Tetrahedral and Other M₂L₆ Transition Metal Dimers

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Abstract: This theoretical study shows how three factors influence the geometry and electronic structure of dimeric tetrahedral and square planar transition metal complexes of the M₂L₆ type. The factors are (1) the geometrical preference of the monomer, (2) the symmetry-restricted opportunities for coupling through the orbitals of the bridging groups, and (3) direct metal-metal overlap. In analyzing the first factor, we find that in tetrahedral d¹⁰ monomers of the MX₂Y₂ type, the angle between the better π acceptors and better π donors should be opened up. The structures of monomeric dinitrosyls are rationalized, including the minor deviations from MNO linearity. Superposition of the calculated MX₂Y₂ monomer structures into a X₂MY₂MX₂ dimer gives a reference point relative to which elongation or contraction of the bridge region as a consequence of through-bond bonding or metal-metal bonding can be evaluated. In the tetrahedral d⁸ dimers we find little direct metal–metal σ bonding, in the d⁶ dimers a strong metal–metal π bond. Locally square planar dimers are studied, with an emphasis on the interconversion of the alternate square planar and tetrahedral geometries. The orbitals of the bridging group are determinative here, with π-donors favoring the square planar extreme. The simple twist interconverting the two structures is symmetry forbidden. We study the hinging distortion in the square planar dimers, failing to find a controlling electronic effect for this soft surface. Other geometries, such as the directly metal–metal bridged Ni₂(CN)₆⁴⁻ type, are also examined.

The thesis of a series of theoretical investigations, of which this is the first contribution, is that there are three determinants of the geometrical and electronic structure of bridged metal dimer complexes: (1) the geometrical preference of the monomer fragment; (2) the opportunity for interaction offered up by the orbitals of the bridging group—a factor we have called in another context “through-bond coupling”; (3) direct bonding or antibonding overlap of primarily metal-centered bonding but especially on the structural consequences thereof; to the contribution of Cotton, who incisively analyzed the entire range of structural deformations in confacial octahedral dimers with respect to an ideal face-sharing structure; and to the work of Mason and Mingson on the role of bridging group orbitals on metal–metal distances. These and other workers have noted that direct metal–metal overlap may not be the sole cause of either a low-spin ground state or a short metal–metal separation. We view as our minor contribution the systematic theoretical analysis of all three factors in the context of the available structural information. This first paper deals primarily with “tetrahedral” metal dimer complexes of the general type 1.

![Diagram](Image)

Subsequent contributions will discuss triply bridging “octahedral” dimers, other less symmetrical structures, and polynuclear chains, while a previously published paper has analyzed weakly coupled systems of the Cu(II) dimer type.¹ ²

Structural Features of Tetrahedral Dimers

Structural information is available for a series of edge-bridged tetrahedral dimers of type 1, having 8, 9, or 10 d electrons per metal, with several examples for each configuration. This provides an ideal opportunity for theoretical investigation of the reasons for structural distortion and the nature of metal–metal interaction in bridged dimer complexes. We begin with an overview of the structural systematics of this type of molecule.

In describing the structure of a symmetrical tetrahedral dimer, it takes one distance, M–M or M–X, and one interior angle, M–X–M or X–M–X, to fix the geometry of the bridging region. A discussion of direct metal–metal bonding generates a natural emphasis on the M–M separation. But an equally valid focus is on the assembly of the dimer from two monomeric units sharing a tetrahedral edge. The perturbation of metal–metal bonding (or antibonding) then manifests itself as a distortion from the simple edge-sharing geometry. From this point of view the natural emphasis would appear to shift to the deviations of the interior angles from their idealized values shown in 2. Fully recognizing the interrelation of the angles and distances, throughout this paper we will speak of elongation or contraction of the bridging region in terms of the M–X–M angle increasing or decreasing. A discussion of this angle allows us to put on one scale diverse examples, many different metals and bridging groups, whose similarities and differences perhaps would be difficult to perceive otherwise. In our structures we will also include the MM distance for more complete specification of the bridge region.

Many tetrahedral dimers are known for metals with filled d shells. In metal halide dimers the geometries are quite similar, with examples shown in 3⁹ and 4⁶. Note the elongation of the bridge region (M–X–M angles greater than 70.5°), and an opening up of the angle between the terminal ligands. The bridge region is presumably stretched by closed shell repulsions. To compensate for the less than tetrahedral angle at the metal one could imagine that sp rehybridization opens up the
angle between the terminal ligands. Yet not all halide bridged d^{10} dimers give the appearance of elongation. Consider for instance the complex 5, with a relatively short Cu-Cu separation and an acute angle at the bridging iodides.\(^9a\) One could again blame rehybridization for the geometrical features—the small external angle imposed by the chelate bite size forcing a larger interior I–Cu–I angle—but perhaps one should first find out what are the geometrical preferences of an unconstrained \(\text{I}_2\text{Cu(NR}_3\text{)}(\text{AsR}_3)^{-}\) monomer. The related Zn(II) monomer (TMED)\(\text{ZnCl}_2\) has a Cl–Zn–Cl angle of 119.4°,\(^9b\) which is not at all different from the I–Cu–I angle of 116.5° in 5.

Structures of main group dimers can be related readily to the ideal tetrahedron because the ligands are generally of a similar electronic type (there are no strongly \(\pi\)-accepting ligands) and the \(d\) levels are usually not involved (they are filled and at lower energy). On the other hand transition metal complexes frequently have both \(\pi\) donor and acceptor ligands, and the high-lying \(d\) orbitals are of great importance to both metal–metal and metal–ligand interactions. It is the transition metal complexes that will receive our primary attention.

To begin our series of tetrahedral dimers we have the formally \(d^9\) species, 6, the structure of which was determined in a crystal with some disorder.\(^10\) The metal and chlorine positions are most accurately known, and it is clear that this dimer is also elongated in the bridge region; in fact, more elongated than in the previously mentioned dimetal hexahalides. However, while 3 and 4 are related to tetrahedral \(\text{MCl}_4\), the “monomer” of 6, the hypothetical \(\text{Co(NO)}_2\text{Cl}_2^{-}\), 7, will not be an ideal tetrahedron. Distortions prior to dimer formation are likely to be more serious, particularly with the \(\pi\) donor Cl and \(\pi\) acceptor NO on the same metal. In the polymeric dinitrosyl cobalt iodide, 8, metal–metal repulsions should open the I–Co–I angle.\(^2i\) Yet that angle is 96°, more acute than tetrahedral, and it is the \(\pi\) accepting nitrosyls which spread apart. Such metal–ligand interactions must be considered before the distortions of a dimer can be attributed to metal–metal interactions. This we will do.

There are several complexes structurally similar to 6, but with two less electrons, among them 9,\(^9j\) \(\text{10,12}\) \(\text{11,13}\) and \(\text{12,14,15}\). The major difference between the \(d^8\) and \(d^{10}\) complexes is the compression in the bridge region. The metal–bridge–metal angles are 70–77°, compared to 92° in 6. This compression and the 18-electron rule have led to the attractive postulate of a direct metal–metal bond in these molecules. However, note that the compression is accompanied by an increase in the interior angle at the metal. At the same time the external angles between the terminal ligands are greater than in 6. This is just what one would expect for a \(d^9\) monomer relative to \(d^{10}\). For instance \(d^{10}\) ML\(_4\) complexes are regular tetrahedra, while the \(d^8\) \(\text{CuCl}_2^{-}\) ion assumes a range of flattened tetrahedral geometries with the precise angle a function of the counterion or crystal packing.\(^16\)\(^17\) How much then of the geometry of the \(d^9\) dimers depends on them being built up from \(d^9\) monomer units and how much depends on the direct metal–metal bonding interaction? We will examine this problem. That the monomer geometry is important is signaled by a number of \(d^9\) \(\text{X}_2\text{MY}_2\text{MX}_2\) structures which are far from locally tetrahedral at the metal. These include \(\text{Cu}_2\text{Cl}_6^{2-}\),\(^18\) numerous o xo-bridged \(\text{Cu(II)}\) dimers,\(^19\) the hydride bridged \([[(\text{C}_6\text{H}_5)_3\text{P(CH}_2)_3\text{P}((\text{C}_6\text{H}_5)_3\text{P})_2\text{NiH}_2]^{2-}\) and the carbonyl bridged \([\text{PPPh}_3\text{Rh(CO)}]^{2+}\).\(^21\) In \(\text{Ni}_2(\text{CN})_6^{4-}\) there is a very short Ni–Ni bond of 2.30 A and no bridging.\(^22\) Nonbridged structures are observed for \(\text{Pt}_2\text{Cl}_4(\text{CO})_2^{2-}\) and \(\text{Pd}_2(\text{CNCN})_6^{2+}\) both with very short metal–metal bonds.

Among the many dimers with eight \(d\) electrons per metal there are three known with locally tetrahedral geometries. These are 13,\(^23\) \(\text{14,24}\) and 15.\(^25\) In 15 the acetylene is considered
to be one ligand, located at the center of the triple bond. The structures are remarkably similar, given how different the ligands are. Compared to the d⁹ dimers, these d⁸ binuclear complexes show a further compression in the bridge region and a dramatic decrease of the angle between the terminal ligands. Application of the 18-electron rule leads to the hypothesis of metal-metal double bonds in these dimers, and there is no doubt that direct metal–metal interaction is important.

Yet another interesting aspect of the structure of these molecules is that they are in fact locally tetrahedral rather than square planar at the metal. A low spin d⁸ monomer would of course be square planar. Indeed there is a host of molecules and structures of d⁸ dimers in which the local coordination at the metal is square planar. These are exemplified by 16 and 17. This common substitution pattern among the examples surveyed in the previous section is X = π donor and Y = π acceptor. We will work up to such a C₃H₆ fragment, X₂MY₄, by beginning with the orbitals of a hypothetical MH₄ species.

The energy of the d block orbitals of an MH₄ complex going from a square planar to a tetrahedral geometry, through a D₂d distortion, 18, is illustrated in Figure 1. The specific extended Hückel parametrization which we use to generate this figure is described in Appendix 2. Departing from D₄h, the high-lying b₂ orbital drops precipitously as overlap with the hydrides decreases, 19. At the same time a pair of e orbitals rises in energy as hydrogens move off the xz or yz orbitals and antibonding overlap increases, 20 → 21. This destabilization is relieved somewhat by interaction with a p orbital, which hybridizes the MO away from the hydrogens, 21. The other orbitals are much less sensitive to this distortion. The xy orbital energy remains constant since the hydrides always lie on the nodes, 22. As the structure deviates from tetrahedral in either direction, antibonding overlap increases, 20 → 21. This nonbonding in the tetrahedral geometry since the hydrogens also lie on the nodes at this point, 24. As the structure deviates from tetrahedral in either direction, antibonding interaction destabilizes the z² orbital.

The geometrical implications of this Walsh diagram are...
clear. A low spin d\(^8\) complex, configuration \((b_1^2a_1^2e^4\))\(^{2}\), will prefer a square planar geometry. A d\(^{10}\) complex will be tetrahedral. A d\(^6\) molecule, with one electron in the \(b_2\) orbital, will be poised between the two geometries. It is no surprise that a range of structures is exhibited by d\(^9\) complexes.

This is the story for MH\(_4\). We proceed toward the \(\pi\) bonded X\(_2\)MY\(_2\) by studying two sets of limited distortions in H\(_2\)ML\(_2\) tetrahedral complexes with \(L = H, Cl, CO\). First, the H–M–H angle was fixed at 110° and the L–M–L angle was varied. In a separate calculation the H–M–H angle was varied while L–M–L was fixed at 110°.

In these C\(_2\)\(_v\) complexes the \(x^2–y^2\) and \(z^2\) orbitals are both \(a_1\), the \(e\) set from MH\(_4\) splits into \(b_1\) and \(b_2\) (an orbital resembling 22 for each pair of ligands), and the \(xy\) orbital has \(a_2\) symmetry.

For d\(^{10}\) complexes the major differences in \(\pi\) donors and \(\pi\) acceptors appear in the orbitals of \(b\) symmetry. Figure 2a shows the relative changes in the energy of a \(b_1\) orbital of an H\(_2\)ML\(_2\) complex as the L–M–L angle is varied, 25. There is an increase in the slope with which the orbital varies with \(\theta\) along the series L = Cl < H < CO. The orbitals are similar in energy at \(\theta = 90^\circ\) but separate at wider angles. At an acute angle this \(b_1\) orbital will resemble 22 with only \(\sigma\) effects operating. At wider angles the \(\pi\) effects diminish and \(\pi\) effects become more important. In H\(_2\)MC\(_l_2\) the \(\pi\) interaction is repulsive, 26, decreasing so as smaller \(\theta\). This lowers the slope of the orbital in Figure 2a. Another way of describing the effect is to say that as the L–M–L angle diminishes from 180° \(\sigma\) antibonding increases but \(\pi\) antibonding decreases. This is for L = Cl. In contrast the \(\pi\) interaction for L = CO is stabilizing, bonding, as shown in 27. As the C–M–C angle closes, the orbital not only turns on \(\sigma\) antibonding but also loses \(\pi\) bonding. Thus the orbital varies more with \(\theta\) than the analogous orbital in the chloro complex.

Figure 2. (a, top): Energy of the \(b_1\) orbital in ML\(_2\)H\(_2\), \(L = H, Cl, CO\), as the LML angle \(\theta\) is varied. The HMH angle is fixed at 110°. (b, bottom): Energy of the \(b_2\) orbital in ML\(_2\)H\(_2\), \(L = H, Cl, CO\), as the HMH angle \(\varphi\) is varied. The LML angle is fixed at 110°.

The conclusion that is to be drawn from the different slopes is that for a d\(^{10}\) H\(_2\)ML\(_2\) at a fixed H–M–H angle the L–M–L angle will be greater between \(\pi\) acceptors than \(\pi\) donors.

Now consider a second distortion, one which varies the H–M–H angle while keeping L–M–L at 110°, 28. The corresponding changes in the \(b_2\) orbital as a function of \(\varphi\) are shown in Figure 2b. \(b_2\) is the other orbital descended from the MH\(_4\) \(e\) set, 29. The slope of this \(b_2\) orbital is smaller for L = CO than for L = Cl. Qualitatively what is happening is that the hybridization of \(b_2\), that is the extent to which a metal p orbital is mixed into \(yz\), increases with decreasing \(\varphi\). Increased hybridization leads to greater \(\pi\) overlap. Recalling that such \(\pi\) bonding is stabilizing for L = CO, destabilizing for L = Cl, we can understand the behavior of the curves in Figure 2b.

Another way of stating the consequences of the second test is to say that in d\(^{10}\) H\(_2\)ML\(_2\) complexes it is easier to close the angle between two ligands (here hydrogens) when L is a \(\pi\) acceptor than a \(\pi\) donor. Very nicely the two separate motions we analyzed give effects which reinforce each other. We extrapolate with some assurance to the X\(_2\)MY\(_2\) complex with \(X = \pi\) donor and \(Y = \pi\) acceptor. In X\(_2\)MY\(_2\) complexes the angle between the \(\pi\) acceptors will be greater.

As the \(b\) orbitals rise, another orbital, \(a_1\) in C\(_2\)\(_v\), but descended from the \(b_2\) orbital of D\(_{4h}\) MH\(_4\), drops. This orbital is mostly \(x^2–y^2\) near the tetrahedral geometry. In d\(^8\) and d\(^{10}\) complexes this is the highest occupied molecular orbital (HOMO), and acts as the brake which prevents the complex from opening to a square planar geometry. At lower energy lies another \(a_1\) orbital, largely \(z^2\). Let us consider the effects of the first distortion, defined in 25, for these two \(a_1\) levels. The results are shown in Figure 3. The behavior of the lower \(a_1\) level is easily interpreted. This level is primarily \(z^2\). As such, it is involved in \(\pi\) bonding near the tetrahedral geometry, decreasingly so as the square planar conformation is approached. The
\( \pi \) bonding, shown in 30 and 31, is stabilizing for \( L = \text{CO} \), destabilizing for \( L = \text{Cl} \).

The slopes of the higher \( a_1 \) orbital are influenced by mixing with a still higher-lying \( a_1 \) orbital, derived from an \( a_2 \) metal \( p \) orbital in square planar MH\(_4\). The important role of this orbital has been discussed by us in another context\(^{17} \). The position of this still higher \( a_1 \) is strongly influenced by the donor or acceptor characteristics of the ligands. For the cases under consideration by us the orbital appears as 32 (\( L = \text{Cl} \)) or 33 (\( L = \text{CO} \)). The combination 33 lies at much lower energy than \( a_1 \) to \( L = \text{M-L} \) bending is much less when \( L = \text{CO} \) than when \( L = \text{Cl} \). Because of this, going from a d\(^{10}\) to a d\(^9\) complex (removing an electron from this orbital) will be removing a more severe restraint to the opening of a Cl–M–Cl than a OC–M–CO angle. Thus, whatever the exact geometry of a d\(^{10}\) tetrahedral complex, the angle between \( \pi \) donors will open more than between \( \pi \) acceptors if an electron is removed from this orbital.

Having analyzed the separate consequences of \( \pi \) donor or acceptor substitution in \( \text{H}_2\text{ML}_2 \), we proceeded to test our conclusions on two more realistic complexes with simultaneous donor and acceptor substitution, \( \text{M(NO)}_2\text{I}_2 \) and \( \text{M(NO)}_2\text{Cl}_2 \).\(^{36} \) Figure 4 shows the d-block levels for \( \text{M(NO)}_2\text{I}_2 \) calculated for \( \text{M} = \text{Fe} \). The diagram for \( \text{M(NO)}_2\text{Cl}_2 \) is very similar. Our conclusions check out for both I–M–I and ON–M–NO angle variation. Thus the \( b_2 \) orbital affected by ON–M–NO bending has a greater slope than does the \( b_1 \) orbital involved in I–M–I bending at a similar angle. The \( a_1 (x^2–y^2) \) is the HOMO for a d\(^{10}\) configuration throughout most of the angular range. It is more responsive to I–M–I than ON–M–NO bending.

Next we allowed both X–M–X and ON–M–NO angles to vary simultaneously and computed for various d electron configurations those angles giving the lowest energy. The results are shown in Table I. Note that for all d electron configurations the angle between the \( \pi \) acceptor nitrosyl groups is greater than between the \( \pi \) donor halides. The angles calculated for \( \text{M(NO)}_2\text{I}_2 \) agree with those found in the Co(NO)\(_2\)Cl polymer 8. Thus we are not surprised by an unusual elongation in dimer 6, even before considering specifically its electronic structure. The distortions in the monomer tend in that direction.

The point should not be lost that we undertook the analysis of the "monomer" distortions with the eventual aim of probing bonding in the dimer. However, a nice side product of our understanding of these monomer distortions is that we can apply what we have learned to a large group of "real" monomers—tetrahedral d\(^{10}\) compounds. For instance, in a number of d\(^{10}\) diphosphine dinitrosyl complexes\(^{37} \) (for instance 34) as well as dicarbonsyls,\(^{38} \) exemplified by (CO)\(_2\)Pt(PPh\(_3\))\(_2 \), 35, as well as mixed carbonyls–nitrosyls,\(^{39} \) the better \( \pi \) acceptors, NO or CO, are spread apart, in contradiction to what one might have expected on the basis of a steric argument.\(^{40,41} \)

### Table I. Calculated M(NO)\(_2\)I\(_2\) and M(NO)\(_2\)Cl\(_2\) Structures

<table>
<thead>
<tr>
<th>Compound</th>
<th>Angle</th>
<th>d electron occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{M(NO)}_2\text{I}_2 ) (^{a} )</td>
<td>I–M–I</td>
<td>97 107 105</td>
</tr>
<tr>
<td>N–M–N</td>
<td>121 124 109</td>
<td></td>
</tr>
<tr>
<td>M–I–M (^{c} )</td>
<td>83 73 75</td>
<td></td>
</tr>
<tr>
<td>( \text{M(NO)}_2\text{Cl}_2 ) (^{b} )</td>
<td>Cl–M–Cl</td>
<td>103 112 105</td>
</tr>
<tr>
<td>N–M–N</td>
<td>120 124 110</td>
<td></td>
</tr>
<tr>
<td>M–Cl–M (^{c} )</td>
<td>77 68 75</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a} \) Computed with M–N–O = 160°, as in the experimental dimer structure (ref 2). \(^{b} \) Computed with M–N–O = 170°, as in the experimental dimer structure (ref 10). \(^{c} \) Extrapolated dimer bridge angle if two such monomers are superimposed. \(^{d} \) High spin configuration.

\( \text{ON} = \text{Cl} \) or \( \text{CO} \). Filled, this pair or orbitals largely cancel out. For \( \text{H}_2\text{MCI}_2 \), the upper \( a_1 \) has a large negative slope and the lower \( a_1 \) a small positive slope (Figure 3). For \( \text{H}_2\text{M(CO)}_2 \), both upper and lower orbitals have a small negative slope as C–M–C is closed. For these angular distortions the energy change of both \( a_1 \) orbitals combined is essentially the same for \( L = \text{Cl} \) or \( \text{CO} \). Filled, this pair or orbitals does not have a differentiating effect on Cl–M–Cl vs. OC–M–CO bending. However, the sensitivity of the \( \text{H}_2\text{ML}_2 \) upper

![Figure 4](image-url)

**Figure 4.** (a, top): Energy levels of Fe(NO)\(_2\)Cl\(_2\) as the ON–Fe–NO angle is varied. (b, bottom): Energy levels of Fe(NO)\(_2\)I\(_2\) as the IM–I angle is varied.

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Copper complexes are known with two phosphine and two π donor ligands in which it is the phosphines which spread apart. However, all of these involve chelates or bridge systems in which the donor–metal–donor angle is restricted, so that sp hybridization effects could be responsible.

Still another distortion that occurs in the dinitrosyls is some departure of the M–N–O unit from linearity. We think that we understand the origins of this deformation. The nitrosyls should bend toward each other at a small N–M–N angle, away from each other at a large N–M–N angle. The argument is given in Appendix 1.

If one electron is removed from our $X_2MY_2$ models, it will come from the high lying $a_1$ (mostly $x^2 - y^2$) orbital. This orbital rises sharply as the angle between donors is increased, but is less sensitive to the angle between acceptors. Thus in a $d^9$ relative to a $d^{10}$ complex the angle between $\pi$ donors should increase, but that between $\pi$ acceptors less so. Our calculations on $\text{M(NO)}_2X_2$ complexes indicate that for $X = \text{Cl}$ or $I$ the $X$–M–$X$ angle will open by $9-10^\circ$ in going from a $d^{10}$ to a $d^9$ metal. The angle between the nitrosyls, however, will open only $4^\circ$ for $X = \text{Cl}$ and $3^\circ$ for $X = I$. Note for further reference that these are also the changes observed in going from the cobalt dimer, 6, to the iron dimers 9–11.

Were a second electron removed from the upper $a_1$ orbital to give a $d^8$ diamagnetic complex, the result would be a square planar structure. An alternative is a high spin $d^8$ system in which the second electron is removed from the highest orbital of $b$ symmetry, the orbital pushed up by the antibonding interaction, 36, with the strongest $\pi$ donor. As noted above, this orbital is highly sensitive to the angle between the other ligand pair. Removing one of the $b$ electrons on going from $d^9$ to high spin $d^8$ releases a severe constraint on that angle. The weakest $\pi$ donors or the strongest $\pi$ acceptors should draw closer together in a high spin $d^8$ (relative to $d^9$) complex, while the angle between the best $\pi$ donors should be relatively unchanged.

The calculated geometries of high spin $d^8$ $\text{M(NO)}_2X_2$ (Table I) behave as expected, the ON–M–NO angle decreasing sharply while the X–M–X angle remains almost unchanged. Experimentally, in the high spin Ni(II) complex $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ the angle between the $\pi$ donor bromines is $123^\circ$ while that between the phosphines is an acute $110^\circ$. Some related cases are also consistent.

The previous analysis has been directed toward the effect of $\sigma$-donors and acceptors on the angular distortions in a tetrahedral complex. The $\sigma$ effects have been by-passed simply because the known dimers are substituted with $\pi$ active groups such as Cl, NO, CO. We now return to the role of $\sigma$-donation and acceptance.

Let us go back to $\text{MH}_4$ and open up one angle $\theta$, defined in the same way as it was in 25. The metal orbitals strongest affected by this motion are the metal $x$ and $x^2 - y^2$, $z^2$ is mildly moved and $xy$ and $yz$ by symmetry remain at constant energy. The effect of $\sigma$ donation or acceptance may be simulated by varying the energy of the two ligand orbitals being moved. In the calculations this is easily done by changing the $H_{\sigma}$ of the two hydrogen.

Both $x^2 - y^2$ and $xz$ are lowered in energy as the ligands moved are made worse $\sigma$ donors (lower $H_{\sigma}$ more electronegative) and both are raised when the ligands are made better $\sigma$ donors (higher $H_{\sigma}$, more electropositive) than the remaining two hydrogens. But the differential effect is greater on the $xz$ orbital. Its slope is diminished for a worse $\sigma$ donor.

increased for a better $\sigma$ donor. Through this controlling effect we come to the conclusion that in a $d^{10}$ tetrahedral complex the angle between the better $\sigma$ donors will be increased, that between the worse $\sigma$ donors decreased from the reference tetrahedral angle.

At times the $\pi$ and $\sigma$ effects may conflict. For instance in diphostine dinitrosyl complex 34 the phosphine is clearly the better $\sigma$ donor and nitrosyl the better $\pi$ acceptor. In this case the $\pi$ effect clearly dominates and the N–M–N angle is wider than the P-M-P angle.

With less $\pi$ active groups it is difficult to assess the relative merits of $\sigma$ donation and $\pi$ acceptance. Perhaps the $\sigma$ effect is relevant to the geometry of the iodide bridged Cu(I) dimer, 5. If we choose as a drastically simplified monomer model $\text{I}_2\text{Cu(NH}_3)_2$ and optimize its geometry, we obtain N–Cu–N 96°, I–Cu–I 126°. We think this distortion is dominated by the relative electronegativity or $\sigma$ donation effects, but obviously the steric bulk of the I ligands could be playing a role. If the dimer (NH$_3$)$_2$Cu$_2$Cu(NH$_3$)$_2$ is constructed as a simple superposition of the calculated monomer units, it would have a Cu–I–Cu angle of 54°. So the observed angle of 63.5° in 5 may actually represent an elongation!

There is no question that the molecular orbital argument leading up to our general conclusion for $Y_2\text{MX}_2$ geometries is a labored one. We were persistent in seeking the argument out, for in dealing with approximate molecular orbital calculations of the extended Hückel type one definitely needs the supporting structure of a symmetry and overlap based explanation. We proceed to combine the $X_2MY_2$ units to form the dimers.

The Electronic Structure of the Dimers

The behavior of all the d levels of $\text{M}_2(\text{NO})_4$ on deformation of the bridge is shown in Figure 5. $D_{2h}$ symmetry is maintained throughout. The rise and fall of all those levels gives a messy appearance to this figure, but hidden in it is a great deal of order. First we draw a schematic representation of the d orbitals at some realistic bridging geometry. This is done in Figure 6. The levels are not arranged in order of energy here, but are grouped in pairs according to their metal character. One immediately recognizes that these ten orbitals are symmetric (S) and antisymmetric (A) combinations, with respect to the xy plane, of the monomer orbitals we have just consid-
Metal–metal interaction is \( \delta \) type and not significant at realistic metal–metal separations.

The \( 2b_{1u} \) pair starts out at a large \( M-\Pi-M \) angle (long \( M-M \)) with \( 2b_{1u} (S) \) above \( 2b_{1u} (A) \). This is again through-bond coupling at work, with halogen orbitals destabilizing the \( 2b_{2u} \) combination. But \( 2b_{1u} \) is metal–metal \( \pi \) bonding and \( 2b_{1u} \) is metal–metal \( \sigma \) antibonding. As the \( M-\Pi-M \) angle drops and correspondingly the metal atoms come together, the direct overlap stabilizes \( 2b_{1u} \) and destabilizes \( 2b_{1u} \). The two levels cross at \( M-\Pi-M < 60^\circ \). The through bond coupling pattern also sets the order \( 2b_{1u} (A) \) below \( 2b_{1u} (S) \) in the \( xz \) pair. Because of the hybridization apparent in Figure 6, the through-space interaction is turned on only slowly, and the crossing of these \( \pi \) bonding levels occurs to the left of Figure 5.

Direct and indirect effects are also operative in the levels descended from the monomer \( a_1 \) pair—\( a_1 \) and \( b_1u \) in the dimer \( D_{2h} \) symmetry. Their analysis is somewhat complicated by the presence of two \( a_1 \) and two \( b_1u \) levels. The mixing of the two could be seen in the comparison of Figures 7 and 4a, where the lower \( a_1 \) and \( b_1u \) energy sum fell more steeply than the lower \( a_1 \) in Figure 7, while the upper \( a_1 \) and \( b_1u \) sum rose more sharply with decreasing \( M-\Pi-M \) angle. A consequence of this mixing is that in each level \( x^2 \) and \( x^2 - y^2 \) mix, and this will still have an impact on our discussion of the evidence for direct metal–metal bonding in the \( d^9 \) dimers.

We proceed to examine the bonding in \( d^{10} \) and \( d^9 \) dimers using the information of Figure 5. In the \( d^{10} \) dimers all ten levels are occupied. The result is a slight repulsion that elongates the dimer relative to the single metal complex. The calculated \( M-X-M \) angles of the \( d^{10} \) monomers are \( 94^\circ \) for \( X = Cl \) and \( 92^\circ \) for \( X = Br \), compared to \( 83^\circ \) and \( 77^\circ \) estimated from superimposing the calculated monomer geometries. Table I. We have already pointed out that the geometry of 6 is unusually elongated, \(^{10}\) with a Co–Cl–Co angle of \( 92^\circ \), because the metal–ligand interactions in the monomer tend in that direction.

If each metal center carries nine \( d \) electrons, then the highest energy orbital in Figure 5, \( 2b_{1u} \), will be vacant. The gap between this orbital and the next highest level is nearly 1 eV at \( M-\Pi-M = 75^\circ \), which should be sufficient to ensure a low-spin diamagnetic complex, as is observed in the cited examples 9-12. The \( 2b_{1u} \) orbital rises sharply as the bridge angle is closed. Thus, when this orbital is vacant, the angle should be smaller than when it is filled. Our calculated geometries do show this trend. The optimum \( M-X-M \) angles calculated for \( d^9 \) com-
plexes are 76° for X = I and 74° for Cl compared to 94° and 92° in the d10 complexes. Experimentally the 73° angle in Fe2(NO)4I2, 9,2 is also more acute than the 92° angle in Co2(NO)4Cl2. 6,10

Is there a direct metal--metal bond in these d9 complexes? Yes and no. Since the b1u orbital rises steeply as the bridge region is compressed and the metals approach one another, there is a temptation to say that this LUMO of the d9 dimer is primarily a metal--metal antibonding orbital. If that is so, it should have a bonding counterpart which decreases in energy with decreasing metal--metal separation. 2a would be one candidate for this bonding role, but, as one can see in Figure 5, it does not have the desired slope. Moreover, 2a is more δ-like than σ over a large range of angles. This was implied in the schematic drawings of Figure 6 and is made more specific by Table II, which lists the composition of the a6 and b1u levels of the dimer as a function of M--X--M angle.

If 2a is not a good candidate for the metal--metal σ bond, we must consider the lower 1a1g. This orbital is primarily z2 and so better fits the σ specification. It falls in energy with decreasing metal--metal distance. If any level is to be identified as the metal--metal σ bond, this must be the one.

Nevertheless, we remain hesitant about saying that direct metal--metal interaction is responsible for the compression of the bridging region in the d9 complexes. First, when we examine the energy of not only the 1a1g, but the entire block of occupied a1g orbitals, 1a1g + 1b1u + 2a, we find that the contribution of the six electrons is almost independent of the bridge angle. Second, and more important, the calculated and experimental d electrons per metal, d0 tetrahedral dimers which are known have either 13-15. Reasoning back from the fact that the angle between the terminal ligands in these dimers (88-100°) is much smaller than in the d9 complexes (116-122°), we infer that the second vacant orbital must rise as these angles close. The b2u and b3g orbitals (Figure 5, redrawn in 37, b2u and 38, b3g) fulfill this requirement. In Figure 5 these levels are buried among the other d orbitals. However, as the terminal ligands move closer together, the average energy of the b2u and b3g will rise much as the b2 orbital does in the monomer (Figure 4a).

The d9 tetrahedral dimers which are known have either phosphido or acetylene bridges, 13-15. We therefore went over to a different model compound, Rh2(CO)4(PH2)2. Figure 8 shows the way that the energy levels for this model vary with deformation of the bridge region. The b3g and b2u orbitals lie below the highest 2b1u level. The levels are nicely separated (1.4 eV at M--PH2--M = 70°) with the metal--metal π-bonding b2u orbital at lower energy. The diamagnetism of the d8 dimer with 2b1u and b3g orbitals vacant is assured. The phosphido bridged dimers have also been the subject of an excellent study by Burdett, 46 where similar level orderings are obtained.

![Figure 8. Energy levels of tetrahedral Rh2(CO)4(PH2)2 as a function of Rh-P-Rh angle. Only selected levels are identified by symmetry type.](image)

### Table II. Occupation of Specified Metal Atomic Orbitals in Fe(NO)4I2

<table>
<thead>
<tr>
<th>MO</th>
<th>AO*</th>
<th>60°</th>
<th>70°</th>
<th>80°</th>
<th>90°</th>
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<tr>
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<td>s + z</td>
<td>2</td>
<td>6</td>
<td>9</td>
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<td></td>
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<tr>
<td>2a</td>
<td>s + z</td>
<td>16</td>
<td>13</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>x^2 - y^2</td>
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<td>45</td>
<td>58</td>
<td>68</td>
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<td>z^2</td>
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<td>8</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>1b1u</td>
<td>s + z</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x^2 + y^2</td>
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<td>7</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>z^2</td>
<td>38</td>
<td>45</td>
<td>53</td>
<td>60</td>
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<tr>
<td>1a1g</td>
<td>s + z</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>x^2 - y^2</td>
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<td>5</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>z^2</td>
<td>62</td>
<td>53</td>
<td>44</td>
<td>38</td>
</tr>
</tbody>
</table>

* We have added together the population of the metal 4s and 4p orbitals.

That the b2u and b3g levels are so nicely split apart in energy is not a consequence of the smaller OC--Rh--CO angle. That angle assures the rise in energy of the b2u--b3g pair, but not their relative ordering, which in our Fe2(NO)4I2 calculations was b2u below b3g, with a level crossing at M--I--M < 60°. The slopes of the b2u and b3g levels are similar in Fe2(NO)4I2 and Rh2(CO)4(PH2)2, but their ordering differs. The change in ordering must come about as a result of the change of the bridging ligands from I or Cl to PH2. This was proved by a calculation on a hypothetical Rh3(CO)4Cl2 (the real molecule has a very different structure, 16) in which the OC--Rh--CO angle was the same as in Rh2(CO)4(PH2)2. The results are shown in Figure 9. Both b2u and b3g are at higher energy, but their ordering is similar to that in Fe(NO)4I2. The hypothetical tetrahedral Rh3(CO)4Cl2 would be a triplet ground state.

Here we see clearly the consequences of a differential through bond coupling effect. The orbitals of the Cl and PH2 bridges obviously have a major effect on the energy ordering of the higher levels of the dimer. It is important to analyze what has happened.

Referring back to 38, we note that as a first approximation the b3g orbital is not affected by the bridging ligands. Indeed a comparison of Figures 8 and 9 shows that the b3g level is essentially identical in the two cases. The b2u level does mix into
Square Planar vs. Tetrahedral Dimers

We now examine the question in the context of alternative geometries 42a and 42b for Rh₂(CO)₄X₂, X = Cl, PH₂. We noted earlier that the locally square planar d⁸ complexes come in two types, all planar, as shown in 42b, and with the coordination planes inclined relative to each other, as in the actual structure of Rh₂(CO)₄Cl₂. 16. The next section will discuss this "hinge" type of distortion, but for reasons of simplicity in comparing the tetrahedral and square planar extremes we assume in this section the D₂h structure 42b. 47

The simplest intramolecular motion which interconverts the two D₂h forms 42a and 42b is a concerted twisting of the two bridging ligands (or the four terminal groups) around the metal–metal axis. This motion was considered in our earlier discussion of Cu₂Cl₄. 3,5 The intermediate symmetry is C₃v. We have constructed potential energy surfaces for these twists. Their presentation is complicated by the fact that the optimum angles at the bridge are very different in the two extremes. For instance, for X = Cl Rh–Cl–Rh = 50° in the tetrahedral geometry, but 97° in square planar. For X = PH₂ Rh–P–Rh is calculated as 64° in tetrahedral, 102° square planar. Instead of presenting a curve that shows an actual twisting energy, we show a correlation diagram, Figure 10, for Rh₂(CO)₄Cl₂ between the above cited optimum geometries in either extreme. The compression–elongation does not break the C₂h symmetry.

The most striking feature of this diagram, as well as of the one for Rh₂(CO)₄(PH₂)₂, is that the twisting motion is accompanied by a level crossing. It is a symmetry forbidden reaction. The vacant levels on the tetrahedral side are b₂u and b₃g. One of these levels correlates across, but the other one does not. The immediate implication is that the existence of isomeric d⁸ dimers, square-planar and tetrahedral, separated by a sizeable activation energy, is in principle a possibility. This interesting prediction is tempered by our realization that the interconversion of the extreme forms 42a and 42b need not necessarily proceed by a simple twist. Alternatively it could come about by an associative equilibrium with other ligands, or by rupture of a single M–X bond.

We still have not answered the question as to why the chloro bridged dimer prefers to be square-planar while the phosphido bridged molecule is tetrahedral. Although metal–metal bonding favors tetrahedral dimers, it is not the sole reason for the different geometries of halide and phosphido bridged complexes. Even if the b₂u (σ) orbital is occupied in a tetrahedral Rh₂(CO)₄Cl₂ complex, the square planar dimer is still lower in energy by 2.3 eV at the respective minima. The phosphido bridged complex, on the other hand, prefers the tetrahedral structure by 0.55 eV over the square planar one. If one compares the PR₂ and Cl ligands, one comes to the conclusion that they differ most in those orbitals which are out of the MXMX plane. We focus our attention on these.

There are two metal orbitals which can interact with out-of-plane bridge ligand wave functions. These are the b₂u and b₁g combinations of Figure 6 (b₁g is also shown in 37). The corresponding orbitals in the square planar complex are 44 and 45. In 44, the square planar counterpart of 37, the d orbitals

![Diagram](image-url)
are no longer in the plane of the terminal ligands. As a result, they are not hybridized toward the center of the bridge system, and so will interact less with the bridge ligand orbitals. At Rh–X–Rh = 101.2°, 44 with Cl bridges is 0.51 eV above the equivalent with PH2 bridges. In the tetrahedral geometry (Rh–X–Rh = 57.8°) 37, with X = Cl, is 1.16 eV above the orbital with X = PH2. With two electrons in these orbitals the difference amounts to 1.3 eV greater preference for the square planar dimer when X = Cl instead of PH2.

The tetrahedral 46 and 45 do not differ in hybridization, but do have considerably different M–X–M angles. This is illustrated in a somewhat exaggerated manner in 46 and 47.

46

The bridge–metal π bonding is greater in the tetrahedral geometry. In the square planar dimer the energy of 47 is 0.66 eV higher with Cl bridges than with PH2 bridges. In the tetrahedral dimer with Cl bridges, 46, is 1.11 eV above the orbital with PH2 bridges. With two electrons in these orbitals the interactions with Cl bridges again favor the square planar geometry more than the same interactions with PH2. This time the difference is 0.9 eV.

The tendency for the dimer to adopt a square planar rather than tetrahedral structure is 2.88 eV greater in Rh2(CO)4Cl2 than in Rh2(CO)4(PH2)2. Of this difference most (~2.2 eV) arises from the out-of-plane interactions we have just described.

The similarity of the acetylene bridged complex 15 to the other dimers is now obvious. Acetylene has no high-lying filled orbitals which are antibonding between the carbons. Such "out-of-plane" orbitals could push the geometry toward square planar, just as they do in the Rh2(CO)4Cl2 case. In general we would expect any d4 four-coordinate dimer to be tetrahedral about the metals if the bridging ligands are π donors. In particular Rh2(CO)4(PR2)2 should be tetrahedral, in contrast to Rh2(CO)4Cl2. If the bridging ligands are good π acceptors, then other distortions, to be discussed below, may yet occur.

The Hinging Distortion in Square Planar Dimers

In the geometries of locally square planar d8 dimers one notices a variation in the "hinge" angle λ, the dihedral angle between the local coordination planes. In many molecules λ = 180°,29 but in a significant subset λ is less than 180°, or the molecule is hinged.28,46 The structures themselves hint that the energies involved in this particular deformation are small, for electronically quite similar species are sometimes planar, sometimes hinged. For instance, in the ubiquitous Pd(II) halide bridged allyl complex series, 49, one has planar geometries for the following allyl substitution patterns: 2-methyl,29 1,1,3,3-tetramethyl,29 2-neopentyl,29h cyclobutyl,29g and the unsubstituted allyl29 while 1,2,3-trimethyl,29h 2-methyl-1-tert-butyl,29h 1,3-dimethyl,29h and cycloheptyl28m are all hinged. Among the Rh(I) chloride bridged dimers X3RhCl2RhY2 one has a planar structure for X2,Y2 = cyclocta-1,5-diene29b but a hinged one for X2 = cycloocta-1,5-diene, Y = P(OPh)3,28g X,Y = ethylene,28f X,Y = CO,2b X2Y2 = 4-methylpenta-1,3-diene,28h and X = CO, Y = PMe3Ph.28f

We have studied the hinging distortion for a model Rh2Cl2(CO)4X2, which has been examined by Burdett as well.46 The calculated equilibrium geometry in our calculations is planar, λ = 180°. This is not the correct geometry, which in the solid state has λ = 124°. However, the computed variation of the energy with λ gives the expected picture of a soft motion. To deform from λ = 180° to λ = 140° costs 3.1 kcal/mol, to λ = 120° 7.5 kcal/mol. The way that the individual energy levels vary with λ is shown in Figure 11. There is no obvious controlling orbital in the picture. Some levels move up, mainly those antisymmetric with respect to the xy plane; some move down, mainly the symmetric ones. But the overall effect is slight. The bridging chlorines provide effective coupling between the metal orbitals over a wide range of λ. The softness of the potential energy curve for hinging was checked by varying the bridging ligand X in Rh2X2(CO)4. For instance for X = PH2 a bent molecule, λ ~120°, was preferred to a planar one by approximately 9 kcal/mol. Unfortunately we see no way at this time to predict whether a given d8 dimer will be hinged or planar. Steric and crystal packing forces are likely to be determinative, for there is no large identifiable electronic effect influencing this distortion.

Dimers with Fewer Electrons and Unusual Geometries

The previous sections have dealt with tetrahedral d8, d9, and d10 dimers and square planar d8 species. We turn briefly to a discussion of the tetrahedral dimers with fewer than eight d electrons and conclude with an account of some less typical geometries.
b\textsubscript{2u}. The lower seven levels are close together, and their spacing is to some extent sensitive to the Fe-SR torsion angle. Again we cannot predict the magnitude of the magnetic coupling, except to say that a very large negative $J$ is unlikely and that the maximum magnetism should correspond to four unpaired spins. The experimental facts are more definitive in giving a $J = -148$ cm$^{-1}$.\textsuperscript{33}

An unusual carbyne bridged series of complexes of Nb and Ta has been synthesized by Mowat and Wilkinson.\textsuperscript{34a} A structure of one compound was determined\textsuperscript{34b} and is shown in 53 ($R = \text{SiMe}_3$). If the CR bridge is viewed as triply negative, this is formally a Nb(V) d\textsuperscript{0} complex. We studied a model compound with $R = \text{H}$. Though the charge on Nb is far from +5, this is like a d\textsuperscript{0} complex in that ten orbitals, identifiable as primarily d, are vacant. Our calculations fully support Wilkinson's view that this is a quasi-aromatic system. The carbyne lone pairs donate to the appropriate symmetry Nb d orbitals, as shown in 54a and 54b. A gap of 1.3 eV between the HOMO and the bottom of the d band is sufficient to yield a diamagnetic complex.

There is a set of d\textsuperscript{9} dimers that do not bridge but form direct metal-metal bonds. Ni\textsubscript{2}(CN)\textsubscript{6}\textsuperscript{4-} and Pd\textsubscript{2}(CNCH\textsubscript{3})\textsubscript{6}\textsuperscript{2+} have had their structures determined.\textsuperscript{22a,c} Each metal is nearly square planar, and the coordination planes are twisted by approximately 90° relative to each other, as shown schematically in 55. The Ni-Ni separation is very short, some 0.2 Å shorter than the supposedly Ni-Ni single bonded bridged dimer 12. The Pd dimer also has a short Pd-Pd distance of 2.53 Å. Pt\textsubscript{2}(CO)\textsubscript{2}C\textsubscript{14}\textsuperscript{2-} has a related structure, but with the coordination planes forming an angle of 60° and the carbonyls transoid.\textsuperscript{22b} It also has a short Pt-Pt separation of 2.58 Å.

Our calculation on Ni\textsubscript{2}(CN)\textsubscript{6}\textsuperscript{4-} in an idealized geometry close to that observed in the crystal structure\textsuperscript{22a} yielded a picture typical of square planar d\textsuperscript{8} systems. A sizeable gap of 2.6 eV separated filled from unfilled levels. A potential energy curve for torsion around the Ni-Ni bond is shown in Figure 12. There is little resistance to a small twist from the observed orthogonal form, but a large barrier to making the molecule planar. The source of that barrier is traced by us to the expected steric repulsion. When those repulsions are removed by incorporating the ligands in a ring, an all planar structure is
feasible. This is found in a recent structure of \((\text{CH}_3)_2P(\text{CH}_2)_3\)Au_2Cl_2.\textsuperscript{22d}

Why do these d\textsuperscript{9} dimers avoid the alternative bridging geometry? To probe this question we studied a model tetrahedral dimer \textsuperscript{56}. Its energy came out 1.2 eV above the observed structure. More important, there was a minute gap of 0.06 eV between the filled and unfilled levels. The tetrahedral dimer would be a high spin complex or would be subject to a second-order Jahn–Teller distortion.

The level pattern in \textsuperscript{56} is quite different from that of the other d\textsuperscript{9} tetrahedral dimers which we have studied earlier. The 2b\textsubscript{1u} level, which in Figure 5 could be seen clearly isolated as the highest d band orbital, in Ni\textsubscript{2}(CN)\textsubscript{6}\textsuperscript{4–} finds a place in the middle of the band. It is depressed in energy by interaction with the relatively low-lying \(\pi^*\) acceptor orbitals of the bridging cyanides—in contrast to in-plane donation in the chloro and phosphido bridged cases discussed earlier. In general the terminal and bridging cyanide \(\pi^*\) levels keep any of the d levels from rising too high and forming a well-defined gap between filled and unfilled levels. We think a similar effect pushes (PPh\textsubscript{3})\textsubscript{2}Rh(CO)\textsubscript{2}Rh(PPh\textsubscript{3})\textsubscript{2} away from an idealized tetrahedral dimer structure and toward the most interesting geometry that it does assume.\textsuperscript{21} In general we expect X\textsubscript{2}MY\textsubscript{2}MX\textsubscript{2} species with Y = \(\pi\)-acceptor to avoid the tetrahedral dimer structure.

While we have examined a number of geometrical extremes, it is clear that our job is far from complete. For instance we have avoided discussion of the pathways interconverting the Ni\textsubscript{2}(CN)\textsubscript{6}\textsuperscript{4–} type dimers with their tetrahedral and square planar counterparts, as well as the possible processes interchanging sites in all these species. We have not discussed the carbonyl type structures, represented by (PPh\textsubscript{3})(NO\textsubscript{2})\textsubscript{2}Ir-Ir(NO\textsubscript{2})\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} or the triply bonded M\textsubscript{2}(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{6} or W\textsubscript{2}(NMe\textsubscript{2})\textsubscript{6}.\textsuperscript{19} These are problems for the future.

The conclusions we come to have been stated in the introductory paragraph of this paper. The geometrical and electronic structure of these tetrahedral dimers is set by three factors: the geometrical preference of the monomer, the differential through-bond coupling, and direct metal–metal bonding. While our simultaneous analysis of all three factors may have been involved, it has led us to a better understanding of the dimers as well as some interesting sidelights on the geometry of d\textsuperscript{10} MX\textsubscript{2}Y\textsubscript{2} complexes and the choice between tetrahedral and square planar dimers.

**Acknowledgment.** We have benefited greatly from discussions with other members of our group, especially Joseph Lauher and David Thorn. Technical assistance in the preparation of this manuscript by E. Kronman and J. Jorgensen is gratefully acknowledged. Our research was supported by the National Science Foundation under Grant GP28137 as well as through the Materials Science Center at Cornell University.

**Appendix I**

**Bending of Nitrosyl Groups in Tetrahedral Dinitrosyl Complexes.** In tetrahedral dinitrosyl complexes the M–N–O angles often depart by moderate amounts from 180°. Thus in 8 the N–Co–N angle is 118° and the nitrosyls are bent toward each other, with a Co–N–O angle ~170°. In (P\textsubscript{3}H\textsubscript{2})\textsubscript{2}Rh(NO\textsubscript{2})\textsubscript{2} the N–Rh–N angle is 157.5° and the nitrosyls are bent away from each other with an Rh–N–O angle of 159°. In the intermediate case 34 with an N–Os–N angle of 139° the bending is less, with an average Os–N–O angle of 177° bent away. Though the extent of bending in these cases is considerably less than in the strongly bent nitrosyls, the variable direction of bending is interesting and has received some attention.\textsuperscript{37a,40,41,53} The degree and direction of this bending can be explained quite easily as a secondary function of the N–M–N angle. The angle between the nitrosyls is set by the factors we have already discussed; that is, the better the possible \(\pi\) bonding with the metal donor orbitals the wider will be the N–M–N angle.

Once the general magnitude of the N–M–N angle is established, it is possible to talk about the bending of the nitrosyls. Two metal orbitals are most affected by this bending motion, \textsuperscript{57} and \textsuperscript{58}. Orbital \textsuperscript{57}, of \(b_1\) symmetry in \(C_{2v}\), is destabilized by the ligand lone pair at acute N–M–N angles. Distortion A, bending the nitrosyls away from each other, enhances this repulsion by placing the lone pair density at an effectively smaller angle. The NO \(\pi^*\) orbitals are not effective in stabilizing this distortion because the N p orbital density will be near the node of the metal d–p hybrid. Distortion B, on the other hand, places the NO lone pair on the node of the metal orbital and allows the NO \(\pi^*\) to stabilize the metal orbital. Thus interactions with orbital \textsuperscript{57} favor distortion B, bending the nitrosyls toward each other.

Interactions with the \(a_1\), predominantly \(x^2–y^2\), orbital \textsuperscript{58}, however, favor distortion A. As the nitrosyls bend apart, the NO lone pair–metal d antibonding overlap decreases, and the \(\pi^*\) orbitals become more metal–nitrosyl bonding. In distortion B this orbital is pushed up by increased repulsions between the
Table III. Bending Preference of Nitrosyls in Co(H)2(NO)2- as a Function of N-Co-N Angle

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<th>N-Co-N°</th>
<th>Co-N°</th>
<th>Co-N-O°</th>
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</tbody>
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° The angles are defined in 59.

Table IV. Metal 4s and 4p Exponents Which Give Reasonable Calculated Metal-Metal Bond Distances

<table>
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<tr>
<th>Compound</th>
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<th>Exptl</th>
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Appendix 2

Computational Details. All the calculations were of the extended Hückel type.44 Parameters used previously44 for carbon, nitrogen, oxygen, and hydrogen were kept fixed during all charge iterations. Exponents for the 3s and 3p orbitals of chlorine and phosphorus were calculated from Burns’ rules.55 Exponents for the 5s and 5p orbitals of iodine are from the work of Clementi and Roetti.56 For metals of the first transition series 3d orbital exponents for the +1 ions were taken from the work of Richardson et al.57 For second-row metals 4d, 5s, and 5p exponents are those determined by Basch and Gray.58

It has been noted59 that the available 4s and 4p exponents for the first transition series 55,56,60 are small compared to the corresponding parameters for the second- and third-row metals.58 Increasing the exponents for the first-row orbitals leads to a larger interaction with ligand σ orbitals and generally better computational results.59,61 In particular the diffuse metal s and p orbitals we have used previously result in small negative metal-metal overlap populations in transition metal dimers, even in complexes such as Fe2(CO)92- which have obvious metal-metal bonds. We have adjusted the metal 4s and 4p exponents to give proper metal-metal distances in dimers with unsupported metal-metal bonds. Except for the metal-metal distance the experimental geometries were maintained throughout these calculations. The exponents of the s and p orbitals were assumed to be equal for a given metal. To emphasize the approximate nature of these parameters they are estimated only to two places in Table IV. In order to check the behavior of the parameters of Basch and Gray58 for the heavier metals the Mo-Mo bond length in Mo2(CO)102- was calculated using these exponents. The calculated Mo-Mo distance was 3.11, the experimental 3.13 Å.61

The exponents for metal 4s and 4p orbitals listed in Table IV are now more in line with the parameters for the heavier metals58 which also seem to give reasonable metal-metal bond lengths. In addition these new 4s and 4p functions are similar to those determined by the Fenske group from maximum overlap criteria.26,59,62
Metal $H_2$ for $Cr$, $Mn$, $Ni$, $Cu$, and $Pt$ were taken from other work. For $Fe$, $Co$, $Nb$, and $Rh$ charge iterations were performed on suitable model compounds ($Fe_2(NoH_4)_4$, $Co_2(NO_3)_2$, $N_2_2CH_2$), and $Rh_2CO_2Cl_2$ assuming a quadrupole dependence of metal $H_2$ on charge. In the iodide bridged dimer the iodine $H_2$ is assumed to vary in a linear way with charge with a slope of 7.9 eV/e for the 5p orbitals. A linear dependence was also assumed for the chlorine $H_2$ in $ClO_2Cl_2$ with a slope of 10.6 eV/e from neutral atom VSOIP's of -25.9 eV for the 3s and -13.8 eV for the 3p orbitals. In the iteration on $Rh(CO)_2C_12$- the $C_13p$ orbitals were assumed to vary on charge. In calculations without charge iteration using the parameters obtained from these models. These are collected in Table V.

References and Notes


(5) For a review of the number of references see the following paper: (a) L. A. Brewer, J. Am. Chem. Soc., 82, 1195 (1960).
(7) Additional structural studies exhibiting this elongation are: (a) $Br_2PbOCl_3$ and $Br_2B(NO_3)_3$; (b) R. C. Evans, F. G. M. Klem, J. A. D. M. Mcdonald, and P. V. M. Borsa, J. Am. Chem. Soc., 92, 1260 (1970); (b) [1,5-cyclooctadiene]CuCl$_2$; (c) J. van den Hende and W. C. Baird, Jr., J. Am. Chem. Soc., 85, 1009 (1963); (c) [Co(CO)$_2$(NO)]Cl$_2$; (d) J. D. Bassi, W. Bollor, M. D. C. Goff, and P. Oliver, ibid., 86, 5427 (1974); (d) (PPh)$_3$AgBr; (e) B. Teo and J. Calabresi, J. Chem. Soc., Comm., 185 (1976).
(11) A similar case is another d$_5$ system, CuI, one can compare the $3s$ angle at bridging $3s$ in $CuCl_2$ with $3s$ in $CuCl_2$ with the corresponding $3s$ angle in the infinite chain structure of $CuCl_2$: W. A. Bashford, I., E. L. Simon, J. Am. Chem. Soc., 43, 2835 (1974), with the corresponding $3s$ angle in the infinite chain structure of $CuCl_2$. (a) J. T. Thomas, J. H. Robertson, and E. G. Cox, Acta Crystallogr., 11, 608 (1958).
(12) W. Clegg (private communication). We are grateful to J. K. Burdett for bringing this work to our attention.
(14) In the structures which contain nitroso groups there is a variable degree of $M-O$-bonding from 0.

A case with azide and nitrosyl substitution that fits this pattern as well is

Throughout this paper we use the abbreviations (a) (PPh3)2Os(N0)2, N-Os-N = 139°, P-Os-P = 103.5°; B. L. Haymore, J. J. Mayerle, R. B. Frankel, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. 0. Hassel, Acta Chem. Scand., C. L. Raston and A. H. White, J. Chem. Soc., Dalton Trans., 11, 2410 (1972); (d) a case that does not appear to fit our generalization J. A. Kaduk and J. A. Ibers, lnorg. Chem., 14, 1105 (1975).


The iodide was calculated with an M-N-O angle of 165°, to simulate the experimental dimer structure (ref 2). In the chloride an M-N-O angle of 170° was used, as observed in the dimer (ref 10).


(a) (PPh3)2Pt(N0)2, C-N-C = 112°, P-N-P = 104°; C. P. Brock and J. A. Ibers, lnorg. Chem., 11, 2120 (1972); (b) (PPh3)2Co(N0)2, C-Co-C = 120°, P-Co-P = 114°; V. G. Albano, P. L. Bellon, and G. Ciani, J. Organomet. Chem., 38, 155 (1972).


Our analysis of the factors influencing distortions in X2MY2 complexes is not complete, for there are some structures in which the observed distortions do not fit the anticipated pattern. For instance, in Cl2Hg(DAsPh3)2 the Cl-Hg-Cl angle is significantly opened to 146.6°, while O-Hg-O is 92.5°; C. I. Branden, Acta Chem. Scand., 17, 1663 (1963). On the other hand, still other Hg(II) structures show angles close to tetrahedral: K. Au-

(42) Throughout this discussion we assume that in X2MY2 complexes the distortion keeps the X-M-X and Y-M-Y planes orthogonal. This is not necessarily so, either in dimers (see ref 19, 20, 21) nor in monomers: see the structure of Cl2Cu(OPPh3)2, A. B. Bertrand and A. R. Kalyanaraman, Inorg. Chim. Acta, 5, 341 (1971).
