

knowledge. The laser Raman instrument purchase was made possible in part through Grant GP-10187 from the National Science Foundation. The assistance of Mr. Wayne M. Butler and Dr. Robert J. Ziegler is gratefully acknowledged.

**Registry No.** Et<sub>4</sub>NReCr(CO)<sub>10</sub>, 54307-62-9; Et<sub>4</sub>NReMo(CO)<sub>10</sub>, 54307-63-0; Et<sub>4</sub>NReW(CO)<sub>10</sub>, 54307-64-1; Ph<sub>4</sub>AsReW(CO)<sub>10</sub>, 54307-65-2.

**Supplementary Material Available.** Table IV, an extensive listing of all observed infrared and Raman bands including their intensities, physical states during measurement, polarizations, and assignments, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40691M.

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## Bonding Capabilities of Transition Metal Carbonyl Fragments

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The energy ordering, symmetry, and extent in space of the valence molecular orbitals of a range of geometries of M(CO)<sub>3</sub>, M(CO)<sub>4</sub>, and M(CO)<sub>5</sub> fragments, where M is a transition metal center, are analyzed in detail. The properties of the fragment orbitals are then used to examine the ability of the fragments to interact with other ligands as well as the geometrical preferences of the isolated fragments. The following problems are discussed: the pyramidalization of five-coordinate fragments, metal-metal bond formation, seven-coordination, stabilization of "umbrella" distortions of fragments, the difference between M(CO)<sub>n</sub> fragments and ML<sub>n</sub>, with L = π donor, geometrical distortions in transition metal hydrides, why Fe(CO)<sub>3</sub> favors bonding with conjugated dienes while Cr(CO)<sub>4</sub> coordinates preferentially with unconjugated dienes.

The usual contemporary way of analyzing the electronic structure of a chemical compound is in terms of molecular orbitals formed as linear combinations of atomic orbitals. For complex molecules of low symmetry these molecular orbitals can be quite delocalized. The practicing chemist, wishing to perceive the main features of the bonding and their chemical consequences, faces the sometimes difficult task of translating the information hidden in the delocalized, complicated wave function, into less exact qualitative concepts.

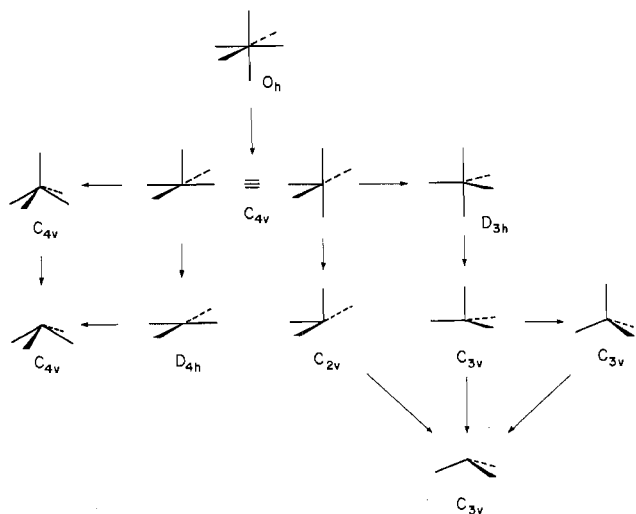
An alternative approach, designed to bridge the gap between the delocalized molecular orbital and the localized semantic structure of the experimentalist, consists of breaking up the molecule into fragments rather than atoms. The orbitals of the simple fragments are easily visualized. The initial bonding follows from the interaction of a limited subset of fragment orbitals, such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO), the valence or frontier orbitals of the fragments. Fragment analysis

has been successfully used for some time for small and organic molecules.<sup>1-3</sup>

For transition metal complexes nothing seems more natural today than the partitioning into metal and ligand orbitals. Yet the decomposition of a complex into an invariant fragment ML<sub>n</sub>, consisting of a metal atom and several ligands, and a variable ligand L' has not been sufficiently exploited.<sup>4</sup> The purpose of this paper is to demonstrate that a consistent analysis of ML<sub>n</sub> fragments may be successfully applied to a wide range of structural problems.

The subject of our study is the set of M(CO)<sub>n</sub> fragments with  $n = 3-5$  and M a metal atom of any transition series. The d-electron configuration is a variable. The specific calculations carried out were of the extended Huckel type, for M = Mn. Details are given in the Appendix. Since many of the conclusions we draw are based on symmetry arguments abstracted from the calculations, our results should carry over to any transition metal center. Our initial hope was that the con-

Scheme I



clusions we reached for  $M(\text{CO})_n$  fragments would hold for other ligands as well. It will be seen later that, while the methodology is the same, the results for an  $ML_n$  fragment with  $L = \pi$  donor can be quite different from our carbonyl case.

The fragment geometries we explored are derived from the octahedron by successive stripping away of one ligand, followed by a sequence of geometrical rearrangements of the remaining  $M(\text{CO})_n$  fragment. Scheme I summarizes the basic geometries studied. For each fragment a range of geometrical distortions, only partially indicated in the scheme, was explored.

The fragments were analyzed with respect to two points.

### (1) Geometrical Preferences of the Pure Fragments.

$M(\text{CO})_n$  fragments by themselves are interesting species. Some of them can, under certain conditions, have a discrete existence.<sup>12</sup> It is also probable that they appear on the pathway of nonconcerted ligand-exchange mechanisms. Coordinatively unsaturated fragments are thought to play an important role in homogeneous catalysis. Where the fragments are known as stable species, we have a calibration point on our calculations.

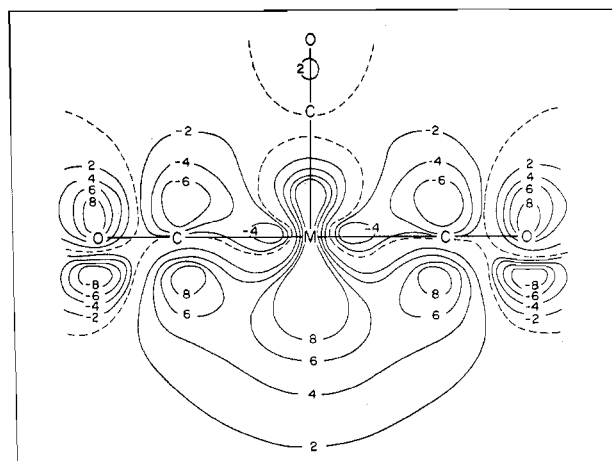
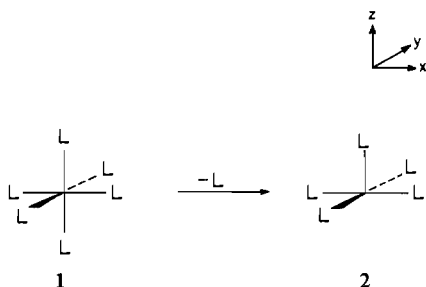
### (2) Ability of the Fragments to Interact with Other Ligands, Forming Stable Compounds.

Here we focused our attention on the relative energy of the acceptor and donor orbitals of the fragment, as well as on the symmetry properties, localization on metal, and spatial extent of these orbitals.

The approach is best illustrated by analysis of a trivial example, the  $C_{4v}$   $M(\text{CO})_5$  fragment.

### Pentacoordinate Fragments: the Flat Square Pyramid $C_{4v}$ $M(\text{CO})_5$

The natural starting point is the octahedral complex  $ML_6$ , **1**. Suppose we remove one axial ligand along the  $-z$  direction, leaving behind the  $C_{4v}$   $ML_5$  fragment of an octahedron, **2**, a "flat" square pyramid. The descriptor "flat" simply is meant to imply that the metal atom is on the basal plane of the square pyramid, to distinguish it from other square pyramids which we will analyze below.



**Figure 1.** The high-lying  $a_1$  orbital of a flat square pyramidal  $M(\text{CO})_5$ . Contours are of  $\psi$ , to be multiplied by  $10^{-2}$ . The dashed line represents a node. The scale of the drawing is set by the  $M-C$  distance of 1.80 Å.

The primary effect of the strong axial perturbation, removal of a ligand, is well known. One member of the octahedral  $e_g$  set, which was metal-ligand  $\sigma$  antibonding, namely, the  $z^2-\lambda L$  combination,<sup>13</sup> moves to lower energy upon loss of part of its antibonding interaction. This is shown schematically in **3**.

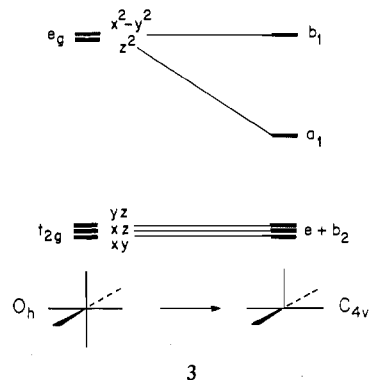


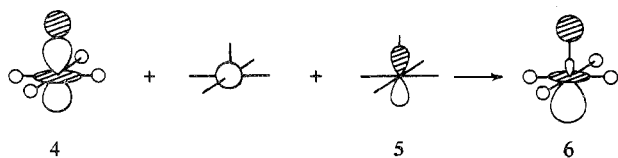
Diagram **3** gives the first and obvious conclusion concerning the  $C_{4v}$  fragment—a low-spin  $d^6$  fragment would be characterized by a low-lying acceptor orbital; a  $d^8$  fragment, by a high-lying donor orbital. The  $M(\text{CO})_5$  calculations show that in place of the missing ligand there grows a nicely directional bare  $a_1$  orbital, mainly localized on the metal and pointing away from the other ligands. Figure 1 shows the computed shape of this  $a_1$  orbital.

The directional character of this orbital is, of course, a result of hybridization, a mixing in of  $(n+1)s$  and  $(n+1)p$  into the  $nd$  orbital. Such hybridization, with consequent enhancement of overlap along certain spatial directions, will be a central feature of the significant orbitals of all our fragments, and so we pause to analyze it in detail here.<sup>14,15</sup>

Hybridization of orbitals is normally a valence-bond concept, a step in the preparation of the best orbitals for electron pair bonding. It is not explicitly present in molecular orbital methods, though it can be introduced *ex post facto* by studying orbital populations. How then does it come into our molecular orbital scheme? We can provide two equivalent rationalizations for this phenomenon.

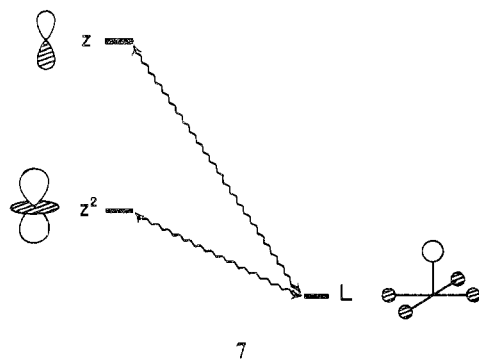
First we note that the reduction in symmetry from  $O_h$  to  $C_{4v}$  allows the mixing into the  $z^2$  orbital,  $a_1$  in  $C_{4v}$ , of other  $a_1$  symmetry orbitals, namely, metal  $s$  and  $z$ . In the octahedral symmetry these could not mix ( $z^2$  being part of  $e_g$ , while metal  $s$  was  $a_{1g}$  and  $p$  part of  $t_{1u}$ ). Since  $s$  and  $z$  are at higher energy than the  $z^2-\lambda L$  combination **4**, these higher orbitals will be

mixed in in a bonding way. The  $z^2-\lambda L$  orbital is strongly metal-apical ligand antibonding and weakly metal-basal ligands antibonding. The important mixing is that of metal



$z$ , for that allows bonding to increase, more precisely antibonding to decrease, by mixing in with the phase relationship shown in 5. The wave function is shaped by hybridization with  $s$  and  $z$  so as to reduce the electron density in the direction of the remaining apical ligand and increase the spatial extension of the orbital away from the five ligands and toward the missing ligand site. With acceptor substituents such as carbonyls, a second beneficial consequence of mixing in  $z$  is that it allows some metal-basal ligand  $\pi$  bonding. This is clearly seen in Figure 1. For  $\text{Mn}(\text{CO})_5$  the calculated composition of the  $a_1$  orbital is as follows:  $z^2$ , 21%;  $z$ , 18%;  $s$ , 4%; apical CO, 1%; all basal CO's, 56%.

A second, more formal, way to rationalize the hybridization mode is to return to the basic metal-ligand interaction diagram, simplified for  $a_1$  orbitals in 7, and to inquire how metal  $z$  (or



$s$ ) can mix into  $z^2$ . In the formal scheme of setting up the interaction between two systems, metal-ligand mixing takes place in first order, but the intermixing of metal orbitals, intrafragment polarization or hybridization, will occur only in second order.<sup>19</sup> The sign of mixing of  $z$  into  $z^2$  will be determined by a matrix element,  $A$ . The interaction overlaps

$$A = \frac{\langle z^2 | L \rangle \langle L | z \rangle}{(E_{z^2} - E_L)(E_L - E_z)}$$

can be chosen positive, as they are in 7, making the numerator in  $A$  positive. The sign of  $A$  is then determined by the energy denominator. From the level ordering  $E_L < E_{z^2} < E_z$  the sign of  $A$  is negative, and  $z$ , with the phase as defined in 7, mixes into  $z^2$  with a minus sign. The result, as before, is hybridization away from the remaining apical ligand.

Having the energy and shape of the significant molecular orbitals of a flat square pyramid  $\text{ML}_5$  in hand, we can ask the question of what sixth ligand it will seek out. In this case the answer is trivial. For a  $d^6$  case, where the LUMO is the  $a_1$  orbital whose composition we have been studying, clearly any  $\sigma$  donor, any base, will do. Such a filled  $\sigma$  orbital will interact nicely with the  $\text{ML}_5$  fragment acceptor orbital to form a  $\sigma$  bond, restoring the octahedral coordination. At this point nothing much has been learned. But if we allow the  $C_{4v}$  fragment its natural degree of freedom, variation of pyramidalness, we will be able to reach some more interesting conclusions.

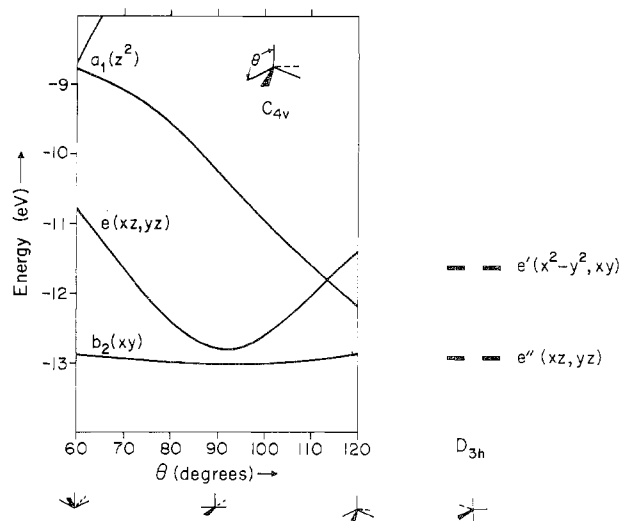


Figure 2. Energy levels of a square pyramid  $\text{M}(\text{CO})_5$  as a function of  $\theta$ . At right are the orbitals of the trigonal bipyramid on the same energy scale. The orbital labels include the d orbital which contributes most, which is not to imply that these orbitals are entirely localized on the metal. The orbital coming in at the upper left in the figure is another e level.

### Pentacoordinate Fragments: Square Pyramid and Trigonal Bipyramid

In our more general study of  $\text{ML}_5$  systems we have explored a square-pyramidal  $C_{4v}$  geometry, 8, allowing the  $L_{\text{apical}}-\text{M}-L_{\text{basal}}$  angle  $\theta$  to vary between 60 and 120°, as well as a trigonal bipyramid, 9.

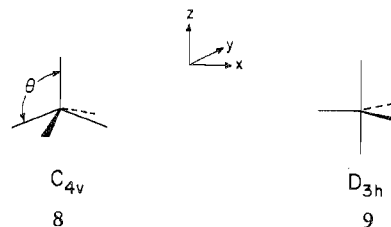
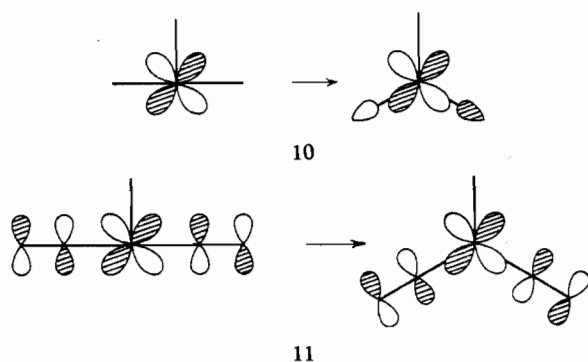


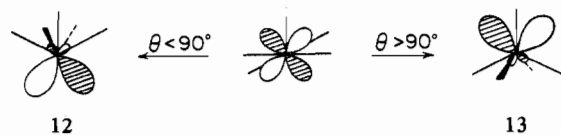
Figure 2 shows the computed energies for 8 as a function of  $\theta$  and for 9, for the four valence orbitals which have a heavy-metal d contribution. The fifth level, mainly  $x^2 - y^2$  in  $C_{4v}$ ,  $z^2$  in  $D_{3h}$ , is so metal-ligand antibonding that it is off-scale in both geometries. The level ordering in square-pyramidal and trigonal-bipyramidal environments is well known.<sup>20,21</sup> We will, however, discuss the variation with angle of the  $C_{4v}$  levels, since the slopes of the individual levels have important chemical consequences.

The lowest d level is  $b_2$ , metal  $xy$  mixed with  $\pi^*$  orbitals of the basal carbonyls. This level is essentially insensitive to the pyramidalness of the molecule. At  $\theta = 90^\circ$ , the next set of orbitals, the degenerate e level, is nearly degenerate with the  $b_2$  level. The direction of the splitting of the octahedral  $t_{2g}$  set, namely  $b_2$  below e, is understandable when one considers that the e set has lost some  $\pi$ -bonding interaction with  $\pi^*\text{CO}$  relative to the octahedral  $\text{M}(\text{CO})_6$ , while the  $b_2$  level retains its maximal  $\pi$  bonding. It must be noted, however, that the relative order of the  $b_2$  and e levels is sensitive to the  $\pi$ -acceptor strength of the ligands.<sup>22</sup>

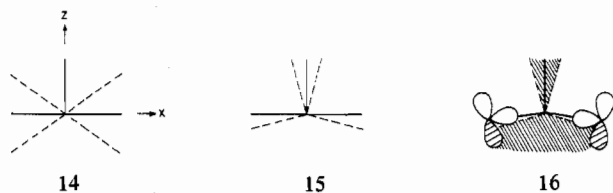
The e set rises steadily in energy as  $\theta$  decreases or increases from  $90^\circ$ . The primary reason for this is the increasing mixing, in an antibonding manner, with basal ligand  $\sigma$  orbitals.<sup>20u</sup> This is shown schematically in 10. A second reason for the rise in energy of the e set is the loss of interaction with  $\pi^*\text{CO}$ , as indicated in 11.



Not only is the  $e$  set destabilized as  $\theta$  departs from  $90^\circ$  but also the orbitals become more and more hybridized, by mixing in  $x$  and  $y$  character. The mechanism of the hybridization is the same as that explicated in detail for the  $z^2$  orbital— $x$  or  $y$  mixes in to minimize the metal  $xz$  or  $yz$ -ligand antibonding character. The hybrids point away from the basal ligands, with a corollary difference in their directionality for  $\theta$  greater or less than  $90^\circ$ . This is shown in **12** and **13** for the  $xz$  component.

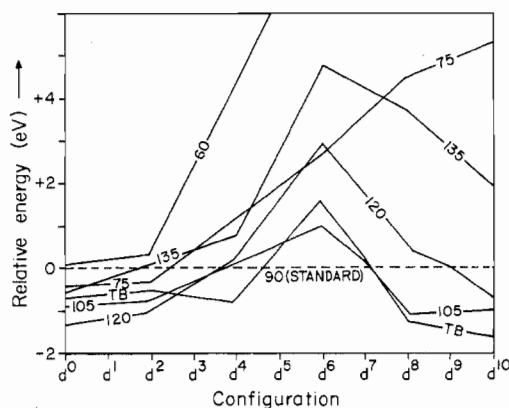


We have discussed the shaping of the  $z^2$  orbital above. Its uniform decrease in energy with increasing  $\theta$  is due to several factors. First there is the shift in metal nodal surfaces caused by hybridization. If we take a cross section of a pure  $z^2$  orbital in the  $xz$  plane, we see nodal lines as shown in **14**. Admixture of metal  $p$  shifts the nodal lines to something like **15**. Now the  $a_1$  orbital is metal-ligand  $\sigma$  antibonding and  $\pi$  bonding. Both interactions can be improved by moving the ligands to  $\theta > 90^\circ$ , toward the nodal surfaces of the  $a_1$  orbital. This is shown in **16**. Motion in the other direction,  $\theta < 90^\circ$ , will increase  $\sigma$  antibonding and decrease  $\pi$  bonding. A second



factor which contributes to the uniform slope of  $a_1$  is ligand-ligand interaction. Examination of **4** shows that the phase relationship of the  $a_1$  orbital, set by  $z^2$ -ligand antibonding, is such that the basal ligand  $\sigma$ -donor orbitals are out of phase with the donor orbital of the apical ligand. An increase in  $\theta$ , which increases the basal ligand-apical ligand separation, will thus lower the energy of the system. This effect was probed computationally by a calculation with model ligands which lacked  $\pi$  orbitals.<sup>21</sup>

Having rationalized the individual level slopes in Figure 2, we can immediately proceed to the specific geometrical conclusions implicit in the figure concerning  $C_{4v}$ , square-pyramidal, complexes: (a) low-spin  $d^6$  complexes will prefer a square pyramid with  $\theta$  near  $90^\circ$ , metal atom in the basal plane; (b) low-spin  $d^8$  and any high-spin systems with less electrons, in which the  $a_1$  orbital is occupied, will favor a pyramid with  $\theta > 90^\circ$ ; (c) no simple  $ML_5$  molecule will have  $\theta < 90^\circ$ ; (d) a hypothetical low-spin  $d^4$  complex should have a double-minimum potential along the  $\theta$  coordinate. The proper consideration of preferred  $ML_5$  geometries must include the trigonal bipyramid. However, there is one important class of molecules in which the  $C_{4v}$  constraint is imposed by a



**Figure 3.** Energies of  $C_{4v}$  and  $D_{3h}$   $M(CO)_5$  geometries for various  $d$ -electron configurations. The number in the curve is the value of  $\theta$ . TB stands for trigonal bipyramid. All energies are relative to the energy of the flat square pyramid,  $\theta = 90^\circ$ .

**Table I.** Optimum  $M(CO)_5$  Geometries

No. of $d$ elec- trons	Optimum symmetry	$\theta$ , deg	No. of $d$ elec- trons	Optimum symmetry	$\theta$ , deg
0	$C_{4v}$	120	5	$C_{4v}$	94
1	$C_{4v}$	116	6	$C_{4v}$	93
2	$C_{4v}$	116	7	$C_{4v}$	98
3	$D_{3h}$		8	$D_{3h}$	
4	$D_{3h}$		9	$D_{3h}$	
			10	$D_{3h}$	

tetradentate ligand. These are the porphyrins.

It is known from crystallographic studies that in (six-coordinate) oxyhemoglobin the iron atom is in the plane of the porphyrin ring but that in the five-coordinate deoxyhemoglobin the metal atom is moved out of the basal ligand plane by some  $0.8 \text{ \AA}$ .<sup>23,24</sup> Accompanying this geometrical and coordination change is a transformation from a low-spin to a high-spin complex. The motion of the iron atom is believed to play an essential role in the cooperativity of oxygen uptake of hemoglobin.<sup>23b,25</sup>

A variety of structures of simple porphyrins determined by Hoard and coworkers confirms the general hypothesis that low-spin  $d^6$  complexes will have the metal atom in plane but that in high- or intermediate-spin  $d^6$  complexes the metal atom will move out of the basal plane.<sup>24,26,27</sup> The effect was explained in terms of the increased ionic radius of the metal atom in the high-spin case where  $z^2$  and/or  $x^2 - y^2$  orbitals, metal-ligand antibonding, would be occupied.<sup>24,27</sup>

It is clear that our analysis, derived from the level trends of Figure 2 and summarized in conclusions (a) and (b) above, is equivalent to the Hoard explanation. A specific calculation was carried out on a model  $Fe(NH_3)_5^{2+}$  system to probe the quantitative implications of our scheme. The low-spin system had an energy minimum at  $\theta = 90^\circ$ . A high-spin system, the configuration  $(xy)^2(xz)^1(yz)^1(z^2)^1(x^2 - y^2)^1$ , had its energy minimum at  $\theta = 112^\circ$ , which corresponded to the Fe atom  $0.77 \text{ \AA}$  out of the plane.

Let us now return to the basic problem of the relative stability of various conformations of the  $ML_5$  fragment, comparing square pyramids of varying  $\theta$  with the trigonal bipyramid. We may defer for a moment the problem of interconversion of the  $D_{3h}$  and  $C_{4v}$  geometries. Figure 3 shows relative total energies of low-spin  $M(CO)_5$  complexes, as a function of electron configuration, for certain values of  $\theta$ . The variation with  $\theta$  was studied in detail, and the optimum geometries for each low-spin  $d$ -electron configuration are given in Table I. There are several points to be noted concerning Figure 3 and Table I. In the  $d^9$  and  $d^{10}$  complexes carbonyl  $\pi^*$  orbitals are occupied. Such complexes are unlikely to be

stable, which is not to deny the existence of perfectly reasonable  $d^{10}$  pentacoordinate molecules, such as  $\text{CdCl}_5^{3-}$ ,  $\text{InCl}_5^{2-}$ ,  $\text{AsF}_5$ , or  $\text{Sb}(\text{C}_6\text{H}_5)_5$ . In such molecules the highest filled molecular orbital is the fifth member of the  $d$  set, the low-lying carbonyl  $\pi^*$  levels being absent. The calculations indicate that the trigonal bipyramid is the most stable geometry for  $d^8$ , in accord with the equilibrium structure of  $\text{Fe}(\text{CO})_5$ .<sup>28</sup> However, the square-pyramidal geometry with  $\theta = 105^\circ$  is not far above in energy, which is consistent with the known stereochemical nonrigidity of iron pentacarbonyl.<sup>29</sup>  $\text{Mn}(\text{CO})_5^-$  is also a trigonal bipyramid in the solid state.<sup>30</sup> Strictly speaking, we should limit our comparison with experiment to carbonyl structures. However, the general scheme, if not the details, of the conformational preferences should carry over to other  $\text{ML}_5$  species. Two pentaamideniobium structures, formally  $d^0$ , are known, both square pyramids.  $\text{ML}_5$  complexes with one to five  $d$  electrons are rare, and those that are known ( $\text{MnCl}_5^{2-}$ ,  $\text{Fe}(\text{N}_3)_5^{2-}$ )<sup>32</sup> are high-spin species, not providing a test of our conclusions. There have been two recent reports of the matrix synthesis of  $\text{V}(\text{CO})_5$ , with somewhat conflicting structural conclusions.<sup>33</sup>

The  $d^8$  configuration is of some interest. Our calculations predict a flat square pyramid,  $\theta \approx 93^\circ$ , as the most stable geometry. There is a large body of spectroscopic evidence for matrix-isolated  $\text{M}(\text{CO})_5$ ,  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ .<sup>12a,c</sup> Most of the evidence has been interpreted in terms of the  $\text{C}_{4v}$  structure,<sup>34</sup> and recent work has assigned a geometry with  $\theta = 93^\circ$  to  $\text{Cr}(\text{CO})_5$ .<sup>35</sup> It is not inconceivable that an intermediate-spin, triplet trigonal bipyramid could come below a singlet square pyramid.

A crystal structure of the  $d^7$  complex,  $\text{Co}(\text{CN})_5^{3-}$ , has recently been reported,<sup>36</sup> yielding an average  $\theta$  value of  $97.5^\circ$ , which is in excellent agreement with our calculated result for  $\text{M}(\text{CO})_5$ . Previous esr studies clearly established a  $\text{C}_{4v}$  structure for  $\text{Co}(\text{CN})_5^{3-}$ , with the unpaired electron in an  $a_1$  orbital.<sup>37</sup> Indication of the matrix synthesis of another  $d^7$  system, monomeric  $\text{Mn}(\text{CO})_5$ , has also been given, along with an assignment of a  $\text{C}_{4v}$  structure.<sup>38</sup> The esr spectrum of this molecule has also been observed.<sup>39</sup>

Crystal structures of several noncarbonyl  $d^8$  complexes are known:  $\text{Ni}(\text{CN})_5^{3-}$ ,<sup>40a</sup>  $\text{Co}(\text{CNCH}_3)_5^+$ ,<sup>40b</sup>  $\text{Ni}(2,8,9\text{-trioxal-1-phosphaadamantane})_5^{2+}$ ,<sup>40c</sup>  $\text{Pt}(\text{SnCl}_3)_5^{3-}$ .<sup>40d</sup> The  $\text{Ni}(\text{CN})_5^{3-}$  structure has two nonequivalent anions in the unit cell, one a square pyramid and the other intermediate in geometry between a square pyramid and a trigonal bipyramid.

This returns us to the question of stereochemical nonrigidity. Nearly all  $\text{ML}_5$  molecules that have been studied (mostly  $d^0$  and  $d^8$ - $d^{10}$ ) show low barriers, less than 10 kcal/mol, to intramolecular dynamic processes interchanging axial and equatorial (or apical and basal) sites. It is likely that the physical process which accomplishes the site interchange is the Berry pseudorotation.<sup>41</sup> A recent study has most graphically traced the pseudorotation itinerary in the very structures themselves.<sup>42</sup> One reason for the stereochemical mobility of these systems is that the Berry pseudorotation is a symmetry-allowed process.<sup>43</sup> That this is true for all low-spin  $d$ -electron configurations except  $d^3$ - $d^5$  is easily demonstrated by the construction of a level-correlation diagram.<sup>21,44</sup> The similar energy of the  $\text{C}_{4v}$  structure with  $\theta = 105^\circ$  and the trigonal bipyramid (Figure 3), for all  $d$ -electron configurations, testifies to the small geometrical difference between these geometries.

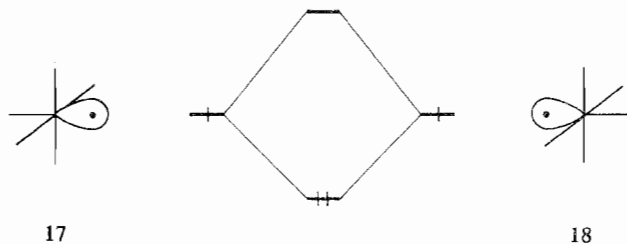
The reader will have noticed that our geometrical conclusions are reached without first-<sup>45</sup> or second-order<sup>46-48</sup> Jahn-Teller considerations. This does not mean that we think such procedures are inapplicable to these problems. The utility of first- and second-order Jahn-Teller arguments has been demonstrated. However, our brute-force approach of con-

sidering all higher symmetry deformations is bound to lead to the same results as a direct Jahn-Teller argument. A prerequisite for application of Jahn-Teller considerations is the knowledge of the level ordering of a complex. We find that the details of the level ordering carry information concerning not only geometrical trends but also the reactivity of the molecule, and it is for this reason we concentrate on the orbital approach.

The conclusions one would reach on the basis of Jahn-Teller arguments do match the orbital-based results.  $d^2$  has a sizable gap between filled and unfilled levels only for a highly pyramidal  $\text{C}_{4v}$  geometry, and this is indeed the optimum conformation calculated.<sup>49</sup>  $d^4$  is closed shell for the trigonal bipyramid but open shell for the square pyramid. The reverse is true for  $d^6$  but only when  $\theta$  is near  $90^\circ$ .  $d^6$  will thus favor a flat square pyramid.  $d^8$  systems are closed shell in both conformations, with sizable energy gaps to unfilled levels. They should be relatively stable to deformation, but the level-correlation diagram for the system<sup>21,44</sup> shows the interconversion to be an allowed process.

We turn to the second aspect of the fragment analysis—the utilization of the fragment orbitals in compound formation. The  $d^6$  case, with the  $a_1$  LUMO prepared to interact with any donor orbital, has been discussed in the previous section.

A  $d^7$   $\text{C}_{4v}$  fragment would have one electron in an  $a_1$  orbital. Previously mentioned observations on  $\text{Co}(\text{CN})_5^{3-}$  and  $\text{Mn}(\text{CO})_5$  confirm this.<sup>37-39</sup> Such a species is much like an organic radical, like a methyl group. It carries its odd electron in a relatively high-lying, directional orbital of  $\sigma$  symmetry. The molecule is beautifully prepared for one typical radical reaction, dimerization, as shown by<sup>50a</sup>



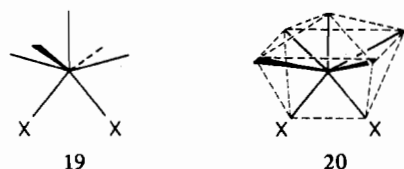
The dimer is the familiar  $\text{Mn}_2(\text{CO})_{10}$ <sup>50b</sup> or the more recently established  $\text{Co}_2(\text{CN})_{10}^{6-}$ .<sup>50c</sup> The first intense electronic transition in  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$  has been unambiguously assigned as just the  $\sigma \rightarrow \sigma^*$  excitation to be expected from the above picture.<sup>50d</sup>

Radical-type reactions of  $\text{Co}(\text{CN})_5^{3-}$  other than dimerization are well known.<sup>51</sup> We should also mention here the important recent theoretical study of the approach of  $\text{RX}$  to  $\text{Co}(\text{CN})_5^{3-}$ .<sup>52</sup>

A square-pyramidal  $\text{ML}_5$  system with five  $d$  electrons would have a low-spin configuration  $(b_2)^2(e)^3$  for  $\theta < 110^\circ$ . The matrix isolation of  $\text{V}(\text{CO})_5$  has recently been reported.<sup>33</sup> A closed-shell configuration with a sizable energy gap between filled and unfilled orbitals could be achieved if an extra electron were put into the  $e$  orbital and the energy of the  $a_1$  orbital were raised. Three electron donors with orbitals of the proper symmetry to interact with the  $a_1$  and  $e$  levels would accomplish this goal.  $\text{V}(\text{CO})_6^-$  and  $\text{V}(\text{CO})_5\text{NO}^{33a}$  and the recently synthesized  $\text{V}(\text{CO})_5(\pi\text{-allyl})$ <sup>53b</sup> are examples of this bonding mode.

An interesting general question is whether unstable conformations of an isolated fragment, such as the "umbrella" geometry, square pyramid with  $\theta < 90^\circ$ , could be stabilized by coordination with certain ligands. For  $\theta < 90^\circ$  both the  $a_1$  and the  $e$  orbitals are hybridized in such a way that they point away from the five ligands. This was shown in **6** and **12**. A pair of donors, for instance halogens, introduced in a geometry such as **19**, would interact with  $a_1$  and one component of the  $e$  orbital, say,  $e_x$ . Low-spin  $d^2$  or  $d^4$  systems become

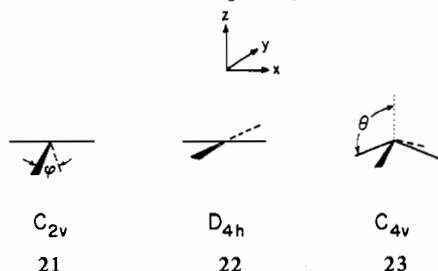
possible. The barrier to rotation of the two X ligands should



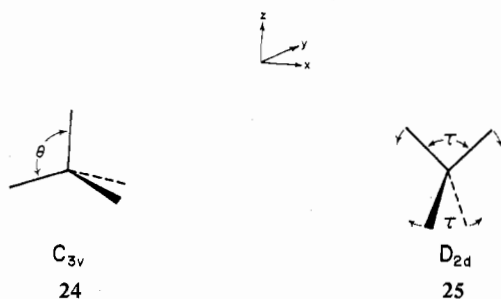
be small, because of the cylindrical symmetry of the e orbitals. If the two extra ligands rotate by  $45^\circ$  from **19**, the resulting seven-coordinate structure can be described as a capped trigonal prism, **20**. A possible  $d^4$  example of this type of coordination may be found in the structures of  $\text{Mo}(\text{CNR})_6\text{I}^+$  and  $\text{Mo}(\text{CNR})_7^{2+}$ ,  $\text{R} = \text{tert-butyl}$ .<sup>54a</sup> These are capped trigonal prisms, with a typical  $\text{IMoC}$  angle in the  $\text{Mo}(\text{CNR})_4\text{I}$  fragment of the former, analogous to our  $\theta$ , of  $82^\circ$ . Related compounds  $\text{MoL}_5\text{X}_2$ ,  $\text{L} = \text{isocyanide}$ ,  $\text{X} = \text{Cl, Br}$ , in which the fragmentation into  $\text{MoL}_5$  and  $\text{X}_2$  is more natural, have been synthesized.<sup>54b</sup> Still other seven-coordinate molecules for which a capped trigonal-prism structure is inferred include the  $d^3$   $\text{Mo}(\text{CN})_7^{4-}$  in the solid phase of  $\text{K}_4\text{Mo}(\text{CN})_7 \cdot 2\text{H}_2\text{O}$ <sup>54c</sup> and the  $d^1$   $\text{Ti}(\text{CN})_7^{4-}$  in  $\text{K}_4\text{Ti}(\text{CN})_7 \cdot \text{KCN}$ .<sup>54d</sup>

#### Tetracoordinate Fragments

By removing two ligands cis or trans from an octahedral  $\text{ML}_6$ , we attain the fragment geometries **21**,  $C_{2v}$ , and **22**,  $D_{4h}$ . First these are related by opening up one angle,  $\varphi$ , from  $90^\circ$  in **21** to  $180^\circ$  in **22**. The square-planar structure can be



distorted to a  $C_{4v}$  square-pyramidal one, **23**. To maintain a relationship with the  $C_{4v}$   $\text{M}(\text{CO})_5$  structure, we measure the pyramidalicity of **23** by the angle  $\theta$  made between a basal ligand and the  $+z$  direction. From Scheme I it is seen that another family of  $\text{ML}_4$  structures, those maintaining a threefold axis, is derived from the trigonal bipyramid by removing an axial ligand. We studied that family of  $C_{3v}$  structures, varying the angle  $\theta$  as defined in **24**. Of course, for  $\theta \approx 109.5^\circ$ , a tet-



rahedral geometry is attained. The tetrahedron can be related to the square-planar geometry by a squashing motion which maintains  $D_{2d}$  symmetry.<sup>42,44</sup> This motion may be measured by the angle  $\tau$  in **25**.

There is no single consistent coordinate axes choice which will serve for all of these geometries. The conventions next to **22** and **24** were the ones used by us and should be noted for further reference. Figure 4 reminds us of the well-known orbitals of one pivotal tetracoordinate geometry, the  $D_{4h}$  square-planar  $\text{M}(\text{CO})_4$ .<sup>55</sup> The energy and composition of the orbitals of the other fragment of an octahedron,  $C_{2v}$  **21**, may be understood by following the distortion from the square-

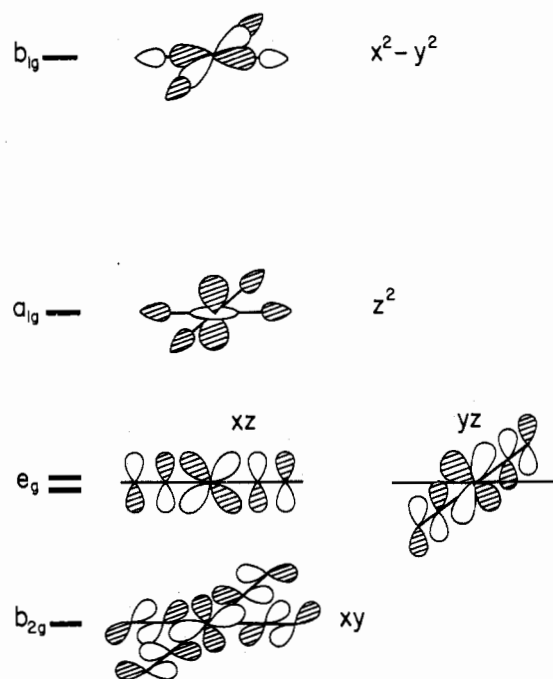


Figure 4. Schematic representation of the d-type valence orbitals of a  $D_{4h}$  square-planar  $\text{M}(\text{CO})_4$ . The vertical energy scale is not realistic—in particular the  $b_{1g}$  orbital is at very high energy relative to the other levels.

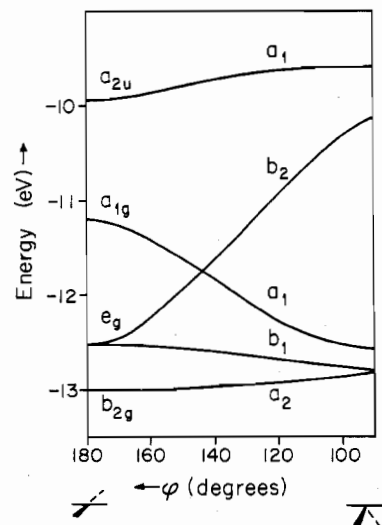
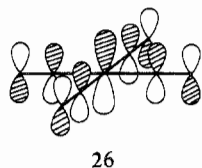


Figure 5. Energy levels of a  $C_{2v}$   $\text{M}(\text{CO})_4$  fragment as a function of  $\varphi$ . The  $D_{4h}$  symmetry labels given at left apply only to the point for  $\varphi = 180^\circ$ .

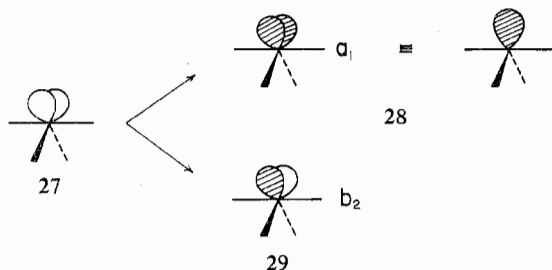
planar geometry. One LML angle, L trans to L, is changed from  $180$  to  $90^\circ$ , while the other trans angle remains at  $180^\circ$ . Figure 5 shows the computed variation of the energy of the four lower d orbitals as this variation in  $\varphi$  takes place. Reference to our discussion of the variation of the  $C_{4v}$   $\text{ML}_5$  geometries with  $\theta$ , Figure 2, shows a number of analogies. The lowest orbital in Figure 5,  $b_{2g}$  in  $D_{4h}$ ,  $a_2$  in  $C_{2v}$ , a mixture of metal  $xy$  and  $\pi^*\text{CO}$ , is virtually unaffected by the distortion. One component of the  $D_{4h}$  degenerate  $e_g$  set, the one which contains metal  $yz$ , rises in energy with decreasing  $\varphi$ , just as did both e components in Figure 2, and for the same reason, namely, the increasing role of  $\sigma$  antibonding. The second  $e_g$  component, containing metal  $xz$ , is essentially unaffected by the ligand motion in the  $yz$  plane. The  $a_1$  orbital, primarily  $z^2$  in  $D_{4h}$ , loses some of its  $\sigma$  antibonding and gains some bonding with carbonyl  $\pi^*$ , just as in the square pyramid. In the lower  $C_{2v}$  symmetry it also is able to mix in some metal  $x^2 - y^2$ .

There is one other crucial feature of this figure. The highest energy level in the diagram is an interesting  $a_1$  orbital. In the square-planar extreme it correlates to  $a_{2u}$  symmetry, which is an in-phase mixture of metal  $z$  (24%) and carbonyl  $\pi^*$  orbitals, **26**. This level did not appear in our schematic



description of orbitals of  $D_{4h}$  ML<sub>4</sub>, Figure 4, for that figure was restricted to those orbitals that carry significant metal d character. Yet in our calculation **26** definitely is the first orbital above the lower four d levels.<sup>56</sup> As the distortion to  $C_{2v}$  fragment proceeds, the  $a_1$  orbital, which was **26**, acquires more and more metal character, becoming a mixture of 9%  $s$  + 22%  $z$  + 3%  $x^2 - y^2$  + 12%  $z^2$  + 54% carbonyl  $\sigma$  and  $\pi$ . Its composition, in terms of metal vs. ligand character, is not that different from the  $b_2$  orbital which rises to meet it:  $a_1$  is 46% metal;  $b_2$  51% metal in our calculations.

The reason for our concern with this  $a_1$  orbital will become apparent when we consider the  $C_{2v}$  ML<sub>4</sub> fragment specifically as  $\text{Cr}(\text{CO})_4$ , derived from the stable octahedral  $d^6$  hexacarbonyl. Just as in our discussion of  $\text{M}(\text{CO})_5$ , we would expect a  $d^6$   $\text{Cr}(\text{CO})_4$  in the geometry of an octahedron minus two cis ligands, **21**, to possess two low-lying acceptor orbitals, pointed toward the missing ligand sites. Such a set of two orbitals, shown in **27**, would be equivalent to a symmetry-adapted set of  $a_1 + b_2$ , **28** and **29**. If we glance at the



right-hand side of Figure 5, we see a cluster of three low-lying orbitals. These are filled in the  $d^6$   $\text{Cr}(\text{CO})_4$ . The orbitals to be identified with **28** and **29** are indeed in the diagram—they are the high-lying  $b_2$  and  $a_1$ . So we need this  $a_1$  orbital, which in  $D_{4h}$  was mainly carbonyl  $\pi^*$ , to give us the required acceptor orbital set.

Structures **28** and **29** are more than symbols for the acceptor orbitals of an ML<sub>4</sub> fragment. Figure 6 shows a contour plot of the high-lying  $a_1$  and  $b_2$  orbitals of **21** ( $\varphi = 90^\circ$ ). They indeed show the directional character imputed to them and required for good overlap with a pair of donors which would reconstruct the octahedron.

The next distortion we study is from the square-planar geometry **22** to a square-pyramidal,  $C_{4v}$ , fragment. The angular parameter  $\theta$ , which measures this deformation, is defined in **23**. Figure 7 shows the computed level energies. The relationship of this figure to the square-pyramidal pentacoordinate fragment is very close. The deformation parameter  $\theta$  is defined in the same way for ML<sub>4</sub> and ML<sub>5</sub>. Every point on the ML<sub>4</sub>  $C_{4v}$  surface of Figure 7 can be related to a corresponding point on the ML<sub>5</sub>  $C_{4v}$  surface, Figure 2, by the addition of an axial ligand. Obviously the ML<sub>4</sub> level diagram is symmetric around  $\theta = 90^\circ$ , the redundant half being put in to show up better the asymmetries of the ML<sub>5</sub> levels. The level slopes and their rationalization are identical for the ML<sub>4</sub> and ML<sub>5</sub> cases. Note the insensitive  $b_2$  orbital, the  $e$  set destabilized with increasing pyramidity, and the  $a_1$  orbital,

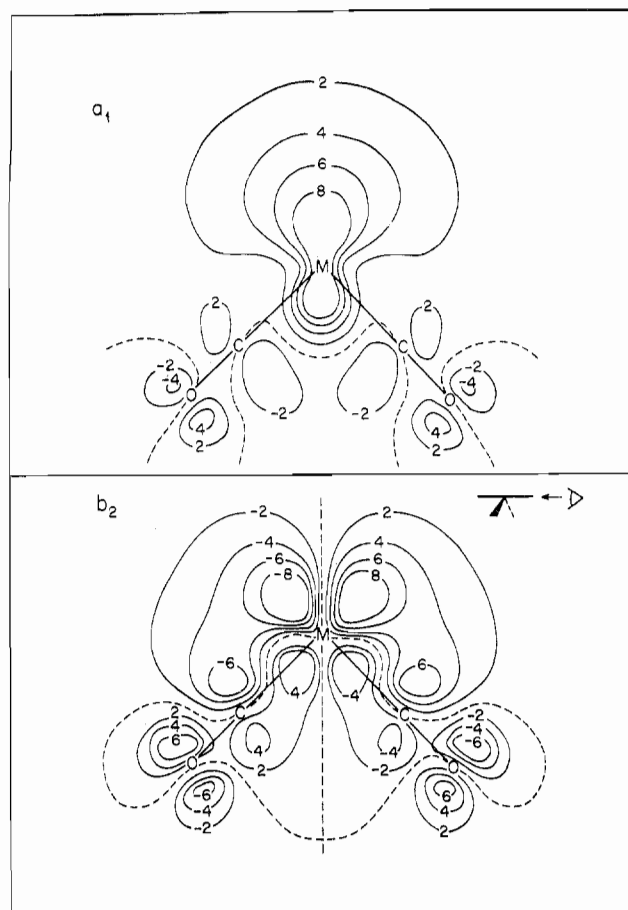


Figure 6. High-lying  $a_1$  and  $b_2$  orbitals of a  $C_{2v}$   $\text{M}(\text{CO})_4$  fragment. Contours are of  $\psi$ , to be multiplied by  $10^{-2}$ . The dashed line represents a node. The scale of the drawing is set by the M-C distance of 1.80 Å.

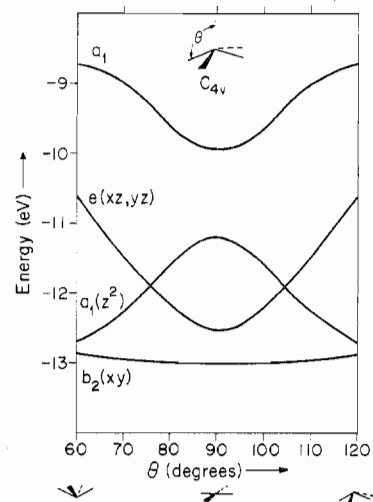
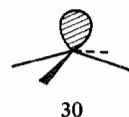


Figure 7. Energy levels of a square pyramid  $\text{M}(\text{CO})_4$  fragment as a function of  $\theta$ .

mainly  $z^2$ , decreasing in energy as  $\theta$  departs from  $90^\circ$ .

A novel, but not unexpected, feature of the ML<sub>4</sub> diagram, relative to the ML<sub>5</sub> one, is the appearance of a low-lying directional hybrid. This higher  $a_1$  orbital is descended from **26**. At  $\theta = 105^\circ$  it is 54% on the metal and looks like **30**. We



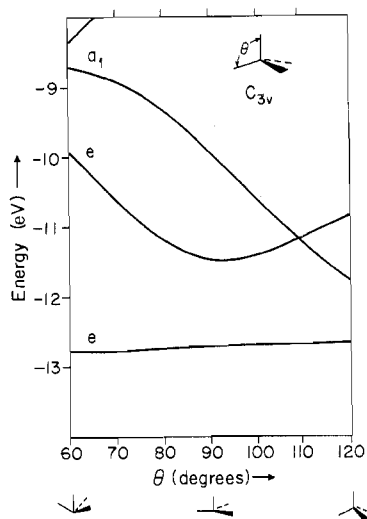
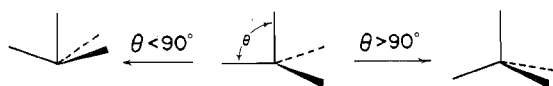


Figure 8. Energy levels of an  $M(CO)_4$  fragment of  $C_{3v}$  symmetry as a function of  $\theta$ .

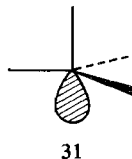
will return to an analysis of the role of these fragment orbitals below.

The next geometrical deformation studied was that of  $C_{3v}$  structures



The level diagram is shown in Figure 8. Once again there are obvious analogies to the  $C_{4v}$   $ML_5$  diagram, Figure 2. In the present case there is a degenerate pair of low-lying levels, insensitive to pyramidalization. The metal contribution in these levels, at  $\theta = 90^\circ$ , a trigonal bipyramid minus one axial ligand, is almost exclusively  $xz$  and  $yz$ . These orbitals are clearly related to the  $e''$  orbitals of the  $D_{3h}$  parent. As  $\theta$  changes from  $90^\circ$ , the  $e$  set acquires more and more metal  $xy$  and  $x^2 - y^2$  character. For instance at the tetrahedral point,  $\theta = 109.5^\circ$ , the  $e$  set is 41%  $xz$ , 21%  $xy$ .

At somewhat higher energy lies another  $e$  orbital. This one is descended from the trigonal-bipyramidal  $e'$  set and at  $\theta = 90^\circ$  contains primarily  $xy$  and  $x^2 - y^2$  at the metal. Just like the square pyramid  $ML_5$   $e$  level, the higher  $e$  in Figure 8 is destabilized as  $\theta$  departs in either direction from  $\sim 90^\circ$ . The highest d-type level at  $\theta = 90^\circ$  is an  $a_1$ . It is beautifully hybridized to point toward the missing ligand, as in **31**. Again



entirely analogous to the trend of the  $a_1$  orbital in the octahedral fragment  $ML_5$ , the  $a_1$  orbital in Figure 8 is stabilized as  $\theta$  increases from  $90^\circ$ , destabilized as  $\theta$  decreases.

The crossing of the  $a_1$  and the upper  $e$  level in Figure 8 does not take place at some arbitrary  $\theta$ , but of course precisely at the  $\theta$  corresponding to the tetrahedral geometry.  $a_1$  and  $e$  become  $t_2$  in  $T_d$ . It should be noted that whereas we get, as we must, the typical tetrahedral d level splitting of  $e$  below  $t_2$ , we do not have the makeup  $e(z^2, x^2 - y^2)$  and  $t_2(xz, yz, xy)$  because our coordinate axes choice differs from that conventionally used for a tetrahedral ligand field.

A further feature of the set of  $C_{3v}$  geometries is that for all reasonable values of  $\theta$  there are no especially low-lying unfilled orbitals above the five illustrated in Figure 8.

The next one-dimensional slice of the  $M(CO)_4$  surface deals with the interconversion of the square-planar and tetrahedral

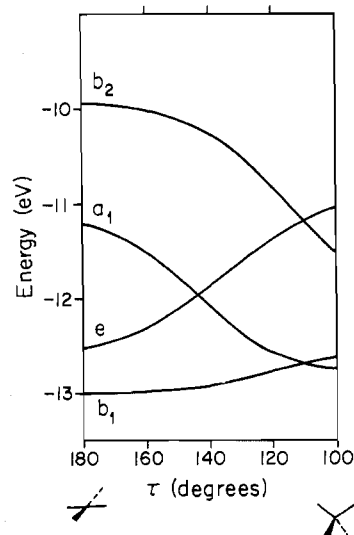
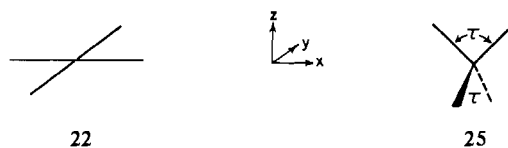


Figure 9. Energy levels of an  $M(CO)_4$  fragment of  $D_{2d}$  symmetry as a function of  $\tau$ , defined in **25**.

geometries **22** and **25**, by a squashing motion which maintains  $D_{2d}$  symmetry. Note that the orientation of the axis system, which is consistent with the square-planar coordination case



studied earlier, leads to an axis orientation for the tetrahedron which is standard but inconsistent with the natural coordinate system for the  $C_{3v}$  surface we just finished analyzing.

Figure 9 shows the computed variation of the level energies with the distortion angle  $\tau$ . From the square-planar side the levels behave in a manner similar to all the cases analyzed above—the  $xy$ - $b_1$  level is unaffected by the motion, the  $(xz, yz)$ - $e$  set rises in energy, the  $z^2$ - $a_1$  orbital falls. From the tetrahedral crossing point at  $\tau \approx 109.5^\circ$  the  $t_2$  level splits into  $b_2 + e$ .  $b_2$ , which is  $x^2 - y^2$ , rises in energy as  $\tau$  is increased, since more and more  $\sigma$  antibonding is encountered. The lower tetrahedral level,  $e$ , splits into  $b_1 + a_1$ .  $a_1$ , which is  $z^2$ , rises in energy with increasing  $\tau$ , as it encounters more  $\sigma$ -antibonding overlap and loses its excellent  $\pi$  bonding. At  $\tau$  equal to the tetrahedral angle the ligands lie precisely in the nodal surfaces of the  $z^2$  orbital.

Figure 9 shows at a glance a pervasive feature of  $d^8$ - $d^{10}$  energy surfaces:  $d^{10}$  will prefer a tetrahedron, while  $d^8$  will be fairly balanced between square-planar and tetrahedral extremes. Of course, on the tetrahedral side a high-spin situation is created for  $d^8$ . We will return to this subject below. We should also note that the essential features of this particular slice of the  $ML_4$  surface have been given earlier by Eaton,<sup>44</sup> in a pioneering study of tetrahalides by Lohr and Lipscomb,<sup>57a</sup> and in an examination of the spectra of  $Ni(CN)_4^{2-}$  by Ballhausen and coworkers.<sup>57b</sup>

Several important slices through the many-dimensional potential energy surface of  $M(CO)_4$  have thus been constructed. We wish to make some statements concerning the geometrical preferences of various d-electron configurations. While reasonably certain that the low energy points would be found along the one-dimensional cuts of Figures 5, 7, and 8, we did carry out a more thorough search. For the case of all MC and CO distances constant, MCO linear, the dimensionality of the total  $M(CO)_4$  surface is 5. If, furthermore, a mirror plane of symmetry is assumed, the number of degrees of freedom is reduced to 3. A full search in the three-



Table II. Optimum Geometries for  $M(\text{CO})_4$  Fragments

No. of d electrons	Optimum symmetry	Angle, <sup>a</sup> deg
0	$T_d$	
1	$T_d$ or $C_{4v}$ <sup>b</sup>	$\theta = 120$
2	$C_{4v}$	$\theta = 117.5$
3	$C_{4v}$	$\theta = 122.5$
4	$C_{4v}$	$\theta = 122.5$
5	$C_{2v}$	$\varphi = 100, \varphi' = 160$
6	$C_{2v}$	$\varphi = 95, \varphi' = 165$
7	$C_{2v}$	$\varphi = 135, \varphi' = 150$
8	$D_{2d}$	$\tau = 150$
9	$D_{2d}$	$\tau = 135$
10	$T_d$	

<sup>a</sup> The relevant angles are given:  $\varphi$  as defined in 21,  $\theta$  in 23,  $\tau$  in 25. <sup>b</sup> Two quite different geometries are very close in energy.

dimensional surface showed that, within the accuracy of the searching procedure ( $\pm 5^\circ$ ), the minima had more than one plane of symmetry, being either  $C_{2v}$ ,  $C_{4v}$ ,  $D_{2d}$ , or  $T_d$ . The tetrahedron is a unique point;  $C_{4v}$  and  $D_{2d}$  are defined by one angular parameter,  $\theta$  in 23 or  $\tau$  in 25. Our previous one-dimensional  $C_{2v}$  cut, passing from one octahedral fragment to another one, does not allow the  $C_{2v}$  fragment full freedom. The optimized structures are described by two angles,  $\varphi$  and  $\varphi'$ , as defined in



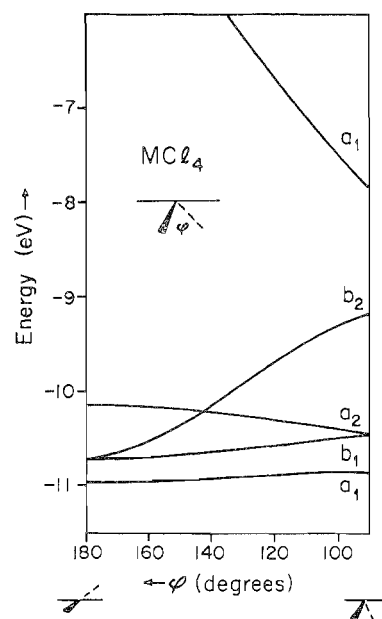
The best geometries are given in Table II. Known stable  $d^{10}$  complexes such as  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{CO})_4^-$ , and  $\text{Fe}(\text{CO})_4^{2-}$  are tetrahedral,<sup>58a</sup> which is a useful check on our calculations. Matrix-isolated  $\text{Cr}(\text{CO})_4$  and  $\text{Mo}(\text{CO})_4$  are known and have been tentatively assigned  $C_{2v}$  geometries.<sup>58b</sup> For the  $d^9$  species our calculations, as well as those of Burdett,<sup>4</sup> give a  $D_{2d}$  structure as the most stable. There is a separate local minimum of somewhat higher energy for a  $C_{3v}$  structure. Experimentally there is some controversy over the geometry of  $\text{Co}(\text{CO})_4$ , with both  $D_{2d}$  and  $C_{3v}$  structures suggested.<sup>58c,d</sup>  $\text{Fe}(\text{CO})_4^-$ ,  $\text{Mn}(\text{CO})_4^-$ , and  $\text{Cr}(\text{CO})_4^-$  have been detected in ion cyclotron resonance studies.<sup>58e</sup>

Table II indicates that the preferred geometry for a low-spin  $d^8$   $M(\text{CO})_4$  system is a  $D_{2d}$  structure with  $\tau \approx 150^\circ$ . In fact the surface is quite flat, with the  $D_{4h}$  structure,  $\tau = 180^\circ$ , lying only 5 kcal higher in energy. Matrix-isolated  $\text{Fe}(\text{CO})_4$  has been assigned a  $C_{2v}$  structure<sup>59a</sup> but is suspected of being a high-spin complex.<sup>59b</sup> Typical low-spin tetracoordinate  $d^8$  complexes are square planar:  $\text{Ni}(\text{CN})_4^{2-}$ ,  $\text{Pt}(\text{NH}_3)_4^{2+}$ ,  $\text{PtCl}_4^{2-}$ , and many others.<sup>60</sup>

Our calculations are for  $M(\text{CO})_4$  and must be viewed with caution when applied to other systems. The apparent disagreement of the calculations for the  $d^8$  case with experimental structures is a good opportunity to discuss this in detail.

First, when we do a calculation with four chlorides as ligands, instead of four carbonyls, we get a clear preference in  $d^8$  for the  $D_{4h}$  structure. The minimum energy point in the  $D_{2d}$  structure, which for  $M(\text{CO})_4$  was 0.23 eV below the  $D_{4h}$  geometry, in  $\text{MCl}_4$  is 0.86 eV above that structure. So the disagreement with experiment was only apparent, based on extrapolating the carbonyl results to other ligands.

This only raises a further question: In what way does the halide fragment case indeed differ? Figure 10 shows the energy levels of  $\text{MCl}_4$  along the same deformation coordinate as was studied for the carbonyl case in Figure 5. Note the following points. (1) The  $a_2$  orbital, lowest among the d levels for  $M(\text{CO})_4$ , is now quite high. This is of course due to the difference in  $\pi$  bonding. In  $M(\text{CO})_4$   $a_2$  is depressed by the carbonyl  $\pi^*$  orbitals, while in  $\text{MCl}_4$  it is raised by the Cl filled

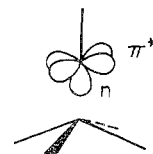
Figure 10. Energy levels of a  $C_{2v}$   $\text{MCl}_4$  fragment as a function of  $\varphi$ .

lone pairs of  $\pi$  symmetry. The  $a_2$  level remains insensitive to the distortion. (2) The behavior of the  $e_g$  set ( $b_1 + b_2$  in  $C_{2v}$ ) is much the same in  $\text{MCl}_4$  as it was in  $M(\text{CO})_4$ . (3) There is no low-lying orbital analogous to the  $a_{2u}$ , 26. The metal p has been destabilized by the chlorine donor orbitals. Instead there is another  $a_1$  orbital, the metal  $x^2 - y^2$ . Over the greater part of the level diagram it lies high in energy, so that a  $d^8$   $\text{MCl}_4$ , to nobody's surprise, should be a poorer acceptor than  $M(\text{CO})_4$ . (4) Most interesting, and important to the deformation, is the slope of the  $a_1$ ,  $z^2$  orbital. In Figure 5 it fell in energy with the deformation to  $C_{2v}$ , while in  $\text{MCl}_4$  it remains constant. To this behavior we can trace the stabilization of  $D_{4h}$  in  $\text{MCl}_4$ . The rationale for the difference may be found in the  $\pi$  bonding. In  $M(\text{CO})_4$   $a_1$  fell in energy because interaction with  $\pi^*$  increased and  $\sigma$  antibonding decreased with the deformation. In  $\text{MCl}_4$  the  $\sigma$  antibonding still decreases but the  $\pi$  effect is now in the opposite direction, being antibonding. The two effects appear to balance.<sup>61</sup> Comparison of the level positions reported by Lohr and Lipscomb for the  $T_d \rightarrow D_{2d} \rightarrow D_{4h}$  distortion of  $\text{CuCl}_4^{2-}$  with the corresponding  $M(\text{CO})_4$  surface slice computed by us (Figure 9) shows the same trend noted in point 4 above: the slope of the  $a_1$  level is very different, smaller in the donor case.<sup>57</sup>

The analysis of the above case shows the differences that may occur in  $\text{ML}_4$  when L becomes a  $\pi$  donor. We will continue with  $M(\text{CO})_n$ , reserving the donor case for another occasion. For less than eight d electrons, low-spin molecules, which are required to test our geometrical notions, are rare, while high-spin species are abundant. This is consistent with the close energetic spacing of the lower levels calculated by us for any sterically reasonable coordination geometry.<sup>62-64</sup>

We turn to the analysis of the interaction between  $\text{ML}_4$  fragments and additional ligands.

In studying the distortion of the square-planar fragment to a  $C_{4v}$  pyramidal one (Figure 7) we noted the presence of two  $a_1$  orbitals—one descended from  $a_{1g}$  of  $D_{4h}$  and the other from  $a_{2u}$ . Let us now consider a fifth ligand brought in along the  $z$  axis, as shown in



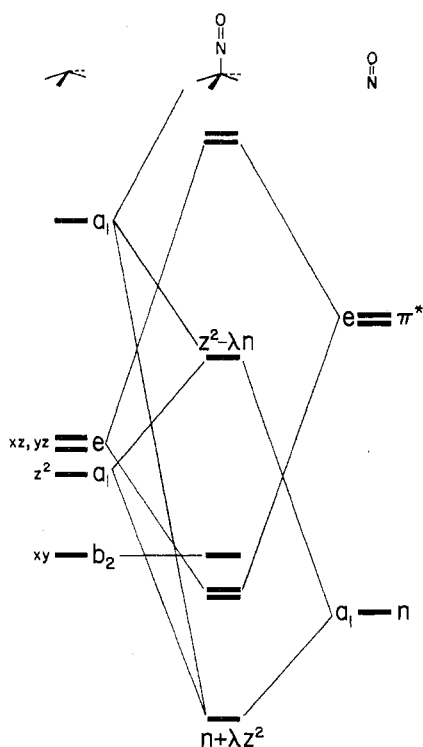


Figure 11. Interaction diagram for a square-pyramidal  $C_{4v}$  fragment (left) interacting with a nitrosyl (right).

Let this fifth ligand carry a donor orbital, marked  $n$ , and a cylindrical  $\pi^*$ -acceptor system. This would be a model for a linear nitrosyl in the apical position of a square pyramid. Figure 11 shows an interaction diagram for such a system—it is essentially a reconstruction of the  $C_{4v}$   $ML_5$  case. There is strong interaction,  $\pi$  bonding, between the fragment  $e$  orbital and the apical ligand  $\pi^*$  set of the same symmetry. The apical ligand donor orbital,  $n$ , interacts with both  $a_1$  orbitals of the fragment. It will be recalled that the higher  $a_1$  orbital has excellent directional properties for overlap with  $n$ .

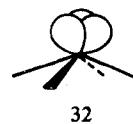
The higher  $a_1$  orbital is important in our scheme, for its presence serves to keep the lower  $a_1$  fragment orbital from moving to too high energy when the fifth, apical ligand comes in. There are two ways to think about this. First we could say that the upper  $a_1$  orbital takes over the main interaction role with  $n$  by virtue of the former's hybridization. Or another way of looking at the result is to say that the lower  $a_1$  and  $n$  interact most strongly but that the antibonding combination  $z^2 - \lambda n$  is prevented from shooting up in energy by the presence of another low-lying  $a_1$  orbital.

The reason for being concerned about the  $a_1$  orbitals is that the middle  $a_1$  level in the interacted scheme of Figure 11 is indeed occupied in stable nitrosyl complexes such as  $IrCl_2(NO)(PPh_3)_2$ .<sup>65</sup> In such complexes we have a  $d^7$  metal atom and a nitrosyl group which contributes three electrons (two in  $n$ , one in  $\pi^*$ ) to the interaction diagram. The five lower levels are occupied. Implicit in Figure 11 is also the tendency of such molecules to bend. By doing so, the middle  $a_1$  orbital can decrease its interaction with  $n$  and gain a stabilizing interaction with  $\pi^*$ . The pentacoordinate nitrosyl problem is an intricate one—it merits more detailed discussion than that given here. Our account of the electronic structure and geometrical distortions of pentacoordinate nitrosyls is presented elsewhere.<sup>66,67</sup>

Important reactions for square-planar  $d^8$  complexes are associative processes in which a fifth ligand is added and oxidative additions with a diatomic molecule. The electronic structure of the  $D_{4h}$  fragment is crucial to the analysis of these

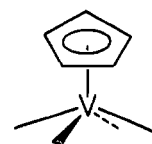
processes, which will be described in a separate study.

A  $C_{4v}$  fragment with  $\theta > 105^\circ$ , represented by the right-hand side of Figure 7, has a nice set of hybridized  $e$  orbitals to play an acceptor role in a  $d^4$  complex. The acceptor set here consists of  $a_1 + e$ . This is of course the representation set subduced by three equivalent hybrids arranged in local threefold symmetry, **32**. A perfect match for such a set of acceptor



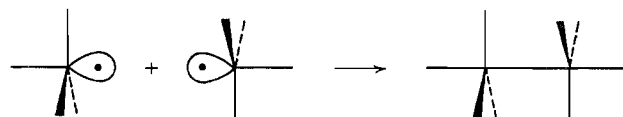
32

orbitals would be provided by a ligand with three equivalent donor orbitals. Such a ligand can be provided by three individual ligands, but it is also available in a  $\eta^5$ -cyclopentadienyl or a  $\eta^6$ -benzene. Indeed  $\eta^5$ -CpV(CO)<sub>4</sub> and CpNb(CO)<sub>4</sub> with this structure are known<sup>68</sup> and numerous CpMo(CO)<sub>3</sub>X derivatives as well.<sup>69</sup>



33

In the  $C_{3v}$  fragment diagram, Figure 8, an interesting point is reached at  $d^9$ , Co(CO)<sub>4</sub>. The odd electron occupies a directional  $a_1$  orbital, and just as in the Mn(CO)<sub>5</sub> case we would expect a facile dimerization

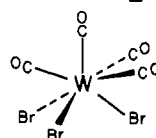


One of the two known forms of dicobalt octacarbonyl results.<sup>70</sup>

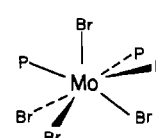
A  $d^4$   $C_{3v}$  fragment (Figure 8) appears to have a set of  $a_1 + e$  acceptor orbitals ideal for interaction with three donors. However, closer examination of the composition of the  $e$  orbitals yields both a worry and an additional insight. The  $e$  orbital, which is the higher of two such symmetry orbitals, is at  $\theta = 90^\circ$  almost entirely  $xy$  and  $x^2 - y^2$ . This follows from its descent from a trigonal bipyramid. The  $xy$  and  $x^2 - y^2$  composition is poor for overlap with an external ligand set—in the pseudoaxial symmetry the  $e$  set is  $\delta$ , but the ligand donors subduce a  $\pi$  set.

A distortion from  $\theta = 90^\circ$  is, however, very effective at mixing  $xz$  and  $yz$  character into the acceptor  $e$  orbital. At  $\theta = 70^\circ$  the  $e$  level has nearly twice as much  $xz$  and  $yz$  as it has  $x^2 - y^2$  and  $xy$ . Effective external hybridization, by mixing in metal  $x$  and  $y$ , is achieved also for  $\theta < 90^\circ$ . In summary such a  $C_{3v}$   $M(CO)_4$  fragment will be an effective six-electron acceptor only when it takes on the sterically uncomfortable "umbrella" geometry, with  $\theta < 90^\circ$ .

Remarkably such a structure,  $M(CO)_4$  plus a six-electron donor, is realized in  $W(CO)_4Br_3^-$ .<sup>71</sup> The resulting coordination geometry, **34**, is a capped octahedron. The  $W(CO)_4$  fragment is indeed umbrella shaped, with  $\theta = 74^\circ$ .

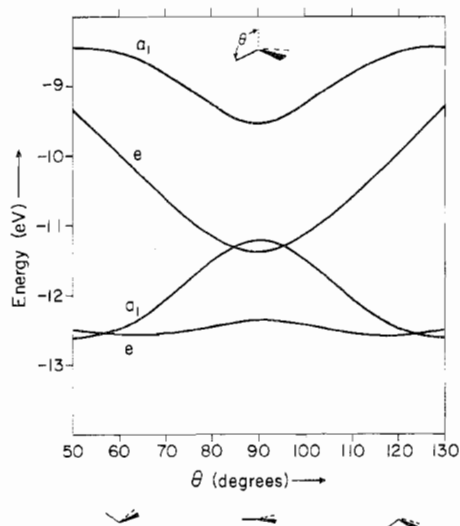


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35

The existence of a  $d^4$  case with a  $C_{3v}$   $M(CO)_4$  fragment, **34**, and another one, the previously mentioned CpV(CO)<sub>4</sub>, **33**,



**Figure 12.** Energy levels of a  $C_{3v}$   $M(\text{CO})_3$  fragment. In the  $D_{3h}$  geometry at  $\theta = 90^\circ$  the lower e orbital is  $e''$ , primarily  $xz$  and  $yz$ , while the upper e orbital is  $e'$ , primarily  $xy$  and  $x^2 - y^2$ . The composition of the two e levels reverses as  $\theta$  departs significantly from  $90^\circ$ .

with a  $C_{4v}$  fragment raises the unsolved question of why one seven-coordinate geometry is preferred to another one and another question as to whether the two geometrical possibilities are separated for any one compound by a large or small energy barrier.<sup>72</sup>

Several seven-coordinate complexes of the type  $\text{MX}_4(\text{PMe}_2\text{Ph})_3$  with  $M = \text{Mo}$  or  $\text{W}$  have been synthesized<sup>73a</sup> and the crystal structure of one, with  $X = \text{Br}$ ,  $M = \text{Mo}$ , has been determined.<sup>73b</sup> The solid-state structure is a capped octahedron, **35**, with  $\theta$  in the  $\text{BrMoP}_3$  fragment being  $74^\circ$ . The geometry is understandable from our analysis.<sup>73c</sup> Furthermore, the level scheme of Figure 8 accounts for the observed paramagnetism of this  $d^2$  complex.

### A Tricoordinate Fragment

Though a number of less symmetric geometries are possible, we concentrate on those that maintain a threefold rotation axis. The angle varied in **36** and Figure 12 is  $\theta$ , measured from the



$+z$  axis, with  $\theta = 90^\circ$  corresponding to the most symmetric  $D_{3h}$  structure. The octahedral fragment, LML angle  $90^\circ$ , is at  $\theta \approx 55$  or  $125^\circ$ . Figure 12 is, of course, symmetrical around  $\theta = 90^\circ$ .

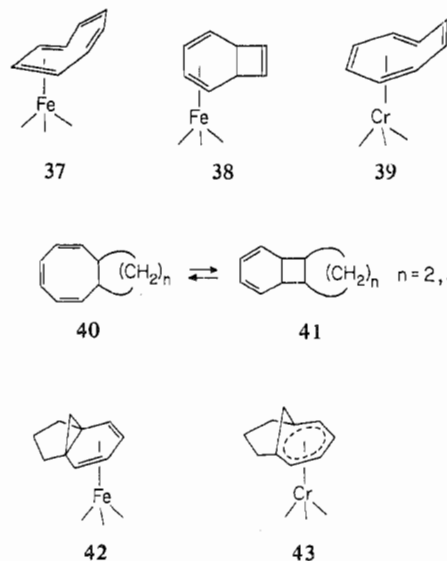
Several obvious points may be noted. (1) The entire diagram is related in a transparent manner to the trigonal-bipyramidal  $\text{ML}_5$  case (Figure 2) and the trigonal-pyramidal  $\text{ML}_4$  case (Figure 8). It is the  $a_1$  level,  $z^2$ , which is strongly affected by the presence or absence of one or two axial ligands. (2) Note the accidental degeneracy of the  $a_1$  and e levels at  $\theta \approx 125^\circ$ . The  $M(\text{CO})_3$  fragment "remembers" its octahedral parentage,  $t_{2g}$  below e. In fact it is much closer in its level structure to the octahedron than it is to another geometry to which it is related, the tetrahedron. (3) The higher e level is primarily metal  $xy$  and  $x^2 - y^2$  at  $\theta = 90^\circ$ , while at  $\theta = 130^\circ$  it is predominantly  $xz$  and  $yz$ . The composition of the lower e level is reversed. In a sense an avoided level crossing has taken place between the two e levels. (4) There is an upper  $a_1$  level, descended from a metal p-carbonyl  $\pi^*$  combination

analogous to **26**, which at  $\theta \neq 90^\circ$  becomes a lovely hybrid of metal s, z, and  $z^2$  pointing away from the fragment.

The  $d^6$  fragment,  $\text{Cr}(\text{CO})_3$  or  $\text{Mn}(\text{CO})_3^+$ , thus has three low-lying levels and a set of three acceptor orbitals,  $a_1 + e$ . As noted above, such a set is equivalent to three localized hybrids oriented as in **32**. Our contribution here is negligible, for such concepts were obvious to the pioneering synthesizers of  $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ <sup>74a</sup> and  $\text{CpMn}(\text{CO})_3$ .<sup>74b</sup>

The  $d^8$  fragment,  $\text{Fe}(\text{CO})_3$ , has two electrons in the high-lying set of three orbitals. It thus should accept two electron pairs in the form of a diene, and optimally so when it can transfer its own high-energy electron pair to an unfilled diene orbital. The last section of this paper will return to a detailed analysis of this fragment.  $\text{Co}(\text{CO})_3$  has three electrons in the high-lying set of three orbitals. Thus  $\text{Co}(\text{CO})_3$ , in its bonding capabilities, is much like CH, while  $\text{Fe}(\text{CO})_3$  is like BH. This analogy is a key component of the elegant systematization of polyhedral transition metal cluster complex structures introduced by Wade<sup>7</sup> and Mingos.<sup>8</sup>

The bonding propensities of  $M(\text{CO})_3$  fragments are best exhibited when two metal fragments of similar steric size form complexes with the same substrate. For instance  $\text{Fe}(\text{CO})_3$  and  $\text{Cr}(\text{CO})_3$  complexes of cyclooctatetraene have long been known. Cyclooctatetraene, which normally exists in a tub conformation, changes its geometry upon complexation with  $\text{Fe}(\text{CO})_3$ , so that the two complexed bonds are in the same plane, **37**.<sup>75</sup> In some cyclooctatetraene derivatives the preference for a conjugated diene is exhibited in a different way: by the  $\text{Fe}(\text{CO})_3$  picking up the bicyclic isomer, **38**, present in equilibrium with the free monocyclic compound.<sup>76</sup> By contrast, in  $\text{Cr}(\text{CO})_3$  or  $\text{Mo}(\text{CO})_3$  complexes of cyclooctatetraene three double bonds are put in the plane, **39**.<sup>77</sup> In the electrocyclic equilibrium **40**  $\rightleftharpoons$  **41**,  $\text{Fe}(\text{CO})_3$  or  $\text{Mo}(\text{CO})_3$



complexes with the appropriate valence isomer.<sup>78</sup> And, while the  $\text{Fe}(\text{CO})_3$  complex of tricyclo[4.3.1.0<sup>1,6</sup>]deca-2,4-diene, **42**, retains the closed cyclopropane ring, the  $\text{Cr}(\text{CO})_3$  derivative opens it to a homoaromatic structure, **43**.<sup>79</sup> This is but a small selection of many analogous examples.

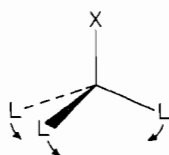
The  $\text{ML}_3$  fragment picture of Figure 12 may also be put to use in explaining the variation of  $\text{ML}_3$  pyramidalities in  $\text{ML}_3\text{X}$  complexes. In a  $d^{10}$  complex the higher e set would be occupied. It is composed primarily of metal  $xz$  and  $yz$  and hybridized by admixture of  $x$  and  $y$  to form a donor set optimally prepared for  $\pi$  bonding with acceptor orbitals of the fourth ligand X. The more pyramidal the structure, the better prepared are the e orbitals for  $\pi$  bonding, in both their energy and their hybridization. We would thus expect that if two

Table III. Optimum Geometries for  $M(\text{CO})_3$  Fragments

No. of d electrons	Optimum symmetry	Angle, <sup>a</sup> deg
0	$C_{3v}$	116
1	$C_s$	96, 96, 125
2	$C_s$	93, 93, 124
3	$C_s$	93, 93, 126
4	$C_{3v}$	116
5	$C_{3v}$	122
6	$C_{3v}$	123
7	$C_{3v}$	117
8	$C_{2v}$	94, 94, 172
9	$C_{3v}$	105
10	$C_{3v}$	98

<sup>a</sup> The angles given are  $\theta$ , defined in 36, for  $C_{3v}$  structures and the three LML' angles for the lower symmetries.

complexes with sterically similar fourth ligands X and X' are compared, the stronger  $\pi$  acceptor will have a more pyramidal  $\text{ML}_3$  part of the complex.<sup>80</sup> This is indicated schematically in



An example may be found in the structures of  $\text{Pt}(\text{CO})(\text{PPh}_3)_3$  and  $\text{Ir}(\text{NO})(\text{PPh}_3)_3$ .<sup>81</sup> Despite the steric bulk of the triphenylphosphine ligands the P-M-N(C) angle rises from  $113^\circ$  in the carbonyl case to  $117^\circ$  for the better  $\pi$  acceptor, the nitrosyl. A similar effect in the structures of  $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ ,  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ , and  $\text{IrH}(\text{NO})\text{L}_3^+$ <sup>82</sup> may have an analogous explanation.

Table III contains the optimized geometries of low-spin configurations. The departures from higher symmetry are easily understood as first- and second-order Jahn-Teller effects. Since the lowest d level is of e symmetry,  $d^1$ - $d^3$  distort naturally to  $C_s$ . A similar effect takes place in  $d^8$ .

Available tricoordinate complexes include an interesting series of high-spin  $d^0$ - $d^3$ ,  $d^5$  trisamides  $M(\text{NR}_2)_3$ , with published structures for  $M = \text{Cr}$  and  $R = \text{isopropyl}$  or  $M = \text{Fe}$  and  $R = \text{Si}(\text{CH}_3)_3$ .<sup>83</sup> A  $C_{3v}$  structure has been assigned to the  $d^6$  species  $\text{Cr}(\text{CO})_3$  and  $\text{Mo}(\text{CO})_3$ .<sup>84a</sup> A  $C_{3v}$  geometry has also been assigned to  $\text{Fe}(\text{CO})_3$ .<sup>84b</sup> Presumably this is the high-spin species,<sup>4</sup> for which we would also predict a pyramidal geometry.

Our calculations prefer a  $C_{3v}$  geometry for the  $d^{10}$  (and high-spin  $d^5$ ) species. This is in disagreement with the calculations of Burdett,<sup>4</sup> which show a  $D_{3h}$  minimum. The pyramid we calculate is quite flat and only 1 kcal/mol lower in energy than the trigonal-planar structure. All known tricoordinate molecules appear to be trigonal planar. These include  $\text{Ni}(\text{CO})_3$ ,<sup>85a</sup>  $\text{Pt}(\text{N}_2)_3$ ,<sup>85b</sup>  $\text{Pd}(\text{N}_2)_3$ ,<sup>85b</sup>  $\text{Pd}(\text{CO})_3$ ,<sup>85c</sup>  $\text{Pt}(\text{CO})_3$ ,<sup>85c</sup>  $\text{Pt}(\text{Ph}_3)_3$ ,<sup>86a</sup>  $\text{HgI}_3^-$ ,<sup>86b</sup> and (trimethylphosphine sulfide)<sub>3</sub> $\text{Cu}^+$ .<sup>86c</sup>

Just as in the  $\text{ML}_4$   $d^8$  case we expect that the change from CO to a donor ligand would affect the geometry predictions. Indeed a calculation on a model  $\text{MCl}_3$  favors a  $D_{3h}$  structure for  $d^0$ ,  $d^{10}$ , and intermediate points where a Jahn-Teller distortion is not operative. A level ordering for the trisamide complexes has been derived.<sup>83</sup> The  $M(\text{CO})_3$  levels of Figure 12 do not match it well, but those of  $\text{MCl}_3$  do.

#### Number of Donor and Acceptor Orbitals of an $\text{ML}_n$ Fragment

The preceding sections have carried a blow-by-blow description of the electronic structure of various fragments. It is appropriate to pause here and view some of our conclusions from a broader perspective.

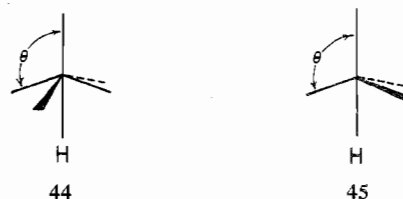
In the energy interval which we have chosen for our figures the total number of available orbitals for an  $M(\text{CO})_n$  fragment varies with  $n$ . The following derivation of the variation is closely connected with the 18-electron rule. Each metal atom has nine orbitals—five d, one s, and three p. In an  $\text{ML}_n$  complex each ligand carries a  $\sigma$ -donor orbital. Each such orbital finds among the set of nine metal orbitals a partner with which to interact. The result is that  $n$  of the 9 metal orbitals are destabilized by  $\sigma$  bonding with the ligands, leaving  $9 - n$  orbitals to either hold metal d electrons or act as acceptor orbitals of the fragment. Nothing is said in this argument concerning the energy, high or low, of the  $9 - n$  orbitals nor concerning their spatial extent or hybridization. But we can deduce immediately the number of valence orbitals—it is four for  $M(\text{CO})_5$ , five for  $M(\text{CO})_4$ , and six for  $M(\text{CO})_3$ .

How many of the  $9 - n$  valence orbitals of an  $M(\text{CO})_n$  fragment lie low in energy and how many lie high is difficult to specify in general, since the energy of the various levels is often sensitive to deformation. For geometries close to the octahedral parent the answer is simply given: three levels are low-lying and  $6 - n$  are relatively high in energy. This follows from the fragments "remembering" the low-energy position of the octahedral  $t_{2g}$  set, stabilized by interaction with  $\pi^*$  orbitals of the carbonyls. Where the fragment departs significantly from the geometry of a piece of an octahedron, the number of low-lying orbitals may be larger or smaller than three [for instance all five orbitals are relatively low in energy for tetrahedral  $M(\text{CO})_4$ , but only one orbital is at low energy for a strongly umbrella distorted  $C_{4v}$   $M(\text{CO})_5$ ].

We could provide a table which lists the number of donor and acceptor electrons, *i.e.*, the number of electrons and holes in high-energy valence orbitals, but we refrain from doing so. In its simplest form such a table contains no more information than a knowledge of the stable carbonyls and the 18-electron rule. It would miss the richness of structural detail that we hope we have demonstrated in the preceding sections where each fragment was analyzed individually. In the following sections we will apply the qualitative ideas developed above to two interesting problems, where not one but several alternative fragments are involved.

#### Deviations from an Ideal Geometry in Transition Metal Hydrides

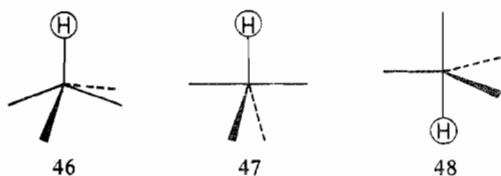
The fact that a hydrogen atom acting as a ligand induces a geometrical distortion is well documented. The question as to whether a hydrogen atom in a metal carbonyl hydride, for instance  $\text{Co}(\text{CO})_4\text{H}$ , occupies a sterically active site or is buried in the metal orbitals has been solved. The first conclusive crystallographic study on this subject was that of  $\text{Mn}(\text{CO})_5\text{H}$ .<sup>87</sup> The observed structure corresponds to a distorted octahedron, **44**,  $\theta = 97^\circ$ , in which the equatorial carbonyls are bent toward the hydrogen atom. A recent electron diffraction structure of  $\text{Co}(\text{CO})_4\text{H}$  shows a distorted trigonal-bipyramidal structure **45** in which the bending angle,  $\theta = 100^\circ$ , is halfway between



a trigonal bipyramid ( $\theta = 90^\circ$ ) and a tetrahedron ( $\theta = 109.5^\circ$ ).<sup>88</sup> The solid-state structure of the isoelectronic  $\text{Fe}(\text{CO})_4\text{H}^-$  is very similar.<sup>89</sup>

We wish to understand the basic structural features of these compounds, and the fragment analysis presents a convenient way of doing so. By way of example let us consider the interaction of a hydride ion with a  $d^8$   $M(\text{CO})_4$  fragment

[Co(CO)<sub>4</sub><sup>+</sup> or Fe(CO)<sub>4</sub>]. The hydride ion is a good donor, a high-lying pair of electrons in a 1s level. The M(CO)<sub>4</sub> fragment will be allowed to assume C<sub>4v</sub>, C<sub>2v</sub>, and C<sub>3v</sub> geometries, 46–48, covering a range of pentacoordinate structures where the hydride is apical in a square pyramid, equatorial in a trigonal bipyramid, or axial in a trigonal bipyramid. The



reader at this point must refer back to Figures 7, 5, and 8 for the electronic structure of the fragments. For a d<sup>8</sup> fragment with C<sub>4v</sub> symmetry all the low-lying d orbitals are occupied. There is the higher a<sub>1</sub> orbital, but at the same time that the hydride s interacts with it, it encounters a destabilizing interaction with the filled lower a<sub>1</sub> orbital. The situation is similar for interaction with a C<sub>2v</sub> fragment, as in 47.

The situation is decidedly different in geometry 48, where the interaction is with a C<sub>3v</sub> fragment. From Figure 8 it is seen that a d<sup>8</sup> C<sub>3v</sub> fragment with  $\theta$  near 90° has its electrons in two e levels. It also has a low-lying empty a<sub>1</sub> orbital prepared to interact in a bonding way with the filled hydride ion.

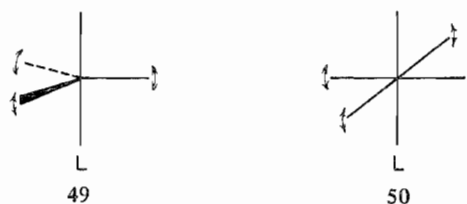
Given that the above line of argument decisively places the hydride ligand in the axial position of a trigonal bipyramid, we still have to rationalize the observed deformation from that structure. The rationalization could, in principle, be a matter of steric size of the hydride relative to the other ligands. Indeed, such a steric explanation has often been presented. Without doubting its validity we wish to construct an electronic argument for the same distortion. That argument goes as follows. The d<sup>8</sup> M(CO)<sub>4</sub> fragment itself has a relatively flat potential energy curve in the region 90° <  $\theta$  < 110° with a minimum at  $\theta \approx 95^\circ$ . The hydride s orbital is closer in energy to the a<sub>1</sub> orbital with which it interacts at the high  $\theta$  end of this range. Therefore the stabilization will be greatest for  $\theta > 95^\circ$ . The energy gap effect dominates the distortion, though it should be pointed out that at  $\theta = 90^\circ$  the s–a<sub>1</sub> overlap is greater than at  $\theta = 110^\circ$ , due to the increased hybridization of the a<sub>1</sub> orbital.

We can analyze the electronic structure of Mn(CO)<sub>5</sub>H in a similar manner, starting from the orbitals of a square-pyramidal d<sup>6</sup> M(CO)<sub>5</sub> fragment in Figure 2.

Another way of thinking about this problem is in terms of the polarity of the M–H bond. If the hydrogen is indeed a hydride ion, H<sup>–</sup>, then we have in the compounds of interest a d<sup>8</sup> M(CO)<sub>4</sub> fragment. For that fragment by itself, within a C<sub>3v</sub> constraint, the calculations favor a trigonal-bipyramidal fragment geometry with  $\theta \approx 95^\circ$ . Were the hydrogen H<sup>+</sup>, then we would have a d<sup>10</sup> M(CO)<sub>4</sub>, which clearly is tetrahedral, *i.e.*,  $\theta = 109.5^\circ$ . d<sup>9</sup> is of course intermediate, with a preferred  $\theta$  of  $\sim 102^\circ$ . In reality the hydrogen is neither H<sup>–</sup> nor H<sup>+</sup>, but some intermediate degree of covalent or partially ionic bonding is established. In a sense the geometry of the hydride is giving us some information on the polarity of the MH bond.

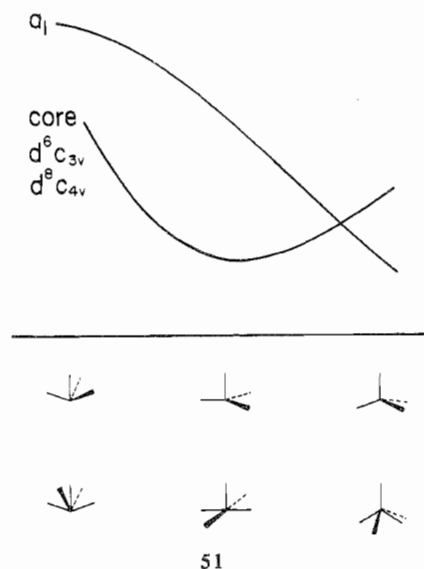
A similar argument may be applied to transition metal dihydrides of the type FeL<sub>4</sub>H<sub>2</sub>. If the hydrogen is formally H<sup>–</sup>, we expect the characteristic d<sup>6</sup> octahedral structure. At the other limit, for an H<sup>+</sup>, the FeL<sub>4</sub> fragment would contain a d<sup>10</sup> metal atom. It should then assume a tetrahedral geometry. Known dihydride structures indeed show geometrical distortions toward the tetrahedral limit.<sup>91</sup> If our argument is correct in attributing an electronic origin to these distortions, it follows that FeL<sub>4</sub>X<sub>2</sub> species in which X is a very good  $\sigma$  donor might show similar distortions of the FeL<sub>4</sub> fragment toward a tetrahedron.

Our theory ties the deformation of these molecules to the strong donor character of the hydride ligand. We can leave the hydride ligand and ask the following more general question. How does the displacement of the carbonyl groups from the idealized equatorial plane in compounds of types 49 and 50



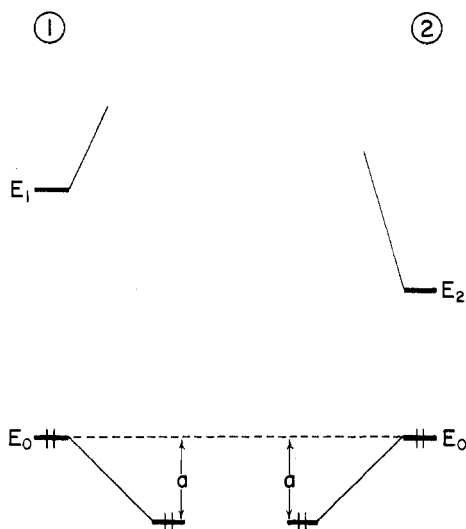
depend on the unique axial ligand L? The effect is a significant one: average L–M–CO angles are 81.7° in H<sub>3</sub>SiCo(CO)<sub>4</sub>,<sup>92</sup> 86.7° in Ph<sub>3</sub>SnMn(CO)<sub>5</sub>,<sup>93</sup> 86.2° in Mn<sub>2</sub>(CO)<sub>10</sub>,<sup>50b</sup> 81.1° in Zn(Co(CO)<sub>4</sub>)<sub>2</sub>.<sup>94</sup> This list is not exhaustive. Generally deformation toward the unique ligand takes place. Two molecular orbital explanations of this effect have been given previously,<sup>18,95</sup> and we regretfully add a third one.<sup>97</sup>

The argument we present focuses on the interaction of the donor ligand, a<sub>1</sub> in either C<sub>3v</sub> or C<sub>4v</sub>, with the a<sub>1</sub> acceptor orbital of the M(CO)<sub>4</sub> or M(CO)<sub>5</sub> fragment. The relevant level diagrams are given in Figures 2 and 8. They may be summarized as follows. There is a set of core levels (b<sub>2</sub> + e in C<sub>4v</sub>, holding six electrons; e + e in C<sub>3v</sub>, holding eight electrons) which raises the energy of the fragment approximately the same amount for either direction of distortion from the “flat” fragment = metal in plane of equatorial ligands. Then there is an a<sub>1</sub> acceptor orbital which behaves unsymmetrically with the equatorial ligand distortion, as shown in 51.



The argument is based on (1) the fact that if the fifth ligand coming to the M(CO)<sub>4</sub> fragment, or the sixth ligand joining M(CO)<sub>5</sub>, is another carbonyl, then the result of interaction on the left- or right-hand side of 51 must be equal by symmetry (bending the equatorial ligands up or down is equivalent in the trigonal bipyramid or octahedron) and (2) the fact that the a<sub>1</sub> acceptor orbital is lower in energy on the right-hand side of 51. Our reasoning follows.

Consider two acceptor orbitals 1 and 2, one at E<sub>1</sub> and one at E<sub>2</sub>, interacting *via* overlap matrix elements H<sub>1</sub> and H<sub>2</sub> with a donor orbital at E<sub>0</sub>. Put E<sub>1</sub> > E<sub>2</sub>; thus 1 is a model for the left side of 51 and 2 for the right side. The donor in question has the special property that its interaction with 1 and 2 is precisely equal when the donor energy is E<sub>0</sub>. This is shown in the diagram



We want to study what happens to the stabilization of the donor when its donor properties are modified by changing its energy from  $E_0$  to  $E_0 + \epsilon$ .

The special constraint on our system is that

$$a = \frac{H_1^2}{E_0 - E_1} = \frac{H_2^2}{E_0 - E_2}$$

*i.e.*, interaction 1 makes up in the overlap-dependent numerator what it loses in the energy denominator. We are using simple second-order perturbation theory with overlap neglected. Next we change  $E_0$  to  $E_0 + \epsilon$ . The difference in stabilization between cases 1 and 2 becomes

$$\text{stabilization 1} - \text{stabilization 2} = \frac{2H_1^2}{E_0 - E_1 + \epsilon} - \frac{2H_2^2}{E_0 - E_2 + \epsilon} = 2a \left[ \frac{1}{1 + \frac{\epsilon}{E_0 - E_1}} - \frac{1}{1 + \frac{\epsilon}{E_0 - E_2}} \right]$$

where the factor of 2 comes from summing over the two electrons in the donor orbital. If we expand in  $\epsilon/\Delta E$  and keep the first term in the expansion variable, we then get

$$\text{stabilization 1} - \text{stabilization 2} = 2a \left[ 1 - \frac{\epsilon}{E_0 - E_1} - \left( 1 - \frac{\epsilon}{E_0 - E_2} \right) \right] = \frac{2a\epsilon(E_2 - E_1)}{(E_0 - E_1)(E_0 - E_2)}$$

Since the denominator of the above expression is positive,  $E_2 - E_1 < 0$  and  $a$  is negative, it follows that

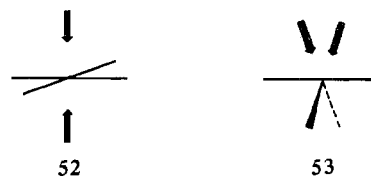
$$\begin{aligned} \text{stabilization 1} - \text{stabilization 2} &< 0 \text{ if } \epsilon \text{ negative} \\ &> 0 \text{ if } \epsilon \text{ positive} \end{aligned}$$

The stabilizations are negative, so it follows that system 1 is more stable than system 2 if  $\epsilon$  is negative and less stable if  $\epsilon$  is positive.

$\epsilon$  positive is to be associated with a ligand which is a better donor than CO;  $\epsilon$  negative, with a poorer donor. Our conclusion is that, in  $M(\text{CO})_4\text{L}$  or  $M(\text{CO})_5\text{L}$ , if L is a better donor than CO, then there will be more stabilization on the right of **51**; that is, the equatorial carbonyls will bend toward L. If L is a poorer  $\sigma$  donor than CO, then the equatorial ligands will bend away from L.

It is not claimed that the factor analyzed here is the only one responsible for this deformation. Indeed the other explanations offered for the effect appear plausible,<sup>18,95</sup> as does, in certain cases such as the hydride, the steric argument. If the electronic factor discussed here is indeed significant, it would be interesting to probe it in two ways: by synthesizing  $\text{Co}(\text{CO})_4\text{L}$  structures where L is a good  $\sigma$  donor but sterically bulky, for instance, L = *tert*-butyl; and by studying compounds where L is a poorer  $\sigma$  donor than CO.<sup>98</sup>

The perturbation argument which we used may have other applications. We illustrate one directed toward understanding the energy difference between *cis* and *trans*  $d^6 M(\text{CO})_4\text{L}_2$  isomers. Consider the approach of two donors to the  $D_{4h}$  and  $C_{2v}$  fragments, as in **52** and **53**. The donor orbitals transform



as  $a_{1g} + a_{2u}$  for **52** and  $a_1 + b_2$  for **53**. Figure 5 shows that in either case a  $d^6$  fragment would present acceptor orbitals of the proper symmetry to interact with these ligand orbitals. The perturbation argument exploits the fact that the acceptor orbitals in the  $D_{4h}$  fragment are at lower energy than those in the  $C_{2v}$  fragment, and yet if the incoming ligands in **52** and **53** were carbonyls, the product of the interaction would be the same, octahedral  $M(\text{CO})_6$ . The conclusion that can be worked out is that in  $M(\text{CO})_4\text{L}_2$ , if L is a better  $\sigma$  donor than CO, then the *trans* isomer will be more stable. If L is a poorer  $\sigma$  donor than CO, then the *cis* isomer will be more stable.

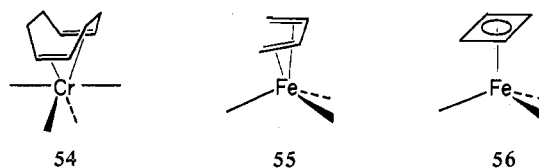
All this ignores the steric effects which loom large in determining isomer stability in octahedral complexes. Whether there is a true electronic component and whether it indeed depends on  $\sigma$  donor strength remain to be seen.

#### Valence-Shell Isoelectronic Fragments:

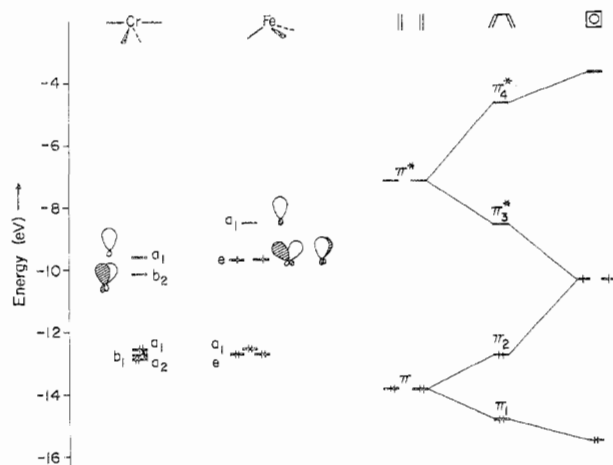
##### $\text{Cr}(\text{CO})_4$ vs. $\text{Fe}(\text{CO})_3$

Until now we have looked only at the problem of stabilizing a fragment with a fixed number of ligands. We next consider groups of two or more fragments with different numbers of ligands and different metal centers but the same number of electrons in the valence shell. By way of illustration we trace some of the differences in the abilities of  $\text{Cr}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_3$  fragments to coordinate with olefins. Both these fragments have 14 electrons in the valence shell, counting the carbonyl donor orbitals, and both form stable 18-electron complexes with two ethylene units. We could add  $\text{Ti}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_2$  to our family of valence-shell isoelectronic fragments, but we will concentrate on  $\text{Cr}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_3$  since these fragments are more common.

Many chromium tetracarbonyl complexes with ligands containing two nonconjugated double bonds are known, for example, complexes with 1,5-cyclooctadiene,<sup>99</sup> **54**, norbornadiene,<sup>100</sup> and hexamethyl(dewar benzene).<sup>101</sup> Some iron tricarbonyl complexes of the same form do exist,<sup>102</sup> but they are relatively few. On the other hand, the iron tricarbonyl fragment gives a variety of stable complexes with conjugated olefins,<sup>103</sup> exemplified by butadiene,<sup>104,105</sup> **55**, or cyclobutadiene,<sup>106</sup> **56**.  $M(\text{CO})_4$  complexes,  $M = \text{Cr}, \text{Mo}, \text{W}$ , of



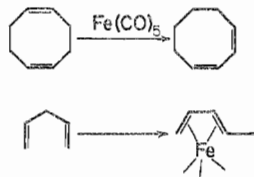
conjugated dienes are rare, represented only by a Cr complex



**Figure 13.** Energy levels of a  $C_{2v}$  octahedral fragment  $M(CO)_4$  and a  $C_{3v}$  octahedral fragment  $M(CO)_3$  plotted on the same energy scale as the  $\pi$  levels of two noninteracting ethylenes, a butadiene, and a cyclobutadiene. Orbital occupations appropriate to  $Cr(CO)_4$  and  $Fe(CO)_3$  are indicated.

of butadiene<sup>107</sup> and several cyclobutadiene complexes.<sup>108</sup> Indeed it appears that, if a  $d^6$   $M(CO)_4$  fragment is offered up a butadiene, it chooses to coordinate two such *via* a single double bond in each: the photolysis of  $M(CO)_6$ ,  $M = Mo$  or  $W$ , in the presence of butadiene yields  $M(CO)_5(\text{butadiene})$  and  $M(CO)_4(\text{butadiene})_2$ .<sup>109,110</sup> Conversely, an  $Fe(CO)_4$  fragment generally prefers to lose another CO and coordinate to both double bonds of a conjugated diene.<sup>111</sup>

Further evidence for the conclusion that iron tricarbonyl prefers to be coordinated to conjugated rather than unconjugated dienes is provided by the isomerization of some ligands during complex formation,<sup>112</sup> as shown in



Molybdenum and tungsten tetracarbonyls can effect the reverse isomerization, from a conjugated 1,3-cyclooctadiene to the nonconjugated 1,5-cyclooctadiene.<sup>113</sup>

Figures 5 and 12 gave the orbitals of  $C_{2v}$   $M(CO)_4$  and  $C_{3v}$   $M(CO)_3$  fragments, respectively. We now place them on the same energy scale in Figure 13. Consistent with their octahedral parentage, these fragments possess three low-lying levels, descended from  $t_{2g}$ .  $M(CO)_4$  has two acceptor levels,  $a_1$  and  $b_2$ , pointed toward the missing ligands, while  $M(CO)_3$  has three such orbitals,  $a_1$  and  $e$ . The electron count introduces a fundamental difference between the two systems. In  $Cr(CO)_4$ ,  $d^6$ , only the lower set of three orbitals is filled. In  $Fe(CO)_3$ ,  $d^8$ , the lower set is filled, but there is an additional electron pair to be placed in the higher lying orbital set.  $Fe(CO)_3$  thus presents to a potential ligand a set of three hybridized orbitals and a high-energy electron pair in them.<sup>7,8</sup>

Let us now consider the interaction of the two fragments with a diene. The acceptor orbitals of  $Cr(CO)_4$  interact effectively with the symmetric and antisymmetric combinations formed from two ethylene  $\pi$  levels. The olefinic ligands act primarily as donors.

The situation is quite different in the  $Fe(CO)_3$  case. Here the fragment itself has electron-donating properties as well as an orbital degeneracy problem. The latter would cause the fragment to distort of its own accord. In interacting with a pair of ligands,  $Fe(CO)_3$  can solve its problems in two ways. If the ligand is a superior  $\pi$  acceptor, then an effective

two-electron transfer can relieve the  $Fe(CO)_3$  of its requirement to distort, or the ligand can provide a good donor orbital of the symmetry of one component of the higher  $e$  level of  $Fe(CO)_3$  and a good acceptor orbital of the symmetry of the other  $e$  component. Interaction with these donor and acceptor levels would split the  $Fe(CO)_3$  level and provide the stabilization that a distortion of the fragment would also provide.

The right-hand side of Figure 13 shows the obvious—butadiene, or for that matter any conjugated diene, is a better donor or acceptor than a nonconjugated diene. The symmetry of  $\pi_2$  and  $\pi_3^*$  of butadiene is also right to split the  $e$  level of  $Fe(CO)_3$ . This explains the preference of  $Fe(CO)_3$  for conjugated olefins.<sup>114</sup> The degenerate orbital of a square cyclobutadiene is low-lying and half-filled. The result of its interaction with the  $Fe(CO)_3$  will be a net transfer of electrons from iron to the ligand. The complexed cyclobutadiene will approach the characteristics of an aromatic  $6\pi$  system, in agreement with the experimental evidence concerning the chemical properties of this complex.

Several of the unconjugated dienes which complex with  $Fe(CO)_3$  may in fact possess a low-lying molecular orbital that makes them a better acceptor than might have been expected from their formal unconjugation. In norbornadiene there is considerable evidence for a significant through-space interaction of the  $\pi$  levels.<sup>115</sup> In bicyclo[3.2.1]octadienyliron tricarbonyl<sup>102e</sup> there is, in addition to the through-space coupling, an allyl cation LUMO.

Supporting evidence for our view of  $Fe(CO)_3$  as a donating fragment comes from the decreased acidity of the 2,4-hexadien-1-ol acid in the  $Fe(CO)_3$  complex as compared with the free acid and the very mild conditions under which the iron tricarbonyl complex of 1-phenylbutadiene can be acetylated.<sup>116</sup> The donor capability has also been probed by a study of  $pK_a$ 's of butadiene and butadieneiron tricarbonyl para-substituted anilines.<sup>117</sup> The cyclobutadieneiron tricarbonyl complex itself is a good donor; witness the stability of cations substituted by that entity.<sup>118</sup>

Suppose that an  $Fe(CO)_3$  group is in fact obliged to bond to two nonconjugated olefins. If it cannot stabilize its high-lying electron pair by donation, it can still bring the electrons to lower energy by distorting the geometry of the fragment itself. The distortion in question is from  $C_{3v}$  to  $C_s$ , a fragment of either a trigonal bipyramid or a square pyramid. The direction of the distortion may be specified by the set of interligand angles. In a  $C_{3v}$  fragment they would be all equal  $\{\chi, \chi, \chi\}$ , with  $\chi \approx 90^\circ$ . The distortion toward a trigonal-bipyramidal fragment makes one angle greater, heading toward  $\{90, 90, 120^\circ\}$ , while the distortion toward a square pyramidal fragment increases two angles, perhaps lowers one, for instance  $\{85, 105, 105^\circ\}$ . When we do a calculation with an  $Fe(CO)_3$  fragment by itself, distorted to one or the other of these geometries, we find that one component of the high-lying  $e$  set is stabilized by more than 1 eV.

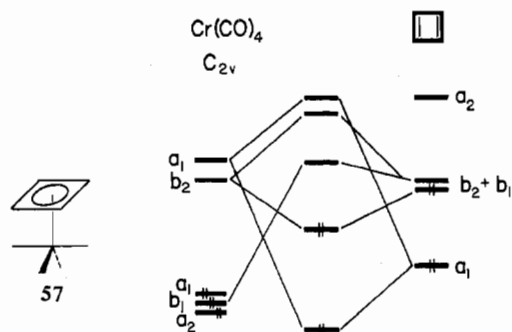
Complexes of conjugated dienes with  $Fe(CO)_3$  do show small distortions from local threefold symmetry in the  $Fe(CO)_3$  moiety.<sup>119</sup> For instance in cyclooctatetraeneiron tricarbonyl the set of interligand angles is  $\{93, 101, 101^\circ\}$ .<sup>75</sup> Still larger distortions in the fragment, to the trigonal-bipyramidal extreme, are found not in  $Fe(CO)_3$  derivatives but in the related  $d^8$  Ir(I) complexes of nonconjugated olefins.<sup>120</sup>

It is interesting to note that the observed distortions in (conjugated diene)iron tricarbonyl complexes are generally in the direction of the square pyramid.<sup>119</sup> The prototype distortion is that of butadieneiron tricarbonyl, **55**.<sup>104,105</sup> The orientation of the double bonds that is attained approximates  $ba\uparrow$ , which in our general account of pentacoordination,<sup>21</sup> is indeed the best orientation of an ethylene in a square pyramid.

A further point concerning  $Fe(CO)_3$  complexes with un-

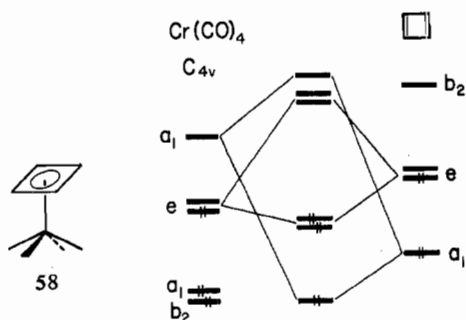
conjugated dienes is that the distortion of the  $M(\text{CO})_3$  fragment that may be one stabilization route may still leave a relatively high-lying electron pair susceptible to attack by acid. Whereas (conjugated diene)iron tricarbonyl complexes protonate at the diene ligand,<sup>121</sup> norbornadieneiron tricarbonyl in strongly acidic media undergoes protonation at the metal.<sup>122</sup>

The level diagram of Figure 13 does not explain the apparent reluctance of conjugated dienes to complex with a  $\text{Cr}(\text{CO})_4$ . The cyclobutadienemetal tetracarbonyl structures ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) are of special interest, and we will subject them to a more detailed analysis. Suppose the  $M(\text{CO})_4$  fragment retains its octahedral geometry, as in 57. The simplified interaction diagram that is obtained is shown. A consequence



of this diagram is that the cyclobutadiene may be somewhat more electron deficient than in the  $\text{Fe}(\text{CO})_3$  complex. Some electrons are transferred from the cyclobutadiene to the  $M(\text{CO})_4$  fragment by the  $b_2$  interaction. There is a reverse transfer by interaction of the  $b_1$  component of the  $\text{C}_4\text{H}_4$  e level with a filled  $M(\text{CO})_4$  level, but we think this effect will be smaller.

The  $\text{Cr}(\text{CO})_4$  need not necessarily retain its octahedral fragment geometry in coordinating with the cyclobutadiene. It can distort to a square-pyramidal fragment, as in 58. The relevant fragment orbitals were given in Figure 7 and are reproduced in the interaction diagram next to 58. The



$\text{Cr}(\text{CO})_4$  e level interacts well with the corresponding cyclobutadiene level, yielding a closed-shell structure. Depending on the relative position of the  $\text{Cr}(\text{CO})_4$  and  $\text{C}_4\text{H}_4$  e levels, the formulation of the cyclobutadiene as being toward the  $\text{C}_4\text{H}_4^{2-}$  or  $\text{C}_4\text{H}_4^{2+}$  extreme is more appropriate. Comparing Figure 13 and Figure 7, it will be noted that the e level of an  $M(\text{CO})_4$  fragment is lower in energy than the e level of an  $M(\text{CO})_3$  fragment. Thus we would expect that in  $\text{Cr}(\text{CO})_4\text{C}_4\text{H}_4$  the cyclobutadiene is more electron deficient than in  $\text{Fe}(\text{CO})_3\text{C}_4\text{H}_4$ .

Our argument cannot at this point decide whether the group VI complexes  $M(\text{CO})_4(\text{C}_4\text{H}_4)$  will have the  $M(\text{CO})_4$  fragment in a square-pyramidal or  $\text{C}_{2v}$  octahedral fragment geometry. The potential energy surface for the  $M(\text{CO})_4$  distortions should be soft.

There are two crystal structures of cyclobutadienemetal tetracarbonyl complexes—one of (benzocyclobutadiene) $\text{Cr}(\text{CO})_3\text{PPh}_3$  and another of (cyclobutadiene) $\text{Mo}(\text{CO})_3\text{PPh}_3$ .<sup>123</sup>

Table IV. Parameters Used in the Calculation

Orbital	$\zeta^a$	$H_{ii}$ , eV
Mn 4s	0.970	-9.75
Mn 4p	0.970	-5.89
C 2s	1.625	-21.40
C 2p	1.625	-11.40
O 2s	2.275	-32.30
O 2p	2.275	-14.80
N 2s	1.950	-26.00
N 2p	1.950	-13.40
Cl 3s	2.033	-30.00
Cl 3p	2.033	-15.00
H 1s	1.300	-13.60

Orbital	$\zeta_1^a$	$c_1^b$	$\zeta_2$	$c_2$	$H_{ii}$ , eV
Mn 3d	5.15	0.51392	1.70	0.69290	-11.67

<sup>a</sup> Slater exponent. Two are listed for the Mn orbital. <sup>b</sup> Expansion coefficients in the double- $\zeta$  wave function.

We are interested in the coordination geometry at the metal atom. This can be measured by the set of six LML' angles, excluding the cyclobutadiene ligand. In an idealized octahedral fragment five such angles would be  $90^\circ$  and one would be  $180^\circ$ . In a square pyramid four angles would be equal, perhaps near  $85^\circ$ , and the two remaining angles would also be equal, near  $150^\circ$ . In the benzocyclobutadiene complex the relevant angle set is  $\{80, 80, 82, 85, 112, 150^\circ\}$ . In the cyclobutadiene structure it is  $\{76, 80, 81, 83, 112, 144^\circ\}$ .<sup>123</sup> Both structures are intermediate in geometry.

The  $M(\text{CO})_4$  complexes do differ significantly in their reactivity from their  $\text{Fe}(\text{CO})_3$  analogs. For example, under conditions where  $\text{C}_4\text{H}_4\text{Fe}(\text{CO})_3$  reacts with  $\text{MeCOCl}$  and  $\text{AlCl}_3$  to yield the acetyl derivative in better than 95% yield the  $\text{C}_4\text{H}_4\text{Mo}(\text{CO})_4$  yields no such derivative.<sup>108</sup> This might indicate a difference in the electron density in the cyclobutadiene ring, but it should be noted that the proton chemical shifts in the  $\text{Fe}(\text{CO})_3$  and  $M(\text{CO})_4$  complexes are quite similar.

A general point we wish to make for a complex  $M(\text{CO})_n\text{L}$  ( $\text{L} =$  an organic group) is that geometry changes are not to be looked for in  $\text{L}$  alone. The  $M(\text{CO})_n$  fragment will adjust its geometry according to the quality of the bonding provided to it by  $\text{L}$ .

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#### Appendix

The computational procedure used by us was the extended Hückel method.<sup>124</sup> To obtain reasonable diagonal matrix elements for a metal center we carried out a complete charge iterative calculation on  $\text{CpMn}(\text{CO})_3$ . At self-consistency the metal atom carried a charge of 0.543+. This calculation resulted in converged metal  $H_{ii}$ 's listed in Table IV. The table also contains the diagonal matrix elements and Slater exponents for all the atoms studied. The Mn 3d function was taken as a linear combination of two Slater functions, with the exponents and coefficients<sup>125</sup> listed in Table IV. The Wolfsberg-Helmholz proportionality constant  $K$  was set at 2.0.

The same metal and ligand parameters were then used in all fragment calculations, irrespective of the d-electron configuration. The following distances were assumed:  $\text{M}-\text{C} = 1.80 \text{ \AA}$ ,  $\text{C}-\text{O} = 1.13 \text{ \AA}$ ,  $\text{M}-\text{Cl} = 2.30 \text{ \AA}$ .



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