should closely follow the trend observed in Figure 3a. For metal-ligand interaction to be more important, the orbital energies in As₅MoCp, where no metal-metal interactions can occur, should match those of the corresponding orbitals in **2**.

We have done both experiments, and the results are given in Figure 3, b and c. The trend in the orbital energies for As₅MoCp closely resembles the picture obtained for **2** in Figure 3a. Therefore, we conclude that a_2'' is predominantly pushed up by the interaction with the ligand orbitals as a consequence of the larger fragment overlap in **2** and **3** compared to "classical" triple-decker compounds such as **5**. Still, we think that metal-metal bonding plays a significant role: in both "inorganic compounds" **2** and **3** there is a metal-metal bond.

Having a picture of the electronic structure of **2** and **3** (undistorted) we proceed to examine the actual distortion. In general, any nonlinear molecule with an incompletely filled degenerate level is susceptible to a structural (first-order Jahn-Teller) distortion¹⁹

(19) (a) Jahn, H. A.; Teller, E. *Proc. R. Soc.* **1937**, *A161*, 220. (b) Burdett, J. K. *Molecular Shapes*; Wiley-Interscience: New York, 1980. (c) Burdett, J. K. *Inorg. Chem.* **1981**, *20*, 1959.

(20) A theoretical analysis has been given for simple structures containing triangular (3⁶) nets of metal atoms and square (4⁴) nets of main group atoms: (a) Tremel, W.; Hoffmann, R.; Silvestre, J. *J. Am. Chem. Soc.* **1986**, *108*, 5174. (b) Silvestre, J.; Tremel, W.; Hoffmann, R. *J. Less-Common Met.* **1986**, *116*, 113. (c) Tremel, W.; Hoffmann, R. *J. Am. Chem. Soc.* **1987**, *109*, 124. (d) Tremel, W.; Hoffmann, R. *Inorg. Chem.* **1987**, *26*, 118.

(21) Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

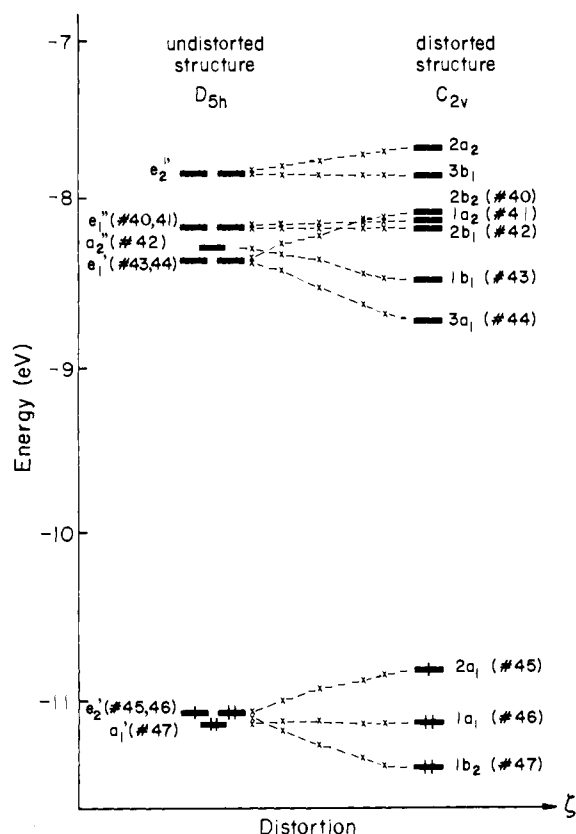
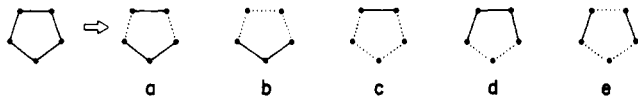


Figure 4. Energy levels of CpMoAs₅MoCp as a function of the distortion parameter ζ that interpolates linearly between the undistorted structure (D_{5h}) and the experimental geometry (idealized C_{2v}).

and **2** certainly falls in this category of molecules. The distortion could be driven by a second-order mixing as well.

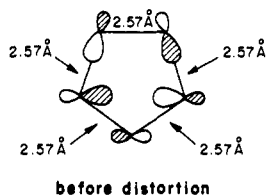
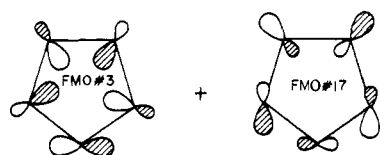
Some of the deformations available to a five-membered ring, strictly speaking a subset of the distortions resulting from Jahn-Teller active vibrations of such a ring, are shown in **12**. For the first case—that encountered in **2**—the evolution of the orbitals close to the HOMO-LUMO gap is shown in the Walsh diagram in Figure 4. We have chosen a distortion parameter ζ that

**12**

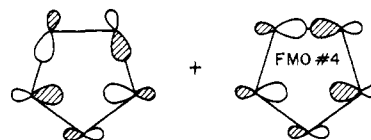
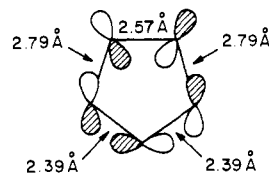
interpolates linearly between the undistorted structure (D_{5h} symmetry) and the experimental geometry (idealized C_{2v} symmetry). The e_2' level (#45,46 in the distorted structure) splits up into two partners (#45 and #47 in the distorted structure), which are stabilized (#45) and destabilized (#47) as the distortion proceeds. In fact, most of the 0.54 eV energy gain for the distorted structure can be accounted for by looking at these orbitals. Since the HOMO which was destabilized is only half filled for **2**, the distorted structure is preferred. The same certainly holds for the monocation. We calculate the monocation still to be more stable by 0.27 eV in the distorted structure. On the basis of these results we expect a (hypothetical) monoanion to be nondistorted and a monocation to be more distorted than the neutral compound. The rationale we are giving here traces the distortion to a first-order Jahn-Teller effect.

However, at the same time as the HOMO e_2' set (#45,46 undis) splits into two partners, the e_1' LUMO (#43,44 undis) splits into two partners as well. Some of the newly formed nondegenerate orbitals may mix, as one would expect from a second-order Jahn-Teller picture. Given the almost identical HOMO-LUMO difference in **2** or **3**, why do we observe a distortion of the central ring in the As compound **2**, but not for the P compound **3**? If the reason is not the energy difference, it should be the orbital composition.

As we mentioned above, there is already a significant admixture of As_3 fragment π^* and σ^* levels into those frontier orbitals of the composite molecule that are affected by the deformation. The second-order mixing (e.g. of #43 (undis) into #46 (undis)) is effective in causing a geometry distortion to the extent that As_3 antibonding orbitals (FMO's #3 and #4 of As_3) are admixed into these frontier orbitals. The evolution of one such mixing is shown in **13** → **14** → **15**. Note how the bonding changes match nicely the observed geometrical deformation.

**13**

The observed orbital pattern in Figure 4 actually allows us to examine the relative importance of first- and second-order Jahn-Teller effects. If there were only first-order mixing, the degenerate levels would split as shown in **16** for the As_3 unit. One partner is stabilized by $\Delta\epsilon_1$ and the other one is destabilized by $\Delta\epsilon_2$, $|\Delta\epsilon_2| \geq |\Delta\epsilon_1|$. For pure second-order distortions the higher lying orbital mixes into the lower orbital in a bonding way. The higher orbital itself is pushed up in energy. In our case the $1b_2$ orbital (#46) is stabilized by first- and second-order effects, and

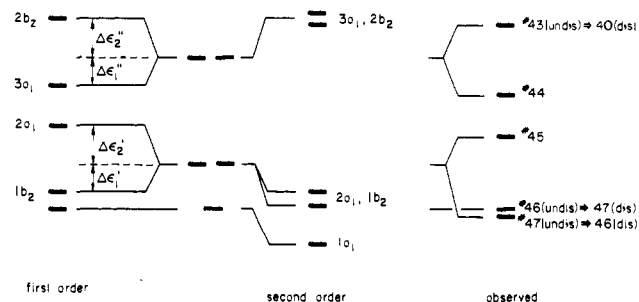
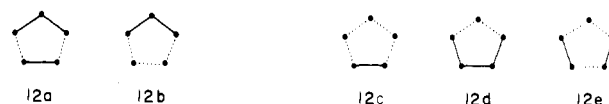
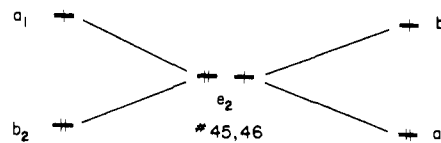
**14**

after distortion

15

the $2a_1$ orbital (#45) is destabilized by first-order and stabilized by second-order interactions. Similarly the $2b_2$ level is destabilized in first order and pushed up in second order by mixing with the $1b_2$ level, the $3a_1$ orbital (#44) is stabilized in first order and destabilized in second order by mixing into $2a_1$ (#45). From the splitting of the degenerate e_2' pair (#45,46) in the distorted structure we can judge the extent of second-order mixing. The $2a_1$ (#45) is pushed up significantly less (0.27 eV) than the $1b_2$ level is stabilized (0.34 eV). This shows that second-order effects are significant and important. Our conclusion is further supported by the evolution of the orbital composition, which we discussed before.

As we mentioned above, one may conceive of other possible distortions of the five-membered ring, not only the one observed in CpMoAs₃MoCp (**2**). We examined the ones drawn out in **12a-e**, under the constraint that the average As-As distance was equal to 2.57 Å. All of the distortions are favored. Some of them stabilize the symmetric a_1 component of the e_2' orbital pair (#45,46) and some the antisymmetric b_2 , as indicated in **17**. The interconversion of distortion isomers within each group is easy, between the groups more costly energetically, being a forbidden reaction. The **12c,d,e** group is calculated to be slightly less stable than the **12a,b** set.

**16****17**

We think that some of these other distortion isomers, not only **12a**, will turn up when one has a wider range of these compounds

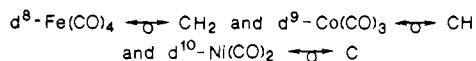
available. Incidentally, from the computed charge distributions we can make a prediction about the effect of introducing heteroatoms in the ring—more electronegative elements should have a tendency to occupy “isolated” positions, less electronegative elements to catenate.

Can we make any other predictions? We mentioned already that the monoanion of **2** should be less distorted than the neutral complex. The corresponding Sb compound, if it can be made, should be even more distorted than **2**. One should point out that our main conclusions here are based on the differences in overlap due to the diffuseness of the orbitals and on electronegativity. There are a number of solid-state examples, where the occurrence of a second-order Jahn–Teller distortion is connected to the relative electronegativity of the constituents.²²

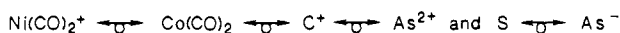
The interaction diagrams in Figures 1 and 2 show that one may expect the monoanions and monocations of **2** and **3** to be stable. Due to the large HOMO–LUMO gap, however, we do not expect compounds with higher electron counts, e.g. sulfur analogues of **3**, to possess this structure. This can easily be rationalized from the polyhedral skeletal electron counting rules.

Analogous Molecules

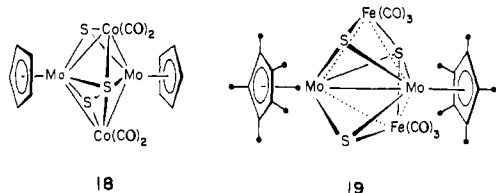
The isolobal analogy²¹ allows us to see the similarity of **2** to a number of recently synthesized metal clusters. The essential relationships are



With the isolobal chains



we can relate the $\text{Cp}_2\text{Mo}_2\text{S}_3(\text{Co}(\text{CO})_2)_2$ (**18**) made by Curtis and Williams²² to the monocation of **2** $\text{Cp}^+\text{MoAs}_5\text{MoCp}^+$. In a similar fashion $(\text{Cp}^*)_2\text{Mo}_2\text{S}_3\text{Fe}_2(\text{CO})_6$ (**19**)^{23a} or the isostructural $\text{Cp}_2\text{Mo}_2\text{X}_3\text{Fe}_2(\text{CO})_6$ ($\text{X} = \text{Se}, \text{Te}$)^{23b,c} and $\text{Cp}^*_2\text{Mo}_2\text{S}_3\text{Co}(\text{CO})_2\text{As}$, (**20**)²⁴ are easily transformed (in our minds!) into



$\text{CpMoAs}_5\text{MoCp}^-$. An isoelectronic compound $\text{CpMoAs}_4\text{SMoCp}$ has recently been made.²⁵ Its structure is similar to that of (**20**),²⁴ where S and one of the As atoms are statistically disordered on the position of the AsS group. The latter structure supports our hypothesis that the more electronegative atoms prefer to be isolated while the less electronegative atoms tend to concatenate. $(\text{MeCp})_2\text{V}_2\text{S}_2\text{Fe}(\text{CO})_3(\text{S}_2)$ (**21**) and $\text{Cp}_2\text{Mo}_2\text{Te}_2\text{Fe}(\text{CO})_3\text{C}_2\text{R}_2$ (**22**) synthesized by Rauchfuss and co-workers²⁷ geometrically

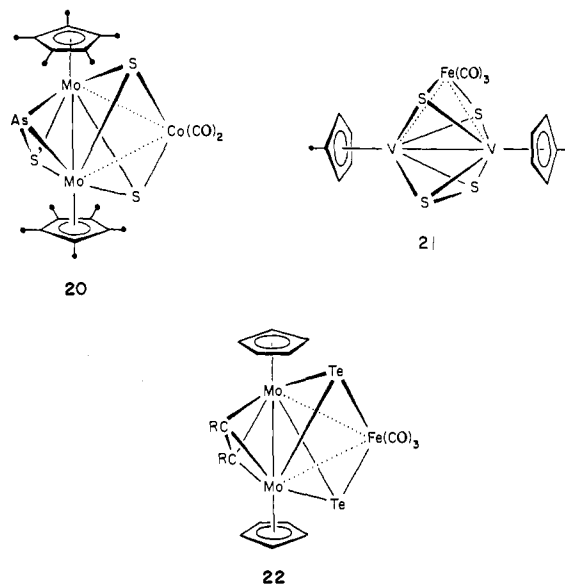
(22) (a) Curtis, D. M.; Williams, P. D. *Inorg. Chem.* **1983**, *22*, 266. For a closely related compound, $(\text{RC}_5\text{H}_4)_2\text{Cr}_2(\mu_3\text{-S})_2(\mu_4\text{-S})\text{Co}_2(\text{CO})_4$, see: (b) Eremenko, I. L.; Pasynskii, A. A.; Orazsakhov, B.; Shestakov, A. F.; Gassanov, G. Sh.; Katugin, A. S.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1988**, *338*, 369.

(23) (a) Cowans, B. A.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1987**, *6*, 995. For the corresponding Se and Te complexes $\text{Cp}_2\text{Mo}_2\text{X}_3(\text{Fe}(\text{CO})_2)_2$ ($\text{X} = \text{Se}, \text{Te}$) see: (b) Cai, Q.; Zheng, B.; Huang, J.; Lu, J. *J. Struct. Chem.* **1987**, *6*, 110. (c) Yang, X.; Huang, J.; Huang, J. *Ibid.* **1985**, *4*, 90. Rheingold, A. L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 585.

(24) Brunner, H.; Kauermann, H.; Klement, U.; Wachter, J.; Zahn, T.; Ziegler, M. L. *Angew. Chem.* **1985**, *97*, 122; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 132. An isoelectronic compound $\text{Cp}_2\text{Mo}_2(\text{S}_2)\text{Fe}(\text{CO})_2\text{S}_2$ is reported in this paper as well.

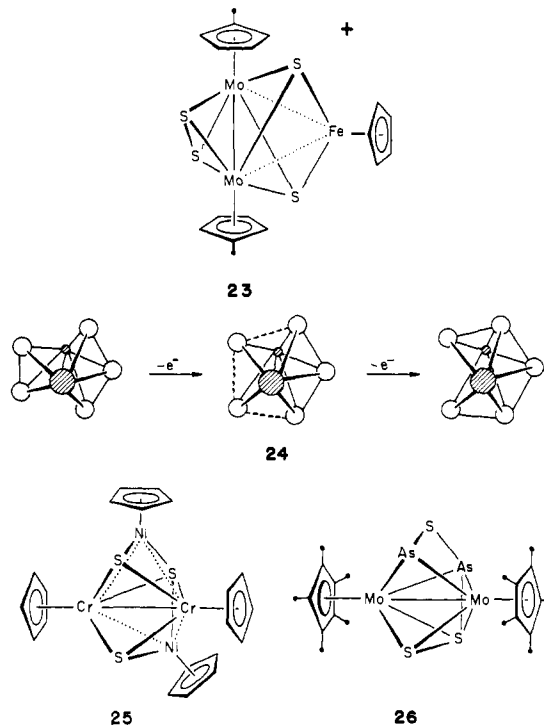
(25) Rheingold, A. L.; DiMayo, A.-L. Private communication.

(26) Bolinger, C. M.; Weatherill, T. D.; Rauchfuss, T. B.; Rheingold, A. L.; Day, C. S.; Wilson, S. R. *Inorg. Chem.* **1986**, *25*, 634.



resemble their isoelectronic congeners **19** and **20**. The latter four compounds show an enhanced 3 + 2 distortion of the middle deck compared to **2**. On the other hand, the middle deck in **18** exhibits a different distortion pattern. **23**, made by Rakowski DuBois and co-workers,²³ has the same electron count.

The structural relationship among these compounds is shown in **24**. Interestingly, the electron count in these compounds can still be increased. $\text{Cp}_2\text{Cr}_2\text{S}_3\text{Ni}_2\text{Cp}_2$ (**25**)²⁸ is the isolobal analogue of $\text{Cp}_2^*\text{Mo}_2\text{As}_2\text{S}_3$ (**26**) which actually has been reported by Wachter and co-workers²⁷ recently.



The electron counts for the last two compounds are 70 and 50, respectively. Taking into account only one Mo–Mo bond we should expect a pentagonal bipyramid where two half bonds (or one full bond) are broken. The electron count for **18** is 66 which would be indicative of a completely bonded polyhedral cluster with

(27) Bogan, L. E., Jr.; Clarke, G. R.; Rauchfuss, T. B. *Inorg. Chem.* **1986**, *25*, 4050.

(28) Pasynskii, A. A.; Eremenko, I. L.; Ellert, O. G.; Novotortsev, V. M.; Rakitin, Yu. V.; Kalinnikov, V. T.; Shklover, V. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1982**, *234*, 315.

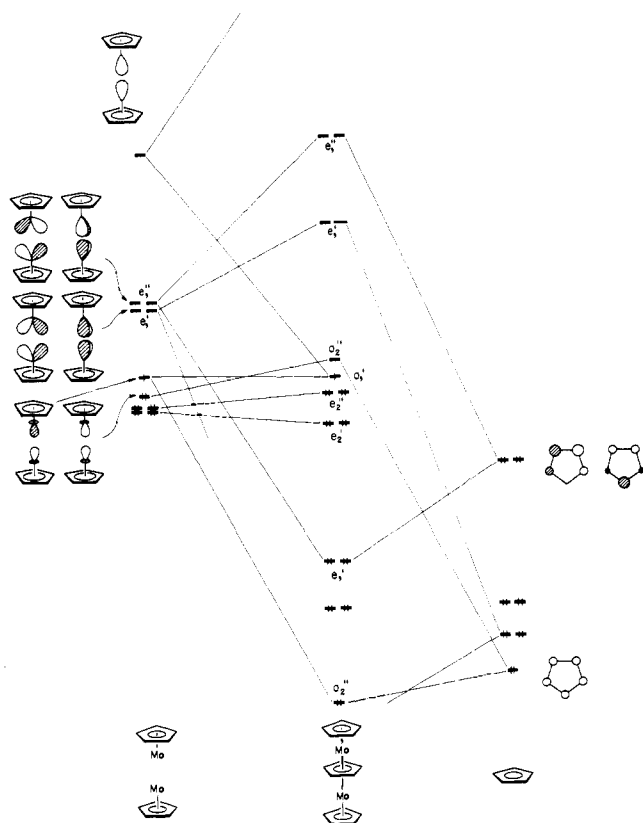


Figure 5. Interaction of two CpMo units and one Cp to form CpMoCpMoCp.

one Mo–Mo bond. Obviously this does not match the observations and one has to modify the magic electron count again, correcting now for the effects of Mo–Fe or Mo–Ni bonding.

The electron counting rules for polyhedral clusters^{11a,29} are more precise. **25** can be viewed as a trigonal bipyramid and a tetrahedron sharing a common edge. The corresponding electron count is $52 + 40 - 34 = 58$, which matches the total electron number in **20**, **21**, **22**, and **23**. The total count for **18** is easily explained from the condensation rules for polyhedral clusters as well. **18** can be viewed as two trigonal bipyramidal entities sharing faces. The total electron count for two face sharing clusters with a and b skeletal electrons is $a + b - 48$ and using $a = b = 52$ (corrected for the S atom in the shared face: $a + b - 38$) in the present case we calculate a skeletal electron count of 66, as observed for **18**.

Other Rings in the Middle

What happens if the size of the central ring is changed, e.g. if one replaces E_3 by Cp or goes to an E_6 or E_4 ring? The first question is answered easily from Figure 5. It shows the interaction of a CpMo...MoCp fragment with a central Cp ring in an idealized D_{5h} symmetry. The Mo...Mo distance is 3.76 Å and the Mo–C distance 2.23 Å. As before, the xz, yz derived e_1' and e_2'' combinations interact strongly with the appropriate symmetry partners of the central ring. The " t_{2g} " set, however, and especially a_2'' stay essentially unperturbed. The reason for this behavior can be understood from a simple geometrical estimation. For the given geometry the carbon atoms lie almost exactly in the node of the Mo z^2 orbitals (z^2 cone angle 54.7° , angle(Mo–Mo–C) 57.5°). Therefore the fragment overlap and the corresponding perturbation are very small. For **2** and **3**, however, the bridging As and P atoms are moving out of the node of the Mo z^2 . So metal–ligand antibonding interactions add to increasing metal–metal interaction.

Furthermore, the interaction between the orbital sets of the CpMo...MoCp and Cp fragments is influenced by their relative

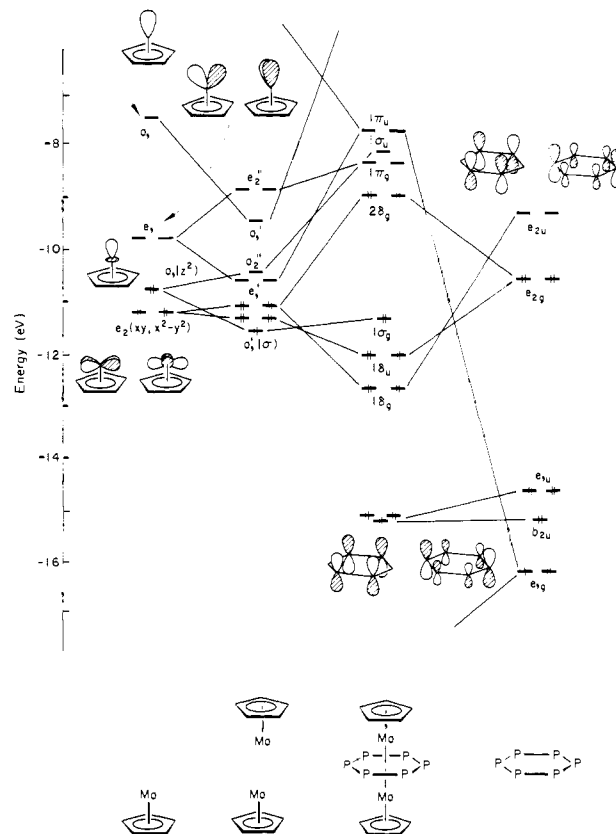


Figure 6. Interaction of two CpMo units and cyclo- P_6 to form CpMo P_6 MoCp.

positioning on the energy scale. The orbitals of the CpMo...MoCp fragment are energetically closer to the relevant orbitals of the Cp ring than to those of the P_3 or As_3 fragment. Therefore, the metal-based orbitals are pushed up substantially giving rise to a sizable gap for 30 electrons. The highest four occupied levels in the complex are within a very narrow energy range. Therefore magnetic behavior is possible for compounds with electron counts ranging between 23 and 29. In fact, the related 26-electron vanadium complex CpVC₆H₆VCp, **27**, was found to be paramagnetic with a quintet ground state corresponding to four unpaired electrons. A calculation on **27** gave results very similar to those obtained from Fenske–Hall calculations and photoelectron spectra.^{30b} The close correspondence between the results of the Fenske–Hall and EH calculations may be considered fortuitous; the general appearance of the frontier levels, however, is caused by the diffuse orbitals of the early transition metal resulting in a substantial orbital spread of the frontier orbitals.

The influence of the σ lone pairs on the bonding of the central rings has not yet been discussed. Their presence in Figures 1, 2, and 5 showed up by the e_1' orbital of the CpM...MCp fragments being pushed up in the composite molecules. In both, the inorganic ring systems and the hypothetical compounds, where the E_n ring is replaced by its carbocyclic analogue, the interaction between the e_1' fragment orbitals is significant. As most other interactions it is larger in the inorganic P-ring system as a consequence of the diffuse P orbitals ($\langle e_1' | e_1' \rangle = 0.34$ vs 0.10 for CpCrP₃CrCp and CpCrC₅H₅CrCp, respectively). Thus, the interaction between the lone pairs and the metal orbitals furnishes quite a substantial stabilization in the inorganic ring systems. This is also true for the As-ring compounds, where the corresponding overlaps have comparable values. Interestingly, we find a correlation between the size of the central ring and the metal–lone pair overlaps. In compounds CpMoP_nMoCp the $\langle e_1' | e_1' \rangle$ overlap increases from

(29) Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1983**, 706.

(30) (a) Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479. A theoretical analysis may be found in: (b) Chesky, P. T.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 5186.

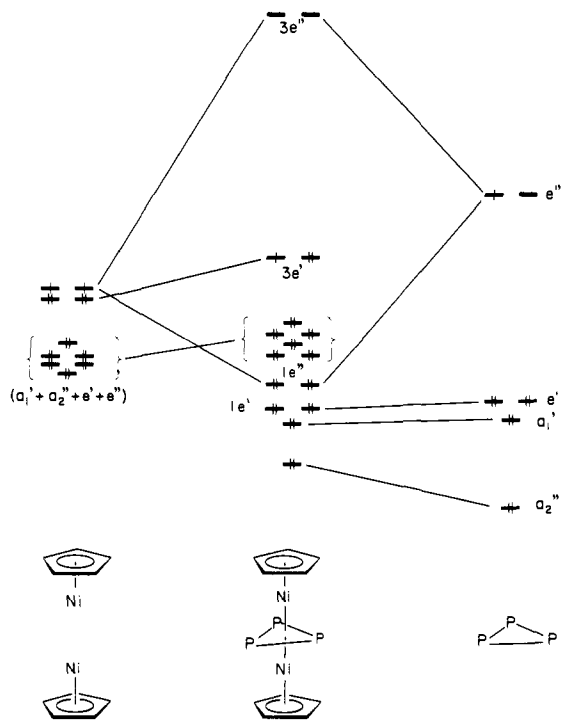


Figure 7. Interaction of two CpNi fragments and cyclo- P_3 to form CpNiP₃NiCp.

$n = 4$ to 6. For $n = 7$ it slightly decreased, leaving us with a six-membered ring as the optimum geometry.

Next the electron count for different sizes of the central ring is examined. Let us look at the E_6 ring first. The magic cluster electron count is $4 \times 8 + 20 + 2 = 54$ electrons, and the actual electron count for **4** is 52 electrons. Again, one can postulate a metal-metal bond and this explains qualitatively why we are short by two electrons. The schematic interaction diagram in Figure 6 is similar to those we have seen before for the E_5 systems. On the left we give the orbitals of the CpMo...MoCp dimer and on

the right those of the P_6 fragment. D_{3h} pseudosymmetry is used in the analysis. The main difference in the interaction diagram in Figure 6 compared to the interaction diagrams in Figures 1 and 2 is a stronger interaction of the δ and δ^* orbitals of the metal fragment with the e_2 and e_2' levels of the P_6 fragment. As a result the HOMO in Figure 6 is pushed up substantially and the calculated HOMO-LUMO gap now is about 0.7 eV. This is rather small; perhaps the calculations err in putting the P_6 e_2 too high in energy. We do not expect a reduced species to be stable; an oxidized compound, however, may be an attractive synthetic goal.

One can speculate about molecules having rings of different size in the middle deck. The next compound in the series would be CpMoP₇MoCp (**28**). The magic electron count (taking into account a metal-metal bond) is 56, which corresponds to a monocation of **28**. The interaction diagram is not very different from those in Figures 1, 2, and 6. Due to the larger ring size the metal-metal separations become smaller for a given M-P distance. For increasing ring sizes, e.g. in a hypothetical CpMoP₈MoCp, the metal atoms come very close to each other; longer M-M distances require longer M-P distances, and the combined geometrical constraints probably do now allow for the existence of such a species. We should mention here that the 26-electron species **27**—a triple-decker compound with a bridging benzene ring—has been reported.^{30a} Presumably due to geometrical constraints of the bridging benzene ligand the metal atoms are at a definitely nonbonding distance of 3.381 Å. Therefore **28** has a triple-decker structure, but the compound is highly electron deficient. From spectroscopic results it could be shown that the complex has a ground state with four unpaired electrons. These findings are supported by our own results in this paper and by Fenske-Hall calculations.^{30b}

For smaller ring sizes, e.g. E_3 and E_4 rings, the situation gets more complicated. A number of triply-bridged species—the Sacconi compounds²—are known. Here the magic skeletal electron count is 42, but as for some other phosphido or sulfido compounds of the late transition metals, these compounds do not conform strictly to empirical electron counting rules. Nevertheless the particular range of electron counts for these compounds can be explained from the interaction diagram in Figure 7. The calculations were done on a CpNiP₃NiCp model complex. On

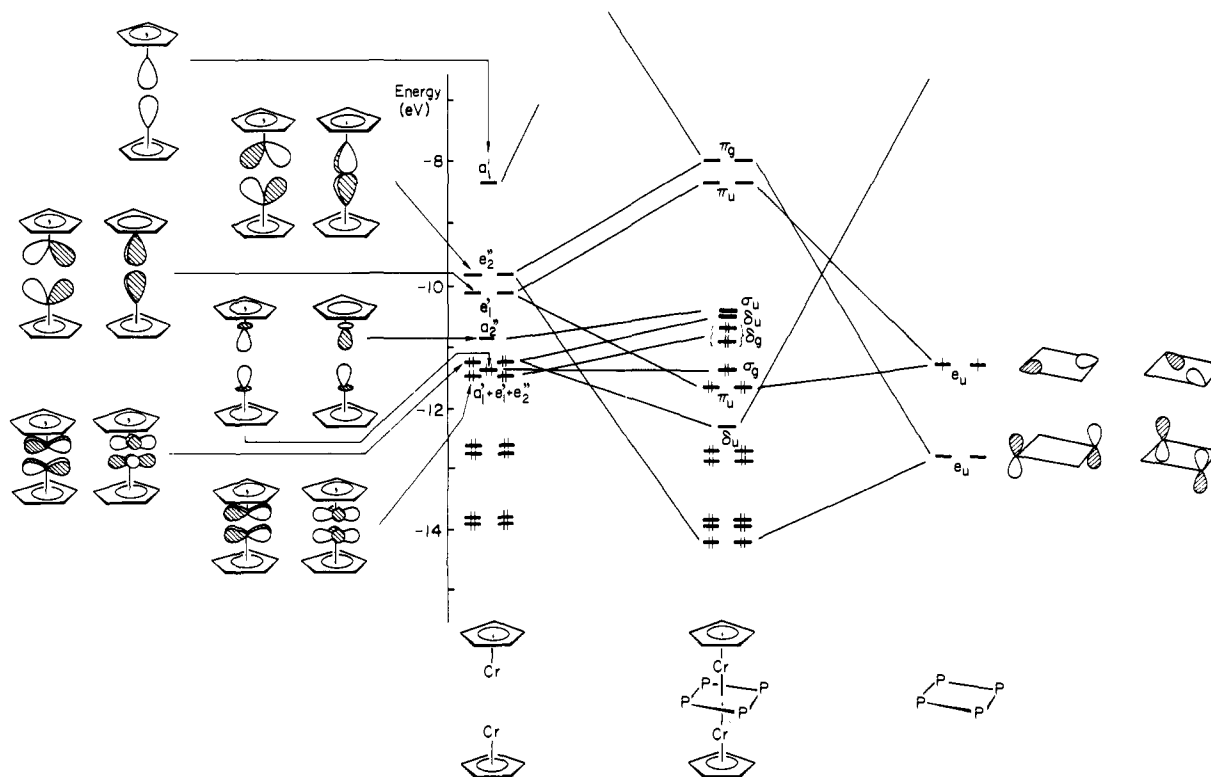


Figure 8. Interaction of two CpCr fragments and cyclo- P_4 to form CpCrP₄CrCp.

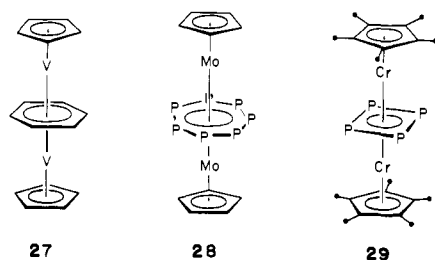
Table I. Parameters Used in Extended Hückel Calculations

orbital	H_{ii} , eV	ζ_1	ζ_2	C_1^a	C_2^a
P	3s	-18.60	1.60		
	3p	-14.00	1.60		
As	4s	-16.22	2.23		
	4p	-12.16	1.89		
S	3s	-20.00	1.817		
	3p	-13.30	1.817		
Te	5s	-20.80	2.51		
	5p	-14.80	2.16		
Cr	3d	-11.22	4.95	1.80	0.5060
	4s	-8.66	1.70		
Mo	4p	-5.24	1.70		
	4d	-11.06	4.54	1.90	0.5899
Ni	5s	-8.77	1.96		
	5p	-5.60	1.90		
Ni	3d	-13.49	5.75	2.00	0.5683
	4s	-9.17	1.825		0.6292
	4p	-5.15	1.125		

^aThese are the coefficients in the double- ζ expansion.

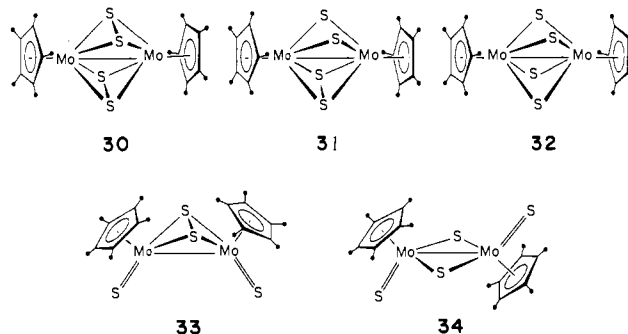
the left are the orbitals of the CpNi...NiCp dimer and on the right those of the P₃ fragment. At a metal-metal distance of 3.8 Å the levels of the individual CpNi fragments are only doubled and no significant level splitting can be found. The main interactions is between the e'' orbitals on both fragments. The e' set on the metal unit is pushed up in energy. If all six low-lying metal-based orbitals are filled as in [(triphos)FeP₃Co(triphos)]²⁺,²⁶ a 30-electron system results (42 cluster electrons) as required by the 30/34 electron rule. A 34-electron count (46 cluster electrons) results from a filling of the e' set, and all known compounds have electron counts between 30 and 34. Compounds with intermediate electron counts must be paramagnetic, and this actually matches the experimental facts.

Only few quadruply bridged compounds are known, probably because the combined constraints of M-E distance, E-E contacts in the bridge, and M-M separation leave only a small "window" for possible structures. Some hydrido and thiolate bridged species have been reported, but to our knowledge no phosphido bridged compounds are known. Let us have a look at a hypothetical CpCrP₄CrCp complex (29).¹⁸ The magic cluster electron count is 46 and the actual electron count is 42, and as such the species is electron deficient. The geometrical constraints of a fully bonded



P₄ ring do not allow a short M-M separation and so we expect a basic level pattern as in the classic triple-decker compounds. The interaction diagram is given in Figure 8. Again, on the left are the orbitals of the CpCr...CrCp dimer and on the right the orbitals of the P₄ fragment. As for 4 and 23 we retain a high pseudosymmetry D_{2h} ; some orbitals are nearly degenerate.

Basically our expectations are fulfilled. A strong interaction of the e₁' lone pair set of the P₄ fragment with the corresponding symmetry combination on the metal dimer pushes the π_u MO substantially up in energy. As a result we see a nice energy gap for a 30-electron species. Our model compound is short of 30 by four electrons. This does not necessarily mean that it should be kinetically or thermodynamically unstable. It may just be electron deficient and paramagnetic, as we have seen for 28 or some of the Sacconi-type species.² On the other hand there are no reports of P₄ bridged compounds,¹⁸ but a number of complexes with four bridging sulfur atoms exists.³¹ These, 30-34, show a fantastic variety of coupling and deformation possibilities in the bridging region and are the subject of a separate paper.³²



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Appendix

All the calculations were performed by using the extended Hückel method^{14a,b} with weighted H_{ij} 's.^{14c} Unless mentioned the experimental bond lengths were used. The values for the H_{ij} 's and the orbital exponents are listed in Table I. The parameters for C and H are the standard ones.^{14a,b}

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(31) (a) A complex CpMo(S₂)₂MoCp has been claimed early on, but no X-ray structure was available: Beck, W.; Danzer, W.; Thiel, G. *Angew. Chem.* **1973**, 85, 625; *Angew. Chem., Int. Ed. Engl.* **1973**, 12, 582. (b) The product originally described as CpMo(S₂)₂MoCp was characterized by X-ray analysis as *anti*-CpMo(S)(S₂)Mo(S)Cp: Danzer, W.; Fehlhammer, W. P.; Liu, A. T.; Thiel, G.; Beck, W. *Chem. Ber.* **1982**, 115, 682. (c) Rakowski DuBois, M.; DuBois, D. L.; Van DerVeer, M. J.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, 20, 3064. Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, 1, 1107. (d) For a review on Cp₂Mo₂S₂(S₂) compounds, see: Wachter, J. *J. Coord. Chem., Sect. B* **1987**, 15, 219. (e) Goh, L. Y.; Mac, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1474.

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