

Theoretical Analysis of Bonding in Monomeric and Polymeric C_5H_5M Compounds

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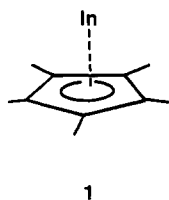
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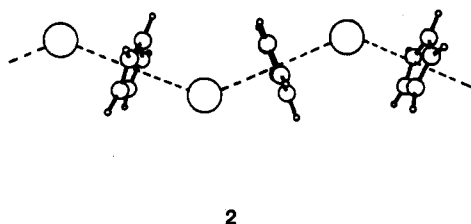
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The structures of monomeric C_5H_5M ($M = In, Tl, Sn^+$) have been optimized with an SCF pseudopotential method with a double- ζ basis set. The results are in good agreement with the experimental information. PES results can also be accounted for. The influence of d orbitals on the thallium atom has been found to be negligible. It is suggested that the bonding between In or Tl and cyclopentadienyl has a large covalent component. The polymeric cyclopentadienylindium was analyzed by means of extended Hückel tight binding calculations. The zig-zag structure of the polymer is shown to be due to a minimization of the repulsive factors. Polyhedral skeletal electron pair counting rules are also applied to this polymer to explain the zig-zag structure. Finally, other distortions in discrete systems are discussed in terms of electron count and molecular orbital pictures.

Indium and thallium cyclopentadienyl (CpIn, CpTl) were prepared by Fischer et al.^{1,2} more than 25 years ago, and since then, the discussion of the bonding in these molecules has been very controversial. The gas-phase structure of CpIn and CpTl was reported by Bartell et al.³ and Tyler et al.,⁴ respectively. It was shown that both species have the half-sandwich η^5 structure 1 originally



suggested by Fischer and Hofmann.² In CpIn the cyclopentadienyl hydrogens were found to bent away from the metal atom by approximately 4° .³ Recently, Jutzi et al.^{5,6} have reported the structure of $(Me_5Cp)Sn^+$ which adopts the same nido structure shown in 1 with the methyl groups bent away as in CpIn. In the solid state, InCp and TlCp adopt a zig-zag chain structure, 2.^{7,8} The M-Cp distances



in the polymer are equal and considerably larger than those in the monomer (3.19 vs. 2.32 Å for CpIn). Each M center is symmetrically positioned between two cyclopentadienyls. Thallium tricyanovinylcyclopentadiene also presents this bent polymeric structure in the solid state.⁹

The bonding in CpIn was initially considered to be mainly covalent,² but Cotton and Reynolds¹⁰ criticized this interpretation and proposed that the molecule was ionic. Tyler et al.⁴ also proposed an ionic bonding for CpTl.

Nevertheless, as Bartell et al.³ pointed out, the In-C distance (2.62 Å) is decidedly shorter than the sum of the ionic radius of In^+ and the van der Waals radius of C (3.0 Å), a fact that strongly argues against the ionic interpretation. In addition, these authors showed by molecular orbital arguments that the bonding in CpIn and CpTl was essentially covalent. Since that time, many experimental studies¹¹⁻¹⁵ have contributed to this discussion on the covalent-ionic nature of the bonding in both the monomeric and polymeric systems. The long distances in the polymeric structures undoubtedly indicate an enhancement of the ionic character in the solid state, but the zig-zag character of the chain also suggests some covalent metal-ligand interaction as pointed out by O'Neill and Wade.¹⁶

Recently, some theoretical studies have been reported. The structure of CpIn has been optimized at the STO-3G level by Hehre et al.,¹⁷ but the results were somewhat discouraging. The In-C distance was computed to be 0.2 Å shorter than the experimental value, and almost no bending (0.6°) for the hydrogens was found. Van Wazer et al.¹⁸ reported pseudopotential SCF calculations on CpTl

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at the experimental geometry with the unexpected result that the d orbitals on Tl have a very important role in the metal-ligand bonding. This was evidenced by the population analysis and by the charge at the thallium that was found to be almost nil. The metal atom was also found to be neutral in the CNDO calculations on CpIn by Lin and Tuck.¹⁹ These authors criticized the interpretation of the photoelectron spectra of CpIn by Cradock and Duncan²⁰ and Edgell et al.²¹ on the basis of these calculations.

This series of conflicting results shows that a clear understanding of the electronic structure of these relatively simple systems has not yet been attained. In this work, pseudopotential SCF calculations with a double- ζ basis set for the monomers and tight binding extended Hückel calculations for the polymers are used to further discuss this problem.

Theoretical Procedure

The pseudopotential method proposed by Durand and Barthelat²² was used for the SCF calculations. This method has been shown to give excellent results for molecules containing main-group elements.²³ The calculations were carried out with a modified version of the HONDO package²⁴ in which the pseudopotential method has been implemented.

The inner-shell core electrons are taken into account through a nonempirical pseudopotential, and the atomic basis set used for the description of the valence electrons is optimized in a pseudopotential SCF calculation for the ground state of the atom by using a quadruple- ζ Gaussian basis set. These four Gaussians were contracted to a double- ζ level through a 3 + 1 procedure. Detailed accounts of the method can be found elsewhere^{22,23,25} and will not be repeated here. A relativistic core was used for In, Sn, and Tl.²⁶ Single-point calculations for the optimized structure of CpTl with a basis set including d functions on Tl ($\eta = 0.1$ or 0.04) were carried out in order to assess the possible role of d orbitals in the bonding scheme.¹⁸ The geometry optimizations for CpIn, CpTl, and CpSn⁺ were done by varying independently all parameters except the CH distances which were kept fixed at 1.08 Å.

The tight binding (LCAO) method of band structure calculation obtained by the extended Hückel method²⁷ was used for the polymeric CpIn. A set of Bloch basis orbitals $\{b_\mu(\mathbf{k})\}$ is formed from the atomic orbitals of a unit cell $\{\chi_\mu\}$ as

$$b_\mu(\mathbf{k}) = N^{-1/2} \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} \chi_\mu(r - R_i) \quad (1)$$

where \mathbf{k} is the wave vector and $R_i = i\mathbf{a}$, \mathbf{a} being the prim-

Table I. Optimized Structures for CpIn, CpTl, and CpSn⁺

molecule	geometry ^a
CpIn ³	C-In = 2.688 (2.621); C-C = 1.421 (1.427) $\varphi^b = 3.4$ (4.5)
CpTl ⁴	C-Tl = 2.832 (2.705); C-C = 1.422 (1.43) $\varphi = 3.7$ (0.0) ^c
CpSn ⁺ ⁶	C-Sn = 2.474 (2.462); C-C = 1.429 (1.39) $\varphi = 5.0$ (4.0)

^a Experimental geometries in parentheses. Experimental values for CpSn⁺ correspond to Me₅CpSn⁺. Distances in angstroms and angles in degrees. ^b Bending of cyclopentadienyl hydrogens. ^c Assumed to be zero.

Table II. Metal-Ligand Overlap Population, Gross Atomic Populations, and Orbital Energies for CpM (M = In, Tl, Sn⁺)

	CpM			
	CpIn	a	b	CpSn ⁺
gross atomic pop.				
M	2.508	2.503	2.557	2.965
C	4.234	4.223	4.222	4.231
H	0.865	0.876	0.867	0.776
Metal-ligand overlap pop.	0.105	0.148	0.180	0.145
orbital energies, au				
3e _g	-0.3076	-0.2854	-0.2857	-0.5410
4a _g	-0.3307	-0.3859	-0.3859	-0.5917

^a Without d orbitals. ^b With d orbitals ($\eta = 0.04$).

itive vector. With these Bloch basis orbitals the crystal orbitals

$$\psi_n(\mathbf{k}) = \sum_\mu C_{n\mu}(\mathbf{k}) b_\mu(\mathbf{k}) \quad (2)$$

and eigenvalues $\epsilon_n(\mathbf{k})$ are obtained by solving the eigenvalue equation

$$H(\mathbf{k})C(\mathbf{k}) = S(\mathbf{k})C(\mathbf{k})E(\mathbf{k}) \quad (3)$$

where $H_{\mu\nu}(\mathbf{k}) = \langle b_\mu(\mathbf{k}) | H_{\text{eff}} | b_\nu(\mathbf{k}) \rangle$. The band structure is determined by performing the above calculation for various values of \mathbf{k} within the first Brillouin zone ($-0.5K \leq \mathbf{k} \leq 0.5K$, where $K = 2\pi/a$).

A repeat unit cell for eclipsed (CpIn)_n contains one CpIn unit for the linear polymer but two for the bent one. Lattice sums were carried out to second nearest neighbors for the former case and to nearest neighbors for the latter. Equation 3 was solved for $\mathbf{k} = 0.0K, 0.1K, 0.2K, 0.3K, 0.4K$, and $0.5K$. The parameters and geometries used in the extended Hückel calculations are given in the Appendix.

Results and Discussion

A. Bonding in the Monomeric CpM Species. The optimized structures for CpIn, CpTl, and CpSn⁺ are reported in Table I. As can be seen, the comparison with experimental data is very satisfactory for CpIn and CpSn⁺. Both the Cp-M distance and the bending angle are well accounted for in contrast with the results from STO-3G calculations.¹⁷ In CpTl the Cp-M distance is somewhat overestimated. The error is of the same order as that found by Almlöf et al.²⁸ in their extended basis set calculations for GeCp₂ and is smaller than the near Hartree-Fock calculations for ferrocene.³²

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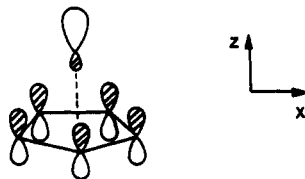
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The highest occupied orbitals (Table II) are a pair of degenerate e_1 orbitals which are the bonding combination of the cyclopentadienyl $e_1(\pi)$ orbitals with the $p_{x,y}$ orbitals of M. The next occupied orbital is the "lone-pair" 3 which results from the antibonding combination of $a_1(\pi)$ with s (out-of-phase) and p_z (in-phase) of M.



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These results confirm the interpretation of the PE spectra by Cradock and Duncan²⁰ and Edgell et al.²¹ and invalidate the criticism of Lin and Tuck.¹⁹ Even the fine details of the spectra are reproduced by the present calculations. Cradock and Duncan²⁰ found that the first ionization energy was only slightly smaller for CpIn than for CpTl (0.18 eV) and that the second ionization energy raised considerably from CpIn to CpTl (0.98 eV). The results in Table II are in full agreement with these data. Both trends can be easily explained. Since the overlap $e_1(\pi)-p_{x,y}$ is of π type and both atoms have very diffuse p orbitals, this interaction is not very different in the two compounds. In contrast, the interaction $a_1(\pi)-s$ is of σ type and consequently is more sensitive to overlap changes. Because of the more contracted nature of the s orbital of the In atom, the destabilizing interaction between the occupied cyclopentadienyl $a_1(\pi)$ orbital and the In s orbital is stronger and the corresponding orbital lies higher. In CpSn⁺ the order of the orbitals is maintained but the energies are considerably lowered because of the electric field.

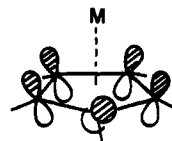
Gross atomic populations and overlap populations are shown in Table II. The computed charges for indium and thallium are +0.5. An ionic model seems not very coherent with this result. In addition, these values are in good agreement with the recent calculation of Almlöf et al.²⁸ on germanocene (a charge of +0.5 was found for each cyclopentadienyl), a molecule for which it is generally accepted that the bonding is covalent.

The InCp and TlCp overlap populations even if small are positive in all cases. The comparison with other ab initio cyclopentadienylmetal systems is difficult due to the persistence of counterintuitive orbital mixing²⁹ in these calculations which often makes this quantity negative. It is interesting to look more closely at these values. The breaking of the overlap population for TlCp shows that the 0.148 value is due to a positive contribution of the e_1 -type terms (+0.186) and a slightly negative contribution (-0.038) of the a_1 contributions. This last contribution comes from a negative part (-0.144) associated to the s orbital and a positive one (+0.106) associated to the p_z orbital. In the language of perturbation theory, the results show that the four-electron destabilization associated with the $a_1(\pi)-s$ interaction is almost canceled by the stabilization afforded by the second-order mixing of the p_z orbital and, finally, the bonding in CpTl comes from the two-electron interactions $e_1(\pi)-p_{x,y}$. A similar analysis for CpIn shows that the $p_{x,y}$ and p_z contributions (+0.198 and +0.135, respectively) are almost the same as in CpTl but

that the antibonding contribution from the s orbital has increased to -0.228, leading to a smaller overall overlap population (0.105). These results are in excellent agreement with the above-mentioned PE results.^{20,21} The analysis of the overlap population from an extended Hückel calculation on CpIn coincides nicely; the total overlap population is 0.154, the contribution from the $p_{x,y}$ orbitals is 0.219 and the ones from the s and p_z orbitals are -0.237 and +0.172, respectively. The agreement between both calculations makes us confident that the analysis is correct and permits us to consider these half-sandwich compounds as π -bonded systems. As the π overlap increases slower with the distance than the σ one, it is very important for the metal atom to have diffuse orbitals since this is the only way in which a sizable π -bonding interaction can be reached without raising excessively the antibonding σ interactions.³⁰ This provides a rationale for the failure of different attempts to synthesize the gallium cyclopentadienyl.³¹

The possible role of d orbitals in the bonding was investigated by performing calculations for the optimized structure of CpTl including d orbitals for Tl ($\eta = 0.1$ or 0.04). The results, which do not show any appreciable dependence on the η value, are shown in Table II ($\eta = 0.04$). It can be seen that the results are very insensitive to the inclusion of d orbitals in the basis. The result is not unexpected. The 6d orbitals lie very high in energy with respect to the occupied cyclopentadienyl π orbitals, and the interactions are very small. The d_z orbital that could assist in relieving the antibonding a_1 interactions has a very small overlap with the $a_1(\pi)$ orbital because of its conical nodal surface which points toward this orbital. Again, the results coincide with the calculations of Almlöf et al.²⁷ on GeCp₂ in which the d orbitals were found to have a negligible role. In our opinion, the result of Van Wazer et al.¹⁸ is due to the inadequacy of single basis sets to describe this type of metal-ligand interactions. It seems well established that a double- ζ basis set is needed for calculations of metal-cyclopentadienyl systems.³²

It is now easy to understand the origin of the bending away of the hydrogens (or methyl substituents) in these systems. This distortion diminishes the antibonding $s-a_1(\pi)$ interaction. On tilting, the $a_1(\pi)$ orbital changes as shown in 4 and this fact has as the main consequence that



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the overlap $a_1(\pi)-s$ decreases and so does the antibonding interaction. The interaction of the p orbitals with the cyclopentadienyl π orbitals [p_z with $a_1(\pi)$ and $p_{x,y}$ with $e_1(\pi)$] does not appreciably change because of the diffuse nature of the In p orbitals. The global effect is stabilizing. This analysis is confirmed by a fragment molecular orbital analysis³³ of the extended Hückel calculations. The overlap population $a_1(\pi)-s$ diminishes from -0.103 to -0.062 when the tilting angle changes from 0 to 10°; the $a_1(\pi)-p_z$ remains almost constant (0.198 vs. 0.202) as does the $e_1(\pi)-p_{x,y}$ (0.109 vs. 0.106). This explanation is different from the one suggested recently by Schleyer et al.³⁴ for similar

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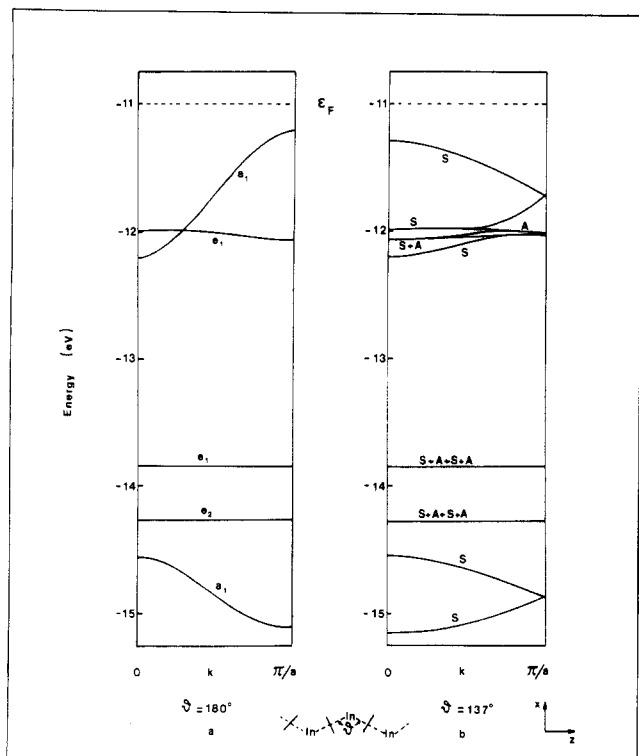


Figure 1. One-dimensional band structure for linear (a) and bent ($\theta = 137^\circ$) eclipsed $(\text{CpIn})_n$. Only the highest occupied bands are shown.

tiltings in second-row half-sandwich compounds which focuses on the $e_1(\pi)-p_{x,y}$ interactions. The reason lies in the much more diffuse nature of the p orbitals in our case.

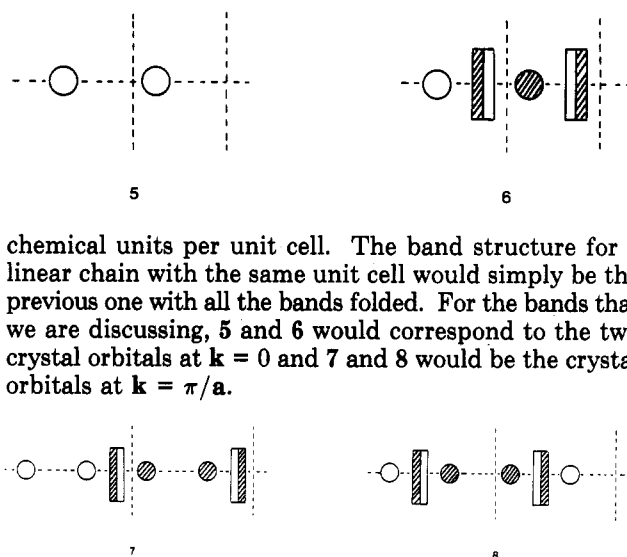
In summary, the present calculations provide a picture of the bonding in CpM compounds in excellent agreement with the experimental information presently available and that fully confirms the bonding description originally presented by Fischer and Hofmann² as well as Bartell and co-workers.³

B. Bonding in CpM Chains. The band structures for the linear and bent ($\theta = 137^\circ$) eclipsed CpIn polymer are shown in Figure 1. In the linear polymer there is a C_5 axis along the chain and the bands have been classified according to the C_{5v} group. In the bent polymer only a symmetry plane remains and the bands have been labeled S or A according to their symmetry with respect to that plane. Note that in the staggered chain there is a screw axis running along the centers of the cyclopentadienyls which leads to folded bands. As the cyclopentadienyls are far from each other, the band structures for the staggered and eclipsed chains are nearly identical. This explains the practically folded nature of the bands in Figure 1b.

The bent polymer is found to be 1.6 kcal/mol more stable than the linear one. The preference for the bent chain is maintained for any choice of parameters but increases considerably by lowering the p orbitals of In. Analysis of the band structure shows that the energy difference for any choice of parameters is only due to the highest occupied band. This is clearly a symmetry-imposed result that could have been derived without recurring to the calculations.

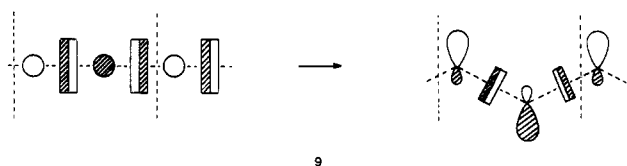
Due to the long Cp-M distances, bands mainly Cp(π) in character will not change at all with bending. Only the bands built from the cyclopentadienyl π_1 and indium s orbitals can change with the distortion (by admixing different degrees of indium p orbitals). The lowest one (lower band in Figure 1a) lies at an energy far from the p orbitals of indium and will also remain unaltered. The remaining

band is built from the s orbitals of indium that mix in some π_1 orbital character. By symmetry, the π_1 orbital cannot mix with the s orbitals at $k = 0$ for the linear polymer 5. At $k = \pi/a$, the π_1 orbitals will mix in an antibonding way with the s orbitals, 6. For the bent structure we have two



chemical units per unit cell. The band structure for a linear chain with the same unit cell would simply be the previous one with all the bands folded. For the bands that we are discussing, 5 and 6 would correspond to the two crystal orbitals at $k = 0$ and 7 and 8 would be the crystal orbitals at $k = \pi/a$.

On going from the bottom (5) to the top of the band (6) we change from a nonbonding to an antibonding metal-cyclopentadienyl situation and so this is a metal-ligand antibonding band. Bending provides a way to relieve this unfavorable situation since by lowering the symmetry, the indium p_x orbitals can mix into the band which becomes essentially nonbonding (as shown in 9 for the top of the band) and is consequently stabilized. This analysis is essentially similar to the one done on Cp_2Sn , the molecular analogue of the CpIn chain, by Hofmann et al.⁶



C. Electron Counting: Distortions and New Compounds. The electron-counting rules derived by Wade, Mingos, Rudolph, and others³⁵ have proved to be very useful in many areas of inorganic chemistry. Essentially these results are based on the fact that the maximum stability for a polyhedral cluster is reached when all the bonding and nonbonding skeletal orbitals are occupied. If extra electrons are added, antibonding orbitals are occupied and bonds must be broken.³⁶

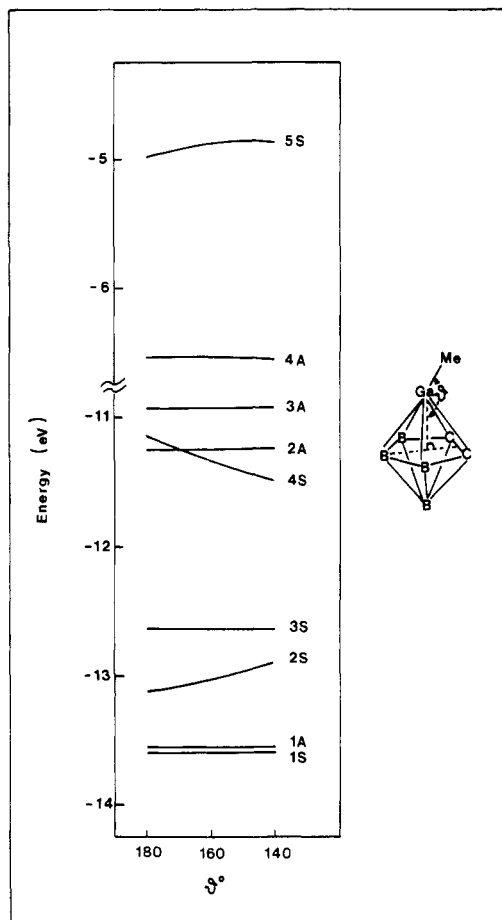
In fact the CpIn and CpTl chains could be considered as a series of condensed pentagonal bipyramids (or condensed closo clusters). Each polyhedron has seven vertices, and thus, according to these rules, eight pairs of electrons should be assigned to each unit in order to have a stable structure. The carbon atoms afford a total of 15 electrons and the two shared indium atoms will provide a total of three electrons to each polyhedra. This is a total of nine pairs per polyhedron, one more than needed to maximize

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Table III. Total and Orbital Energy Changes^a For Bending in $1-CH_3GaC_2B_4H_6$

θ , deg	E_{total}	$2(\epsilon_{4S} + \epsilon_{2S})$
180	4.5	4.3
170	2.0	2.0
160	0.4	0.5
152	0.0	0.0
140	1.1	0.7

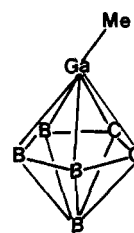
^a kcal/mol relative to the most stable geometry.Figure 2. Walsh diagram for $GaCH_3$ bending (θ) in $1-CH_3GaC_2B_4H_6$. Orbital 3A is the HOMO.

the skeletal bonding. But the polymer has a way to eliminate this extra pair of electrons without breaking any bond—it must simply bend.

The same electron-counting argument could be used to provide a simple explanation of some distortions in discrete molecules. In $CpSnCl$ ³⁷ the chlorine atom is strongly tilted. It was suggested that the solid-state structure could be the result of intermolecular interactions. In our view, this is a six-vertex nido structure with a total of nine skeletal electron pairs, one more than needed. By bending the Sn-Cl bond, the optimum count is reached since two electrons pass into an external Sn nonbonding orbital. This molecule is interesting because according to the electron-counting rule the bending could be prevented by simple substitution of two cyclopentadienyl carbons by borons. The bent structures of germanocenes,²⁸ stannocenes,³⁸ and plumbocenes³⁸ are further examples of the same electron counting at work.³⁹

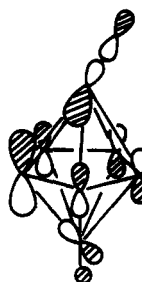
(37) Bos, K. D.; Bulten, E. J.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* 1975, 99, 71.(38) Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* 1981, 925.

These distortions should not be confused with those observed in compounds having the correct electron count. One example is the bending observed in $1-CH_3GaC_2B_4H_6$, 10, in which the Ga-CH₃ bond makes an angle of 23° with

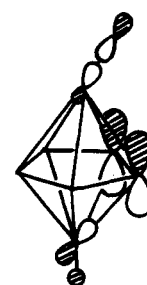


10

the Ga-B apical line. Grimes et al.⁴⁰ have attributed the bending to the gallium d orbitals. Extended Hückel calculations without d orbitals reproduce well the bending (Table III) and provide a different explanation. Figure 2 is a Walsh diagram for the bending. Only two orbitals, 2S and 4S, change appreciably. The orbital 4S, 11, is

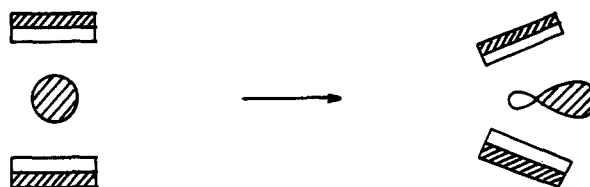


11



12

strongly concentrated on the gallium and on the central boron. Bending of the $GaCH_3$ group increases the overlap between the carborane and the $GaCH_3$ fragments (0.290 for $\theta = 180^\circ$ vs. 0.360 for $\theta = 150^\circ$), and the orbital is stabilized. The orbital 2S, 12, can be described as $\pi_{C=C} + \sigma_{GaCH_3}$. By bending, the overlap between the fragments decreases (from 0.197 in $\theta = 180^\circ$ to 0.137 in $\theta = 150^\circ$) and the orbital is destabilized although to a lesser extent than orbital 4S is stabilized. In summary, the distortion increases the skeletal bonding in contrast with the other cases in which the distortion is needed to relieve anti-bonding interactions (e.g., 13)



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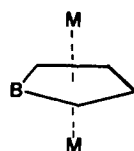
In what conditions an inverse sandwich structure containing In or Tl could be possible? Two electrons of each M could be located in the lone-pair orbitals and would not

(39) Different distortions of clusters that do not satisfy the Wade rules have been examined. Cox, D. N.; Mingos, D. M. P.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* 1981, 1788; O'Neill, M. E.; Wade, K. *Inorg. Chem.* 1982, 21, 464. King, R. B. *Polyhedron* 1982, 1, 132. Lauher, J. W. "XI International Conference on Organometallic Chemistry", Pine Mountain GA, 1983.(40) Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F.; Greene, P. T. *J. Am. Chem. Soc.* 1972, 94, 1865.

Table IV

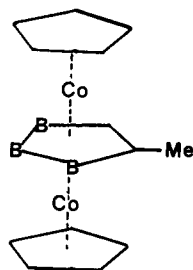
atom	orbital	H_{ii} , eV	ξ
In	5s	-12.60	1.903
	5p	-6.19	1.677
Ga	4s	-14.58	1.77
	4p	-6.75	1.55

participate in the skeletal bonding. The appropriate electron count (eight pairs) can only be obtained if one of the carbons in the ring is substituted by one boron. So, 14 is a likely candidate. One of the metal atoms in 14 could



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be substituted by an Sn-R group without changing the electron count. With use of the isolobal analogy, one of the metals can be substituted by a group like FeCp and the bonding characteristics are not altered, or conversely we could use a CoCp group and substitute another carbon atom by a boron in the central cyclopentadienyl. Substitution of the remaining M by another CoCp and replacing another carbon by a boron, without altering the



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number of skeletal electrons, give us the well-known $\text{Co}_2\text{Cp}_2(3\text{-CH}_3\text{-2,3-C}_2\text{B}_3\text{H}_4)$ (15). These inverse sandwich structures are then the inorganic equivalent of the triple-decker compounds. A rich chemistry of indium and thallium is probably still uncovered.

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Appendix

The exponents and parameters for In and Ga were taken from Clementi and Roetti⁴¹ and Hinze and Jaffe,⁴² respectively. The modified Wolfsberg-Helmholtz formula was used.⁴³ The parameters for B and C were the standard ones.⁴⁴ Distances C-C = 1.42 Å and C-H = 1.08 Å were used for cyclopentadienyl. The experimental Cp-In distances were used for monomeric (2.32 Å) and polymeric (3.19 Å) CpIn. Experimental structural data⁴⁰ were used for $1\text{-CH}_3\text{GaC}_2\text{B}_4\text{H}_6$ (Table IV).

Registry No. 1, 34822-89-4; CpTl, 34822-90-7; CpSn⁺, 77220-40-7.

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The Unusual Bonding Capabilities of a Tetrametal Butterfly Cluster Fragment: Electronic Structures of $\text{HFe}_4(\text{CO})_{12}\text{CH}$ and $\text{HFe}_4(\text{CO})_{13}^-$

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Different coordination geometries of the CH^- and CO^{2-} ligands on the tetrairon butterfly cluster $\text{HFe}_4(\text{CO})_{12}^+$ are explored by using the Fenske-Hall quantum chemical technique. The known preference for η^2 rather than η^1 ligand binding is examined for both. It is demonstrated that the complexes $\text{HFe}_4(\text{CO})_{12}\text{CH}$ and $\text{HFe}_4(\text{CO})_{13}^-$ are aptly described as having a primary triiron-CH or triiron-CO core, thereby supporting a simple geometrical analysis of their structures. Possible mechanisms for the weakening of the ligand C-H and C-O bonds in these complexes in going from η^1 to η^2 geometries are presented and compared. The results suggest that the versatile nature of the metal butterfly causes the CO^{2-} ligand to be increasingly activated on tilting primarily by loss of charge from a CO π -bonding orbital, whereas the CH^- ligand is activated both by charge loss from filled CH σ -bonding orbitals and by charge transfer into a CH σ -antibonding orbital. The major contributory factor to this mechanistic difference is the lack of dinuclear π orbitals on CH. Finally, the difference between the η^2 and η^1 geometries for CH^- are subtle ones whereas those for CO^{2-} are more obvious.

The class of compound in which a main-group "ligand" bridges the wingtips of a homonuclear tetrametal butterfly cluster fragment is becoming increasingly exemplified.¹⁻⁷

Clusters of the type $\text{HFe}_4(\text{CO})_{12}\text{X}$ can be formulated in terms of the metal fragment $\text{HFe}_4(\text{CO})_{12}^+$ and, for example,

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