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Comparative Bonding Study of Conical Fragments

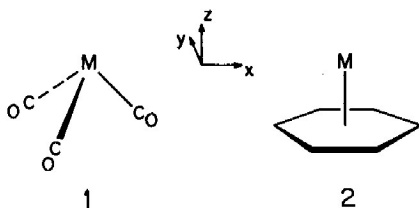
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A detailed construction of the frontier orbitals of $M(\text{CO})_3$ and $M(\text{benzene})$ fragments leads to a general analysis of $M(\text{CO})_3$ and $M(\text{CH})_n$, $n = 3-8$. The number, symmetry properties, energy, and extent in space of these frontier orbitals determine their interaction with other ligands completing the metal coordination sphere. An overlap analysis of the bonding capabilities of $M(\text{CO})_3$, $M(\text{benzene})$, and $M(\text{cyclopentadienyl})$ leads to the conclusion that in interaction with another metal $M(\text{C}_6\text{H}_6)$ or MCp has a stronger σ interaction, but $M(\text{CO})_3$ is better at π bonding. In interaction with a main-group probe oxidation state effects appear to dominate. Structural information on pertinent replacement pairs is surveyed to evaluate the validity of these theoretical conclusions. The bending of hydrogens out of the carbon plane in $M(\text{CH})_n$ complexes is traced to π interactions and a reorientation of the ring π orbitals for better overlap. The result is bending toward the metal for large n and away from the metal for small n . Pyramidal deformations in $M(\text{CO})_n\text{L}_m$ are predicted in response to the donor capability of L.

Between a set of three carbonyls and the cyclic polyene or polyenyl systems $(\text{CH})_n$, $n = 3-8$, one has covered the majority of ligand types in known transition metal complexes. These ligands are often interchangeable. Our interest is in the obvious similarities and the subtle differences of $M(\text{CO})_3$ and $M(\text{CH})_n$ fragments and the consequences of these similarities and differences on their bonding capability. We begin with a detailed comparison of $M(\text{CO})_3$, **1**, with $M(\eta^6\text{-C}_6\text{H}_6)$, **2**, and



then turn to the general features of $M(\text{CH})_n$ fragments. At the end of the paper we attempt to correlate our theoretical conclusions with the available structural information on $M(\text{CO})_3$, $M(\text{arene})$, and $M(\text{Cp})$ complexes.

Theoretical Comparison of the $M(\text{CO})_3$ and $M(\text{benzene})$ Fragments

Interaction diagrams for the formation of **1** and **2** from a metal atom and three carbonyls or a benzene are shown in Figure 1. These diagrams, as well as the other computations referred to below, are derived from extended Hückel calculations for $M = \text{Mn}$, with parameters and geometrical details given in the Appendix. Only those levels which figure in our discussion are shown.

The differences between the frontier orbitals of **1** and **2** are ones of energy (indicated in Figure 1), of extent in space, and of shape (to be discussed below). The origin of these differences lies in the low-lying empty orbitals of the carbonyls, which find no counterpart in benzene. The following specific comparisons may be made.

1. The similarities of fragments **1** and **2** are the expected ones. For a d^6 configuration both **1** and **2** have a set of three low-lying acceptor orbitals of a $+e$ symmetry, marked¹ "hy", xz , and yz in Figure 1. The shapes of these orbitals will be discussed below. Here it suffices to say that they are directed away from the $(\text{CO})_3$ or C_6H_6 and may be adequately described as a set of three hybrids **3**. They are ideally prepared to interact with another six-electron donor system.

2. The first difference between $M(\text{CO})_3$ and $M(\text{C}_6\text{H}_6)$ is in the energy of the z^2 orbital. In **1** z^2 is stabilized by a dominant interaction with an a_1 combination² of $(\text{CO})_3$, while



in **2** z^2 is destabilized by a filled a_1 . It is interesting to note that our calculations indicate that in this destabilization the lowest benzene π orbital; a_{2u} , is not as important as a still lower energy radial type σ orbital of a_{1g} symmetry.³ The reason for this is that at a typical metal-benzene distance the 2p orbitals of the benzene ring lie approximately in the nodal plane of the z^2 orbital. To the extent that the z^2 orbital in **1** is stabilized by mixing in the carbonyl π^* a_1 combination there will be a net transfer of electrons from the metal to $(\text{CO})_3$, providing z^2 is occupied.

3. In both fragments the xy and $x^2 - y^2$ orbitals are slightly stabilized. In **2** symmetry restricts interaction to the LUMO's of benzene, e_{2u} . In **1** mixing is allowed with all e orbitals. The most important interaction seems to be with $2e$, derived from the carbonyl π^* set. The calculation shows larger overlap in the $(\text{CO})_3$ case, which would again lead to greater stabilization and metal to ligand charge transfer when these orbitals are filled. It should be noted that in $M(\text{CO})_3$ there is some mixing of the $(x^2 - y^2, xy)$ and (xz, yz) sets.

4. Metal xz and yz are destabilized by filled orbitals of e symmetry. A concomitant effect is the mixing in of x and y orbitals with a phase such that hybrids pointing away from the $(\text{CO})_3$ or C_6H_6 are produced.⁴ In **4** and **5** are shown contour diagrams of one of these orbitals. In $M(\text{CO})_3$ there is supplemental mixing with unfilled carbonyl orbitals, so that the d character of the orbitals we label xz and yz is somewhat reduced. Also the extent of hybridization with x and y is greater in $M(\text{CO})_3$. The left-right asymmetry of **4** is a consequence of the mixing with xy and $x^2 - y^2$ mentioned above.

5. The orbital labeled "hy" (for hybrid) shows some significant differences in the two fragments. In **2** it is nearly a pure hybrid of s and z while in **1** there is added some z^2 character and some delocalization to the $(\text{CO})_3$. The detailed breakdown of the electron density in this a_1 orbital is given in Table I. A detailed rationale of the composition of these orbitals can be given by utilizing higher order perturbation theory.⁵ The salient features of the analysis are the following. In $M(\text{C}_6\text{H}_6)$ there is a second-order mixing of metal s and z through their mutual overlap with the benzene a_{2u} . The benzene orbital does not itself mix in because the system of s , z , and a_{2u} is similar to an allylic π system, with s playing

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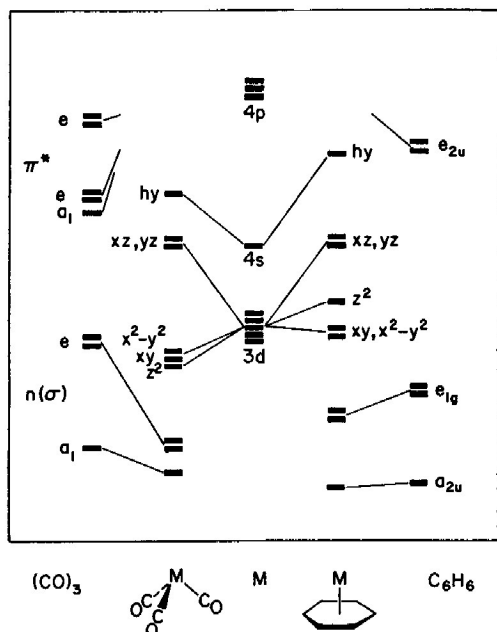
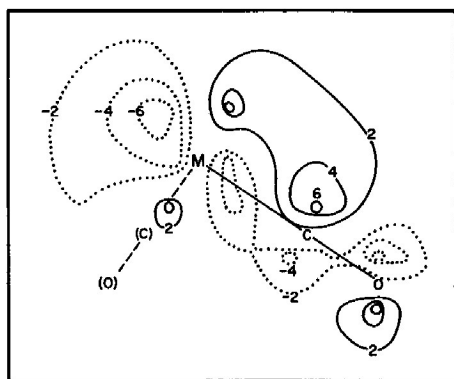
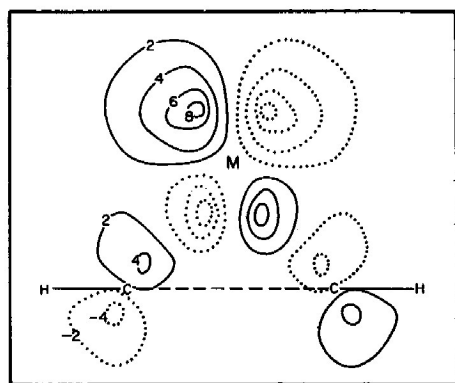


Figure 1. Interaction diagrams for the construction of the orbitals of $M(\text{CO})_3$ and $M(\text{C}_6\text{H}_6)$ from the metal orbitals (at center) and the ligand orbitals (at left and right). The resulting fragment MO's are labeled according to their metal character.



4



5

the role of orbital 1, a_{2u} orbital 2, and z orbital 3. The middle-energy orbital of an allylic system has little or no density at the central orbital, even though one can think of that orbital as coupling centers 1 and 3. In $M(\text{CO})_3$ the lowest vacant a_1 orbital of $(\text{CO})_3$ dominates the coupling pattern, both taking electron density from s and mixing z^2 into s . The

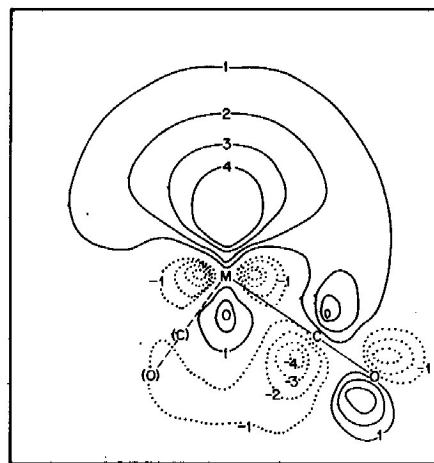
Table I. Electron Density in "hy" Orbital, in %

Orbital	Ligand(s)		
	$(\text{CO})_3$	C_6H_6	C_5H_5
s	21	52	54
z	34	45	44
z^2	18	0	0
Ligand(s)	27	3	1

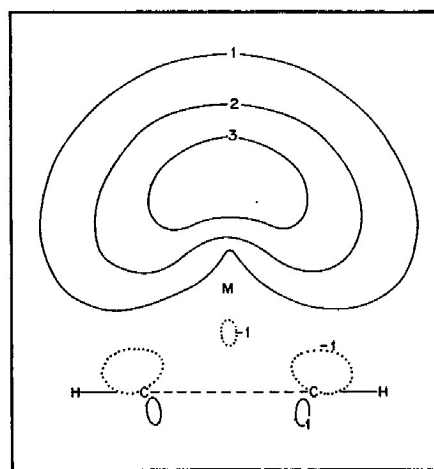
Table II. Transformation Properties of $(\text{CH})_n \pi$ and Metal Orbitals

n	$(\text{CH})_n$	Metal d
3	$a_1 + e$	$a_1 + 2e$
4	$a_1 + e + b_2$	$a_1 + e + b_1 + b_2$
5	$a_1 + e_1 + e_2$	$a_1 + e_1 + e_2$
6	$a_1 + e_1 + e_2 + b_1$	$a_1 + e_1 + e_2$
7	$a_1 + e_1 + e_2 + e_3$	$a_1 + e_1 + e_2$
8	$a_1 + e_1 + e_2 + e_3 + b_1$	$a_1 + e_1 + e_2$

differing shapes of the hy orbital are shown in contour diagrams 6 and 7.



6



7

Though we have dwelled upon some of the differences between the $M(\text{CO})_3$ and $M(\text{C}_6\text{H}_6)$ fragments, we urge the reader to view these differences as minor perturbations superimposed on a basically similar pattern. $M(\text{CO})_3$, $M(\text{C}_6\text{H}_6)$, and $M(\text{Cp})$, which we will discuss later, can be termed *isolobal*. By this word we mean to imply that the number, symmetry properties, extent in space and energy of the frontier

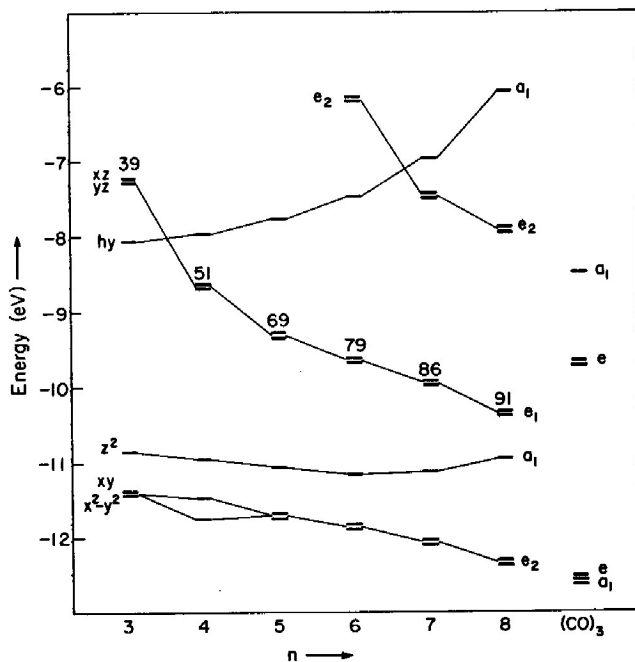


Figure 2. Frontier orbitals of $M(CH)_n$, $n = 3-8$, and $M(CO)_3$. For the e_1 orbital the percent electron density on the metal is indicated by a number. For $n = 3$ the e_1 and e_2 labels do not apply—both levels are e . For $n = 4$ the level set which is e_2 -like is nondegenerate.

orbitals of the fragments are similar—not identical, but similar.

The above discussion has correlated the frontier orbitals of $M(CO)_3$ and $M(C_6H_6)$ fragments. What matters, of course, is the way that the resemblance or dissimilarity of these fragments is translated into the manner in which they bind to some other ligand. We will return to a comparison of the relative bonding capabilities of the two fragments later. At this point it is appropriate to enlarge our discussion to include other $M(CH)_n$ species.

Molecular Orbitals of Other $M(CH)_n$ Fragments

The known cyclopolyene or cyclopolyenyli rings found in transition metal complexes range in size from 3 to 8.⁶ The polyene orbitals and their interactions with transition metal atoms are well-known, so that to some extent we run the risk of repeating in this section what is common knowledge.⁶⁻⁸

In the reduced C_{nv} symmetry the π orbitals of planar $(CH)_n$ rings and the atomic orbitals of a transition metal transform as shown in Table II. The metal s and p orbitals subduce in each case the $2 a_1 + e$ representations. Of course, it is the cylindrical $C_{\infty v}$ pseudosymmetry which is more important than the actual C_{nv} symmetry. Thus the metal d orbitals are $\sigma + \pi + \delta$ in all cases, and the cyclopolyene orbitals can be reclassified accordingly. A perfect match for the metal d orbitals is found in the $a_1 + e_1 + e_2$ orbitals of a cyclopolyene for $n \geq 5$. From that point on, the differences among the various $M(CH)_n$ species are only quantitative, depending on the relative energies of the cyclopolyene and metal orbitals.

All of the interaction diagrams are in fact qualitatively alike, as shown in Figure 2. This illustrates the frontier orbitals of $Mn(CH)_n$, along with those of $Mn(CO)_3$ for comparison. In the $Mn(CH)_n$ geometries which we utilized, the $Mn-C$ distance was kept fixed at 2.19 Å. In all $M(CH)_n$ we recognize a cluster of three relatively low-lying orbitals, mainly on the metal, composed of z^2 , xy , and $x^2 - y^2$. These are characteristic of an octahedral fragment. At higher energy (at least for low n) there is an $a_1 + e_1$ set of hybrids directed away from the metal. For high n there comes in an e_2 orbital, primarily localized on the ligands. We proceed to detailed examination of the various frontier orbitals.

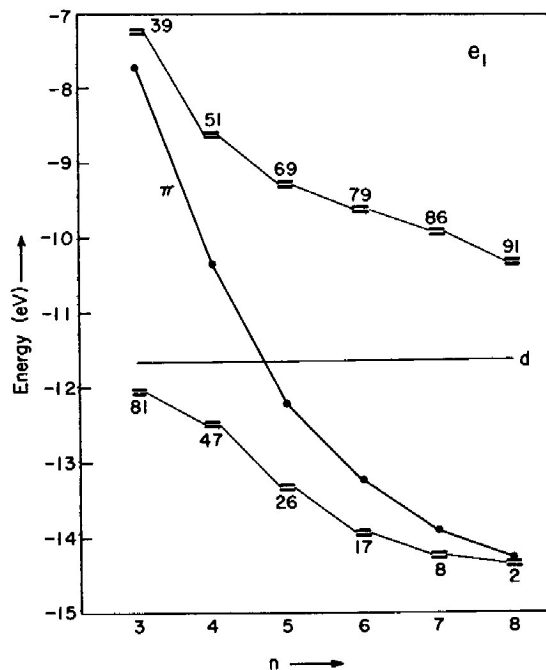


Figure 3. Construction of the e_1 frontier orbitals from the interaction of a variable-energy C_nH_n e_1 and a fixed-energy xz, yz set. π labels the energy of the e_1 set in the cyclopolyene. The numbers are percent metal character.

The low-lying xy and $x^2 - y^2$ set, of e_2 symmetry, moves to lower energy with increasing n . At the same time its delocalization to the ligands increases. The energy and delocalization trends are of course a reflection of increased interaction with a $(CH)_n$ e_2 orbital, of δ pseudosymmetry. For $n \geq 5$ such a π orbital is present, at increasingly lower energy for higher n . Note for these higher n values the presence in the diagram of the higher e_2 combination, metal-ligand antibonding. For an account of the role of the e_2 orbitals the reader is directed to the important contributions of Green, de Liefde Meijer, and their co-workers.⁸

Not far from the $xy, x^2 - y^2$ set lies an a_1 orbital, which varies relatively little in energy and composition with n . Both this z^2 orbital and hy are highly localized on the metal, 92-98% on the metal over the entire range of n . The energy of hy changes as a result of a change in sp hybridization, from 59% s and 39% z at $n = 3$ to 40% s and 56% z at $n = 8$.

The most dramatic variation is in the e_1 or π orbitals. They drop in energy with n , become more localized on the metal, and mix in less x and y character. What is happening is made explicit by Figure 3. It shows the energy of the $(CH)_n$ e_1 orbitals as a function of n , as well as the (assumed!) straight-line energy of the metal d orbitals. The two e_1 orbitals which result from the interaction are very clearly the result of an "avoided crossing" and a strongly avoided one at that. The lower e_1 set, which was not drawn in Figure 2, starts out as mainly metal and ends up as primarily ligand. The upper e_1 set, metal-ligand antibonding, is primarily ligand at low n and is changed continuously to heavily metal character at high n . The change in hybridization can also be explicated by application of second-order perturbation theory.

A comparison with $M(CO)_3$ shows that for no n can the $(CH)_n$ hy orbital match the acceptor capability of the corresponding $M(CO)_3$ orbital—the latter is always at lower energy. This is for interactions with a main-group probe. The e_1 xz, yz set may play either a donor or an acceptor role, depending on the d^n configuration. If e_1 is empty, then in $M(CH)_n$ it can achieve energetic parity with $M(CO)_n$ or even surpass it in acceptor capability, for $n \geq 6$. If e_1 is occupied, then it becomes a better donor than $M(CO)_n$ for $n \leq 5$.

Table III. Overlaps between ML_n Acceptor Orbitals and NO and MnH_3 Probe Orbitals

	Overlaps with NO		Overlaps with MnH_3	
	$\langle hy n \rangle$	$\langle xz \pi_x^* \rangle$	$\langle hy hy \rangle$	$\langle xz xz \rangle$
$M(CO)_3$	0.178	0.133	0.622	0.205
$M(C_6H_6)$	0.134	0.151	0.820	0.171

Table IV. Metal-Probe Overlaps

ML_n metal orbital	N		Mn		
	2s	2p _z	4s	4p _z	3d _{z²}
4s	0.30	0.02	0.59	0.50	0.02
4p _z	0.44	0.01	0.50	0.24	0.03
3d _{z²}	0.24	0.17	0.02	0.03	0.06

Relative Bonding Capabilities of $M(CO)_3$ and $M(C_6H_6)$ Fragments

We now return to our primary objective of assessing the relative interactions of $M(CH)_n$ and $M(CO)_3$ with external ligands. $M(CO)_3$ and $M(C_6H_6)$, whose orbital structure has been analyzed in detail above, will serve as a departure point. Of course there is an infinite variety of ligands which can bind to these fragments. The common feature that otherwise disparate potential bonding partners for ML_n will carry is a donor function. This will interact strongly with the acceptor orbitals of $M(CO)_3$ or $M(C_6H_6)$. Which of the six frontier orbitals serve as donors or acceptors of course depends on the d-electron configuration. The most common 18-electron cases will be d^6 – d^{10} , so that the acceptor orbitals will be hy , xz , and yz .

One of the several ways that we explored for judging the bonding capability of the ML_n moiety was to calculate overlaps between the hy , xz , and yz orbitals and appropriate symmetry group orbitals of a bonding partner. It became apparent that it was important to distinguish between main and transition group partners. As an example of the former, we chose a nitrosyl group, with its nitrogen atom placed 1.71 Å from the metal atom.⁹ This ligand has a well-developed lone pair, denoted as n , and a set of low-lying π^* orbitals. As a transition metal bonding probe we chose a hypothetical MnH_3 fragment placed 2.9 Å away from M . The MnH_3 has σ and π orbitals quite analogous to those of the ML_n system we have discussed. Table III shows the computed overlaps between hy , xz , and yz and the corresponding symmetry probe orbitals.

The ordering of the interactions in Table III merits explanation. In interpreting the various overlaps with hy , it is useful first to recall (Table I) that in $M(CO)_3$ hy is a mixture of metal s , z , and z^2 and is somewhat delocalized to the carbonyl groups. In $M(C_6H_6)$ hy is a nearly pure mixture of metal s and z . Table IV lists the computed overlaps between metal s , z , z^2 , and various σ orbitals of the probe.

Consider first the ML_n –N overlap. The metal s and z orbitals are so diffuse that they overlap nearly equally with both the positive and negative lobes of N z . This accounts for the small overlaps with N z . Metal z^2 , reasonably contracted, has significant overlaps with the main-group probe s and z orbitals. Since the distinction between $M(CO)_3$ and $M(C_6H_6)$ is primarily that the former carries z^2 character, we can understand why in Table III the overlap of the $M(CO)_3$ hy with the main-group probe orbital, which is a mixture of 2s and 2p_z, is greater than that of $M(C_6H_6)$ hy . The more p character in the coupling lone pair, the greater the differential. Conversely, if the donor orbital is mainly s (for instance, a hydride) $M(CO)_3$ and $M(C_6H_6)$ should possess similar σ -bonding capabilities.

While the group overlaps of Table III indicate that an $M(CO)_3$ fragment should have a somewhat stronger σ in-

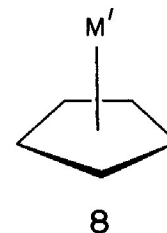
teraction than $M(C_6H_6)$, we were concerned that the conclusion rested on overlap differentials involving metal 4s and 4p orbitals. The shape of these orbitals is uncertain, the particular Slater exponent assumed by us being little more than a guess. We therefore repeated the ML_n -probe calculations with different 4s and 4p exponents. These were judged appropriate for $M = Ni$ (see Appendix) and gave considerably more contracted 4s and 4p functions. The group orbital overlaps of Table III in fact are sensitive to the metal wave function, for the trends noted were reversed by a little. We are not left with a definitive comparison of the $M(CO)_3$ and $M(\text{arene})$ σ -bonding capability—from the theoretical point of view the fragments appear roughly equivalent.

In contrast to the above discussion it is $M(C_6H_6)$ that should be more effective at bonding with another metal. At the distances of 2.5–3.0 Å characteristic of metal–metal bonding the primary overlap is between the diffuse s and p orbitals of the metal. The noded and relatively contracted d functions provide a poor overlap with other metal d orbitals or s and p functions, as may be seen in Table IV. The $M(CO)_3$ fragment, with its admixture of z^2 , should be less effective at bonding with another metal than $M(C_6H_6)$. We also note that the trends in interaction with a metal probe are insensitive to the choice of metal wave function.

In evaluating the π interactions the important points are that xz and yz in $M(CO)_3$ are both more delocalized to the $(CO)_3$ and more hybridized with metal x and y than is the case in $M(C_6H_6)$. The greater delocalization away from the metal is responsible for the smaller $M(CO)_3$ π overlap with a main-group probe. The hybridization, on the other hand, enhances overlap with a metal atom center.

The conclusions which we obtain from the preceding laborious discussion are the following: *For coupling with another metal probe $M(C_6H_6)$ definitely has a stronger σ interaction, but $M(CO)_3$ is better at π bonding.* The σ effect appears to be dominant. For main-group probes our comparison of σ and π interactions of $M(CO)_3$ and $M(C_6H_6)$ is inconclusive. Given this situation for the overlap factor, one could fall back on the role of the residual charge on the metal. This would imply that an $M(CO)_3$ group is a worse π donor and better σ acceptor than $M(C_6H_6)$.

Our next concern is to compare these conclusions with the experimental evidence that is available. A comparison of $M(CO)_3$ and $M(C_6H_6)$ is relatively restrictive, for indeed the most common replacement is of $M(CO)_3$ by $M'(\eta^5\text{-cyclopentadienyl})$, $M'(\text{Cp})$, 8. There is a slight problem with an

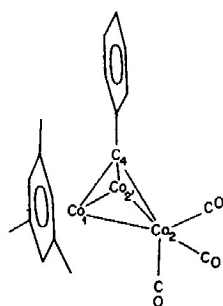


analysis of the latter two systems due to the fact that in order to obtain a truly isoelectronic interchange one must change the transition metal as well, from M to $M' = \text{metal with atomic number } M + 1$. For instance interchangeable pairs are $Fe(CO)_3$ and $Co(C_5H_5)$; and $Co(CO)_3$ and $Ni(C_5H_5)$. We prefer to have only one part of the system change, not both the metal and the ligands. Fortunately the symmetry properties and overlaps of cyclopentadienyl ligand are very similar to those of benzene. This allows us to make an analysis of 1 and 2, where the metal atom is the same. At selected places in our discussion we will point to the possible perturbation caused by changing the metal.

Structural Information on Matched $M(\text{CO})_3$, $M(\text{C}_6\text{H}_6)$, and $M(\text{Cp})$ Complexes

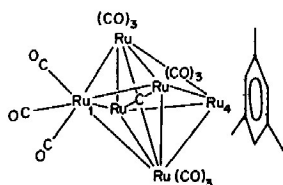
An examination of the experimental evidence relevant to our theoretical conclusions must be prefaced by three general comments. First, there is little thermochemical information on these molecules.¹⁰ We must draw whatever conclusions we can concerning the differential bonding from the results of structural studies. Some indirect information may be forthcoming from spectroscopic studies, but we have not attempted to review it. Second, despite the generality of the replacement of $M(\text{CO})_3$ by $M(\text{C}_6\text{H}_6)$ or $M'(\text{Cp})$ there are relatively few structures to compare. It may be that the assurance that has built up that such groupings are indeed replaceable has operated against the allocation of precious time to carry out several structural studies. Third, for the few structures that we have we are put in the uncomfortable position of comparing structural investigations often of disparate quality. A few accurate structural studies would quickly clear up the questions posed by the replacement, but for the present we must ask the reader to bear with us as we review the evidence that is available.

For metal-metal interactions we have several pertinent examples. The structure of phenylmethynitricobalt hexacarbonyl,¹¹ **9**, offers an interesting internal comparison of



9

$\text{Co}_1\text{-Co}_2 = 2.44 \text{ \AA}$
 $\text{Co}_2\text{-Co}_2' = 2.48 \text{ \AA}$
 $\text{Co}_1\text{-C}_4 = 1.87 \text{ \AA}$
 $\text{Co}_2\text{-C}_4 = 1.90 \text{ \AA}$

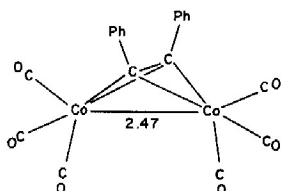


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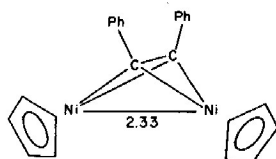
$\text{Ru}_1\text{-Ru} = 2.86, 2.90 \text{ \AA}$
 $\text{Ru}_4\text{-Ru} = 2.85, 2.86 \text{ \AA}$
 $\text{Ru}_1\text{-C} = 2.12 \text{ \AA}$
 $\text{Ru}_4\text{-C} = 1.88 \text{ \AA}$

$\text{Co}(\text{CO})_3$ and $\text{Co}(\text{mesitylene})$. Note that the bonds with the $\text{Co}(\text{mesitylene})$ fragment are consistently shorter, as expected. A related comparison of $\text{Co}_4(\text{CO})_{12}$ ¹² with $\text{Co}_3(\text{CO})_9(\text{arene})$ ¹³ is hampered by crystallographic problems due to disorder in the crystal of the former molecule. A ruthenium carbonyl carbide cluster,¹⁴ **10**, also shows shorter Ru(arene) to C and Ru distances.

Another metal-metal comparison is available from the acetylene complex structures **11**¹⁵ and **12**.¹⁶ The Co structure



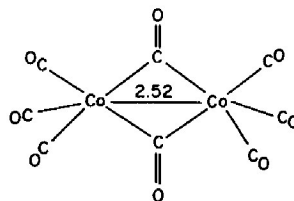
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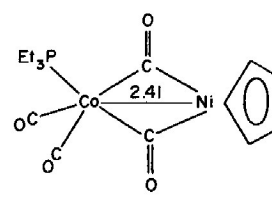
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is an early one, with a large *R* factor. The Co-Co distance is longer.

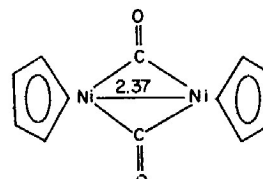
The series **13**,¹⁷ **14**,¹⁸ and **15**¹⁹ provides a stepwise replacement of $(\text{CO})_3\text{Co}$ by CpNi . The metal-metal separation decreases along the series.



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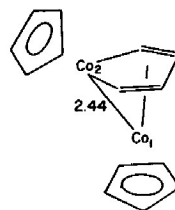


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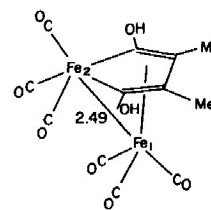


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In structures **16**²⁰ and **17**²¹ there is a double fragment



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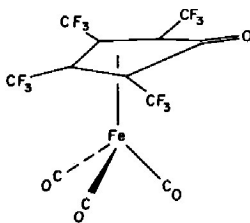
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substitution. As expected, the CpCo-CoCp distance is shorter than $(\text{CO})_3\text{Fe-Fe}(\text{CO})_3$. The average $\text{Co}_1\text{-C}(\text{MC}_4 \text{ ring})$ distance of 2.03 \AA is shorter than the corresponding Fe-C distance of 2.13 \AA . Also the average $\text{Co}_2\text{-C}$ distance in the MC_4 cycle, 1.87 \AA , is shorter than the $\text{Fe}_2\text{-C}$ distance of 1.94 \AA . The shorter CpCo -main group bond lengths are not in agreement with our expectations, and perhaps this is the appropriate place to face up to the problems of interpretation caused by the cyclopentadienyl ligand.

The symmetries, distances and overlaps of C_5H_5 and C_6H_6 fragments are very similar and, were it not for the different metal atom that must be coupled to these to achieve iso-electronic fragments, the donor and acceptor orbitals of $\text{C}_6\text{H}_6\text{M}$ and CpM' would be nearly identical. The difference between *M* and *M'* is one of atomic number and oxidation state— $\text{Fe}(0)$ and $\text{Co}(1)$; $\text{Co}(0)$ and $\text{Ni}(1)$. The effect of the increased oxidation state is in principle felt in two ways: (1) through an increased splitting of metal *s* and *d* levels, with a corollary decrease in hybridization, and (2) through a contraction in the size of the atom.²² Of course, electroneutrality to some extent tempers the distinction implied by the oxidation-state formalism. Nevertheless, one would expect a $\text{Ni}^{\text{II}}\text{-L}$ distance to be inherently shorter than a $\text{Co}^{\text{I}}\text{-L}$ separation. Whenever we contrast the bonding capabilities of $(\text{CO})_3\text{Co}$ with CpNi , we will have to remember that any electronic effects that we postulate are operating on top of this background.

The nitrosyl ligand serves as a simple main-group probe in $(\text{CO})_3\text{Co}(\text{NO})$ and $\text{CpNi}(\text{NO})$. An electron diffraction structure is available for the former,²³ while for the latter we have a microwave structure^{24a} as well as an electron diffraction structure.^{24b} If the NO is viewed as NO^+ , these are d^{10} systems. The NO group is a good σ donor and an excellent π acceptor. The Co-N distance is 1.67 \AA and Ni-N is 1.63 \AA , which again may be due, at least in part, to a change in oxidation state.

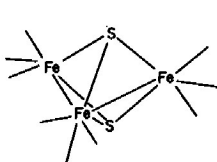
The structures of tetrakis(trifluoromethyl)cyclopentadienone complexes with $\text{Fe}(\text{CO})_3$ and CoCp are available.²⁵ The structural type is shown in **18**. The two structures show



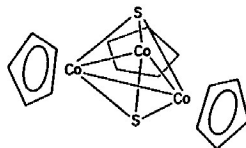
18

similar angles of bending up of the carbonyl group and metal-ring distances and a somewhat longer set of C-C distances in the cyclopentadienone ring for the CoCp complex. But the structural parameters are not of high accuracy, so that little significance can be attached to the variations.

As a final structural comparison we cite the clusters $(\text{CO})_9\text{Fe}_3\text{S}_2$, $(\text{CO})_9\text{Fe}_3\text{Se}_2$, $\text{Cp}_3\text{Co}_3\text{S}_2$, and $\text{Cp}_3\text{Co}_3\text{S}_2^+$. The first two low-spin compounds possess an open C_{2v} structure,^{26,27} 19, with one Fe-Fe distance much longer than the other two.



19



20

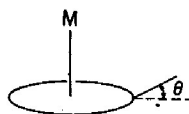
$\text{Cp}_3\text{Co}_3\text{S}_2$, which is a triplet at room temperature,^{28,29} is a closed D_{3h} structure,²⁸ 20. Its cation is slightly distorted to a C_{2v} geometry with one Co-Co distance slightly shorter than the other two. A qualitative MO scheme²⁹ rationalizes perfectly well the geometrical distortions in this system. In a D_{3h} geometry two electrons occupy an antibonding e' orbital.³⁰ A distortion to C_{2v} breaks the degeneracy. It is understandable that a high-spin two-electron system would maintain the D_{3h} geometry, while a low-spin state would distort.

The general picture that emerges from an examination of these structures is one of agreement with our theoretical conclusions on stronger metal-metal bonding with an $M(\text{C}_6\text{H}_6)$ or $M'(\text{C}_5\text{H}_5)$ fragment. For the metal-main group bonding the theoretical result was not clear, and the experimental picture seems to be dominated by oxidation-state arguments.

Pyramidal Deformations in $M(\text{CH})_n$ and $M(\text{CO})_3$

In this section we discuss two small but interesting distortions in $M(\text{CH})_n$ - and $M(\text{CO})_3$ -containing structures. The first of these concerns the noncoplanarity of the cyclopolyene hydrogens with the carbon plane, and the second deals with the variable pyramidalities of the $(\text{CO})_3$ grouping.

Accurate structural investigations show that when a cyclopolyene is coordinated to a transition metal center, the hydrogens or other ring substituents may be bent toward or away from the metal. In examining such structures we exclude highly unsymmetrically substituted molecules and complexes in which not all of the $(\text{CR})_n$ centers are coordinated to the metal. A significant set of distortions remain. Let us define the deformation by an angle θ between the C-R axis and the ring plane, as shown in 21. Positive θ will correspond to



21

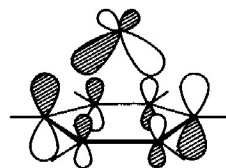
bending toward the metal; negative θ , to bending away.

Table V. EH Optimized θ in a Series of $M(\text{CH})_n$ Fragments

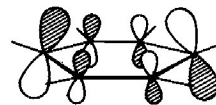
Fragment	Co- (C_3H_3)	Fe- (C_4H_4)	Mn- (C_5H_5)	Cr- (C_6H_6)	V- (C_7H_7)	Ti- (C_8H_8)
Optimal θ	-26°	-6°	0°	3°	9°	13°

Let us first consider coordinated benzene rings. A neutron and crystal diffraction study of benzenechromium tricarbonyl³¹ gives an average bending angle of $+1.7^\circ$. Similar positive θ deformations are observed for bis(benzene)chromium,^{32,33} but negative θ deformations, away from the metal, have been found for hexamethylbenzenechromium tricarbonyl³⁴ and the η^6 ring in bis(hexamethylbenzene)ruthenium.³⁵ The entire range of deformations is small, and no one would be surprised if the observed distortions were a consequence of crystal packing forces. Nevertheless, it is interesting to study the problem theoretically—there is no constraint holding the cyclopolyene substituents in the carbon plane.

An optimization of θ in a d^6 $\text{Cr}(\text{C}_6\text{H}_6)$ fragment yields an energy minimum for hydrogens bent toward the metal by 3.2° . The bending can be traced to an e_1 orbital, the in-phase combination of metal xz and yz with the benzene e_{1g} orbital. The shape of one component of this orbital for a planar benzene is illustrated in 22. The reason that this orbital



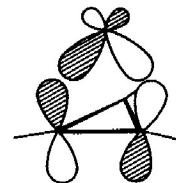
22



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combination is stabilized for a distorted benzene with hydrogens bent toward the metal is that the metal-benzene overlap is increased by such a distortion. Bending the hydrogens up reorients³⁶ the benzene MO's in such a way that the e_{1g} orbital (e_1 in the reduced C_{6v} symmetry) lobes tilt to point in at the metal, 23. This orbital deformation increases the overlap with metal xz and yz . A similar explanation in terms of ring p orbital reorientation for better M-ring bonding has been given earlier by Kettle.³⁷

If we accept this explanation for the small positive θ deformation, then we must attribute the negative θ distortions in hexamethylbenzenes to steric effects. The overall credibility of our rationalization is however enhanced by surveying the analogous distortions as a function of cyclopolyene ring size. If the crucial bonding effect is the $(xz, yz)-e_1$ interaction, then for large rings overlap will be maximized by a tilting in of the e_1 π orbitals (as shown in 23), and θ would be positive. But for small rings the ligand π set should tilt out, as in 24, to



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increase overlap with xz and yz , and the optimum θ should be negative. Extended Hückel optimizations of θ on a series of $M(\text{CH})_n$ fragments lend support to this argument. A tabulation of these results is given in Table V. There is a continuous trend of the hydrogens approaching the metal as the rings increase in size.

What is known experimentally for various ring sizes is the following: θ is an average $+4.1^\circ$ for the methyl groups of bis(1,3,5,7-tetramethylcyclooctatetraenyl)uranium.³⁸ A better example perhaps is to be found in the structure of $[\text{C}_8\text{H}_8-$

TiCl₄, where the hydrogens in each C₈H₈Ti unit are displaced toward the Ti.³⁸ In ferrocene θ is positive;⁴⁰ in (C₅Me₅)Rh(dba)⁴¹ and in (C₅Me₅)Fe(CO)₂SO₂CH₂CH=CHPh,⁴² negative. In less symmetrical ferrocenes there appears to be no significant trend, with θ being sometimes positive and sometimes negative.⁴³

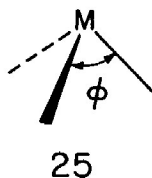
Substituents on complexed cyclobutadienes consistently bend away from the metal. θ is -10.8° in (C₄Ph₄)Fe(CO)₃⁴⁴ and also negative in two less symmetrical systems: [C₄Me₄NiCl]₂⁴⁵ and [C₄Ph₂(*t*-Bu)₂]₂Fe₂(CO)₃.⁴⁶

Complexed cyclopropenyl groups show a significant bending of ring substituents away from the metal. Thus the average bending angle is -20° in CpNi(C₃Ph₃)⁴⁷ and -19° in Cl(py)₂Ni(C₃Ph₃).⁴⁸

Our analysis further predicts that in M(CH)_{*n*} complexes the crossover between positive and negative θ , which in complexes of the first transition series appears to occur at $n \approx 5$, should shift to larger n for M in the second or third transition series. The corresponding metal *xz* and *yz* orbitals are more diffuse. For a large ring they require less reorientation for maximal overlap.

Parenthetically we might mention that the typical bending away of substituents on a complexed ethylene may be readily understood as a limiting case for application of the arguments cited above.

Let us discuss a different deformation, the modification of the pyramidal of the M(CO)₃ fragment. A measure of this is the angle ϕ in 25. As discussed earlier,⁴ the *a*₁ and *e* (*hy*,



xz, *yz* in Figure 1) orbitals of the M(CO)₃ fragment will both decrease in energy with increasing ϕ , i.e., the more planar the M(CO)₃. In a quasi-tetrahedral d¹⁰ system (CO)₃ML *xz* and *yz* are filled and play a donor role. It follows that the stronger the π -acceptor capability of L (and the worse its σ -donor function) the more pyramidal the M(CO)₃ grouping. For related (PR₃)₃ML systems the experimental evidence is in accord with this.⁴⁹

For a quasi-octahedral d⁶ system (CO)₃ML₃ *hy*, *xz*, and *yz* are all empty and act as acceptor orbitals for the incoming donor orbitals of three L groups. The stronger the donating capability of L the less pyramidal should be the M(CO)₃ fragment. The same should hold true if L₃ is replaced by a cyclopolyene, (CH)_{*n*}.⁶⁻ⁿ In Figure 3 we note that the energy of the π orbital (and hence the donor strength) rises with decreasing n . Therefore the pyramidal of the carbonyl cone in (CH)_{*n*}M(CO)₃ is expected to decrease with n . Experimental confirmation of this is found in the structures C₆H₆Cr(CO)₃,³¹ C₅H₅Mn(CO)₃,⁵⁰ and C₄Me₄Fe(CO)₃⁴⁴ where the average ϕ is 88, 92, and 97°, respectively. A comparison of C₆H₃(NO₂)₃Cr(CO)₃ (average $\phi = 89^\circ$)⁵¹ with C₆H₆Cr(CO)₃, however, seems to indicate that ϕ is relatively insensitive to substituents on the ring.

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Appendix

Extended Hückel calculations⁵² were carried out using the following geometries and atom parameters. M(CO)₃ had the idealized octahedral fragment geometry with angle CMC = 90°. Bond distances were M-C = 1.80 Å and C-O = 1.13 Å. M(CH)_{*n*} bond distances were M-C = 2.19 Å, C-C = 1.40 Å, C-H = 1.08 Å. The ring was kept planar with M above its center. NO was set at 1.71 and 2.10 Å from the metal fragments with N-O = 1.17 Å. MH₃ was calculated at 2.90 Å from the metal with angle HMH = 90° and M-H = 1.5 Å. Table VI summarizes the extended Hückel parameters used.

Table VI. Extended Hückel Parameters for Nonmetals

Orbital	Slater exp	H _{ii} , eV	Orbital	Slater exp	H _{ii} , eV
H 1s	1.30	-13.60	N 2p	1.950	-13.40
C 2s	1.625	-21.40	O 2s	2.275	-32.30
C 2p	1.625	-11.40	O 2p	2.275	-14.80
N 2s	1.950	-26.00			

Table VII. Extended Hückel Parameters for Metals

Orbital	Slater exp 1	H _{ii} , eV	Slater exp 2	Coeff 1	Coeff 2
Mn 4s	0.97	-9.75			
Mn 4p	0.97	-5.89			
Mn 3d	5.15	-11.67	1.7	0.5139	0.6929
Ni 4s	1.825	-9.75			
Ni 4p	1.125	-5.89			
Ni 3d	5.75	-11.67	2.0	0.5683	0.6292

To span a range of metal wave functions we used the exponents of Mn and Ni, keeping the H_{ii} the same in both cases (see Table VII). The metal d functions were taken as double- ζ functions.⁵³ In the series of calculations, such as Figures 2 and 3 and Table V, the metal parameters were constant. Only the number of electrons changed.

References and Notes

- Throughout this paper we use the abbreviated notation *z*² for d_{z²}, *z* for p_z, etc.
- The arrangement of three carbon monoxides into the geometry they occupy in an M(CO)₃ fragment introduces CO-CO overlaps large enough to produce a significant mixing and consequent reorientation of all orbitals of the carbonyls— σ , π , π^* , σ^* . The block of low-lying unfilled orbitals *a*₁ + *a*₂ + 2 *e* is still recognizable as primarily π^* .
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- This distance is between the observed M-N distances in Co(CO)₃NO and CpNiNO. Being as short as it is, it may not be typical of ML_{*n*}-main group interaction. With this in mind we repeated our calculations for the NO probe, but placing it 2.1 Å away from the metal. All conclusions were qualitatively similar.
- See J. D. Cox and G. Pilcher "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. Some recent measurements on the strength of aren-Cr(CO)₃ bonds are summarized by F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. L. Leung,

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