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Bridged and Unbridged M_2L_{10} Complexes

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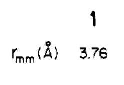
Abstract: Remarkably there are several structural alternatives to quadruple-bonded d^4–d^4 complexes of the Cotton type $Re_2Cl_8L_2^{2-}$, namely, the bridged, double-bonded edge-sharing bioctahedral Vahrenkamp complex $V_2(CO)_8(\mu\text{-}PR_2)_2$, and metal–metal nonbonded, high-spin, bridged complexes of the Walton type, $Re_2Cl_4(dppe)_2(\mu\text{-}Cl)_2$. This observation leads to a general theoretical analysis of M_2L_{10} structures. Walsh diagrams for $Y_4M(\mu\text{-}X)_2MY_4$ bioctahedral geometries with X, Y = donor, acceptor are constructed. The M–X–M angle θ is taken as the measure of deformation. The total energy is a sum of the d-block contributions and a core d^0–d^0 potential which has steep walls and limits sharply the ability of the d electrons to control the geometry. For instance, it forces the Walton complexes to be high spin. The energy wall at low θ in the bioctahedral complexes is dominated by repulsions among the axial substituents, while the precise location of the minima is governed by the bridging atoms. Superimposed on the d^0–d^0 energy there is a variable contribution due to metal–metal interaction, which may be attractive or repulsive, depending on electron count. After a brief analysis of the unsupported dimers the interconversions of the two types of geometries are studied. The transformation of d^4–d^4 Cotton and Vahrenkamp complexes is forbidden while that of d^7–d^7 $M_2(CO)_{10}$ compounds is allowed.

Structurally variegated dimers, trimers, polyhedra, quadruple bonds, fluxional ligands, cluster catalysis, ferredoxin and nitrogenase models, one-dimensional conducting chains—what a magnificent assemblage of static and dynamic chemical phenomena has been presented to us, within the short span of a dozen years, by the area of metal–metal interactions.

From the flasks of their makers there have come entirely new structural types, of marvelous intricacy. The natural course of science has transformed initially unique cases into familiar families. With time, this being still an experimental science, eventually, a degree of theoretical understanding of each class of molecules is achieved. But the very intensity of effort within each line of research, the concentration that is required to synthesize, characterize, and understand each specific structural type, sometimes postpones a consideration of the question which is a fundamental test of our degree of understanding: "Why do these molecules have the structures that they do?" Why do they choose static structure A when another electronically similar class chooses B? Let us try to make this question come to life with a specific example.

In 1978 Vahrenkamp prepared a lovely series of diamagnetic $M_2(CO)_8(PMe_2)_2$ (M = Mn, Cr, V) compounds, **1–3**. He found



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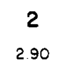

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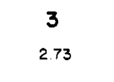

3

r_{mm}(Å) 3.76 2.90 2.73

all of them to be edge-sharing bioctahedral D_{2h}, with two bridging phosphido groups. Note the remarkable range of MM distances in the series. This could be taken to indicate a progression from no MM bond for Mn to a single bond for Cr to a double bond for V, in agreement with the 18-electron rule.[1,2]

Edge-sharing bioctahedral complexes of the $M_2(CO)_8(\mu\text{-}X)_2$ type, hereafter designated as the Vahrenkamp compounds, are quite common.[3] But there is something special about the V complex. If the PR_2 group is taken as mononegative, one plausible electron-counting convention, this is a d^4–d^4 complex. There is another group of d^4–d^4 complexes that forms one of the most beautiful chapters of modern inorganic chemistry. This is the set of quadruply bonded dimers, the Cotton compounds, exemplified by $Re_2Cl_8^{2-}$.[4] While the paradigm is M_2L_8, a sixth ligand easily enters the axial coordination site of each metal (e.g., $Re_2Cl_8(H_2O)_2^{2-}$, $Tc_2(O_2CCMe_3)_4Cl_2$). Thus a set of directly metal–metal

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(1) Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472.

(2) For a review and leading references on metal–metal bonding see: Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379–392.

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(4) For reviews see: (a) Cotton, F. A. *Chem. Soc. Rev.* **1975**, *4*, 27. (b) *Acc. Chem. Res.* **1978**, *11*, 225. (c) Trogler, W. C.; Gray, H. B. *Ibid.* **1978**, *11*, 232–239.

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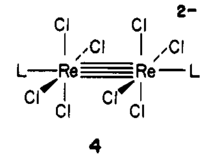
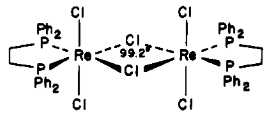
bonded, and strongly so, d^4–d^4 complexes of type **4** lies before us.



4

Re-Re 2.22 Å

There is a third class. These are $M_2L_8(\mu\text{-}X)_2$ d^4–d^4 bridged complexes, prepared by the Walton group.[5] These are also bioctahedral, bridged structures, exemplified by **5**. **5** differs from the Vahrenkamp compounds by having a very long metal–metal bond (what a fantastic change in the Re–Re distance occurs in replacing two Cl^- and two H_2O's by two diphos ligands, **4** → **5**!) The Walton compounds are in general paramagnetic, high-spin complexes.



5

Re-Re 3.809 Å

The problem, made crystal clear in its definition through the ease of crystallographic structure determinations, lies before us. There are at least three very different types of M_2L_{10} complexes, all d^4–d^4, all locally octahedral. There are the quadruply bonded, unbridged Cotton dimers, the still metal–metal bonded yet bridged Vahrenkamp complexes, and the paramagnetic Walton compounds, which have no metal–metal bonding to speak of. *What makes a certain ligand set favor one of these geometries over the other?*

One could argue for one preference or the other by analogy with other structures, by invoking the propensity of certain groups to be terminal or bridging. But that will not get one very far. Chlorides, which refuse to bridge in the Cotton complexes, and carbonyls, which similarly do not go into the bridging sites in the Vahrenkamp compounds, both are among the most common bridging ligands. Even the bridging propensity of phosphido, well exhibited in a multitude of complexes, is occasionally broken.[6] There must be other factors at work here.

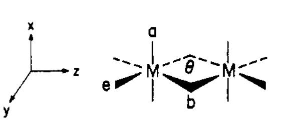
The very specific question of structural choice that we asked of the d^4–d^4 complexes can be repeated across the periodic table. The literature is replete with Walton-type compounds (all donor ligands) all the way from d^0–d^0 to d^6–d^6. Among these are simple M_2L_{10} dimers as well as polymers in which a bridged bioctahedral repeating unit occurs in every conceivable form.[7] Yet another class extends the abundance of bridged complexes to d^7–d^7 and d^8–d^8. The compounds are of the type $M_2(CO)_8(\mu\text{-}A)_2$ where A is an acceptor group such as $SiPh_2$ (counting the silene group as an acceptor, neutral, rather than as SiR_2^{2-} is a point we will have to return to) in $Mn_2(CO)_8(SiPh_2)_2$,[8] or A = CRR', R = OMe, R' = $p\text{-}MeC_6H_4$, in $Re_2(CO)_8(CRR')_2$.[9] Bridging carbonyl, nitrosyl, and isocyanide are also common in many d^7–d^7 complexes of the $Cp_2M_2(CO)_2(\mu\text{-}A)_2$ type (Cp = cyclopentadienyl, isolobal with three carbonyls), M = Fe or Ru.[10] These fluxional compounds exist side by side with $M_2(CO)_{10}$ (M = Mn, Tc, Re),[11] $Co_2(CN)_{10}^{6-}$,[12] and $Mn_2(CO)_8(PEt_3)_2$,[13] which are all also d^7–d^7 but unbridged, simply MM bonded.

There is a wealth of data at hand, and no lack of interrelated questions that can be asked. The main one has already been posed: (a) Why do these molecules have the structures that they do? It is supplemented by the following: (b) What factors determine the metal–metal distance in the bridged complexes? (c) What are the magnetic properties expected from the different classes of compounds? (d) When should one expect a facile bridged to MM-bonded interconversion or a fluxional molecule?

We will try our best to answer these questions. The reader is warned that the argument will be involved at times. We seek a comprehensive understanding and the task of obtaining that understanding is an arduous one.

Geometrical and Electron-Counting Preliminaries

The edge-sharing bioctahedral complex M_2L_{10} has many degrees of freedom, even if the ten ligands are identical. The maximum symmetry is D_{2h}. There are terminal equatorial (L_e), axial (L_a), and bridging (L_b) ligand sites, **6**. The complexes may depart from D_{2h} symmetry in many ways, perhaps the most interesting of which is a puckering of the central rhomboid from planarity. But even within the D_{2h} constraint there is a wide range of deformations. The L_eML_e and L_aML_a angles may change from their idealized octahedral values of 90 and 180°, respectively. The latter change is a particularly interesting one because it can be alternatively described as (a) axial ligands moving toward or away



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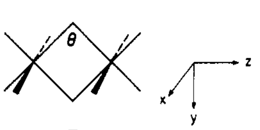

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from each other or (b) the metal atoms moving off their idealized octahedral sites. This deformation is a common one in infinite edge-sharing octahedral chains, and we plan to discuss it elsewhere in the future.

Most of the variability in these structures, and the natural focus of concern about metal-metal bonding, is in the inner rhomboid, in the bridging region. If the $\overline{\text{M–L}_\text{b}\text{–M–L}_\text{b}}$ grouping is planar, as it is, or very nearly is, in most structures of interest, it takes one distance (M–M, M–L_b, or L_b–L_b) plus one angle (M–L_b–M, L_b–M–L_b, or M–M–L_b), or two distances, to fix the bridging region. The traditional emphasis, for obvious reasons, has been on the metal-metal separation.[14] That distance is always important to know, and within an identical ligand set (same M, L_b) it is an excellent gauge of the strength of metal-metal interactions. However, if one wants to examine and intercompare a wide range of metals and bridging ligands, it is critical to supplement the description by defining an internal measure or standard of no metal-metal interaction, one that is sensibly independent of the radii of M and L_b. In this context Cotton and Ucko,[15a] Dahl, Rodulfo de Gil, and Feltham,[15b] and we [16] have found useful the ML_bM angle θ, defined in 7. An ideal edge-sharing bioctahedral complex will have $\theta = 90°$. Deviations of θ from that value are not by themselves indicators of metal-metal bonding or antibonding—they may be a consequence of the electronic or steric asymmetry of the ligand set, the d-electron count on the metal, or steric repulsions between axial ligands. All these factors one will have to worry about, but still by paying attention to θ one can put different metals and bridging ligands on the same scale.

Electron counting is a thorny matter. Though everyone knows that it is just a heuristically useful formalism, a conceptual device for classification of metals in molecules, nevertheless people become fixed in their attitudes here with a rigidity approaching that of political debate. We need that organizing tool here, no doubt about it. So we must face up to the ambiguities of any scheme and make our own convention clear. There is no disagreement on typical terminal ligands, neutral two-electron Lewis bases such as phosphine or carbonyl. Chloride, or halide in general, and phosphido, we will count as an anionic four-electron donor when it is bridging, X^- or PR_2^-, and assign it a similar charge when it is terminal, and similarly for mercapto, SR^-.

Problems begin to arise for bridging carbonyl or carbene, CR_2, or the related group 4 carbenoids, SiR_2, SnR_2, and GeR_2. We will count these as neutral two-electron bridging groups. The choice for carbonyl is forced by the desire to have the ligand count the same in the oxidation-state formalism whether it is terminal or bridging. But for group 4 ER_2 ligands the ambiguity of the formalism emerges full-blown. These could be viewed as either ER_2 or ER_2^{2-}. The former view makes them analogous to carbonyl or ethylene. The latter choice, an obvious one in view of the geometrical similarity of these ligands to phosphido, makes them bidentate, isoelectronic with PR_2^-, AsR_2^-, etc. The formalism is just that, a formalism. Our assumptions really are unimportant, as long as we are consistent, for the final molecular-orbital picture will restore the proper balance. But it is important to recognize the ambiguities, and we will return later, in the section on acceptor bridges, to a discussion of the problem of bridging carbonyls and carbenes.

The calculations which we will use are of the extended Hückel type, with parameters given in the Appendix. This approximate molecular orbital method has well-known deficiencies, but it is a transparent procedure, and one amenable to the perturbation theoretic analysis that is our interpretative tool. We have found it useful in a series of investigations of metal-metal bonding.[16,17]

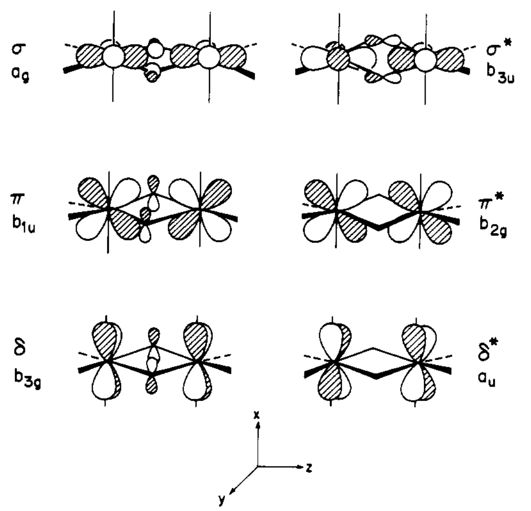
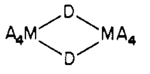


Figure 1. The six lower d-block orbitals of a bioctahedral M_2L_{10} complex. No energy ordering is implied.

There are special problems associated with the limits of a single-configuration treatment of metal-metal bonding, even in the large overlap region. We will refer to these later. There are also inherent difficulties with trying to build a comprehensive picture, applicable to a wide range of molecules, for the individual cases may deviate in detail. While we are aware of these problems and limitations we are not paralyzed by them. Our approach is to build a model, as wide-reaching and as detailed as possible, and explore its consequences.

There are four possible classes of compounds to be considered, depending on the identity of the bridging ligands and the terminal ligands. These can be either donor groups, D, such as halogens, phosphides, etc., or acceptor groups, A, which have low-lying empty orbitals, such as CO and CH_2. The four combinations **8–11** are shown below. The first two have been already designated



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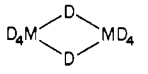

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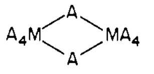

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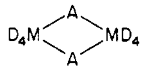

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as the Vahrenkamp and the Walton compounds, respectively. The other two, **10** and **11**, will be called simply acceptor bridged compounds. In addition we have the multiply bonded unbridged Cotton compounds, and their similarly unbridged but singly bonded homologues with higher electron counts.

It should be made clear at the outset that we have called these complexes the Cotton, Vahrenkamp, and Walton compounds, not intending the least slight to the extensive and informative researches of others who have synthesized, characterized, and otherwise studied these compounds. Their work is referred to in detail throughout. We use the names simply because we need a mnemonic designator for the three classes of complexes: (a) unbridged, short metal-metal separation, diamagnetic (Cotton); (b) bridged, medium metal-metal separation (Vahrenkamp); (c) bridged, long metal-metal separation, paramagnetic where applicable (Walton).

Let us begin with the Vahrenkamp and Walton complexes.

Donor Bridges: $M_2A_8(\mu\text{-D})_2$ and $M_2D_8(\mu\text{-D})_2$

The compounds that we have studied are $Cr_2(CO)_8(\mu\text{-}PH_2)_2^z$ (z = 2+, 0, 2−) and $Re_2Cl_8(\mu\text{-Cl})_2^z$ (z = 4+ to 4−). The first is

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[14] Though the nonbonded L_b–L_b interactions must not be forgotten—see here the important paper of Ross, F. K.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 4538.

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[17] (a) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884. (b) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *Ibid.* **1976**, *98*, 3219. (c) Dedieu, A.; Hoffmann, R. *Ibid.* **1978**, *100*, 2074. (d) Hoffmann, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *Ibid.* **1978**, *100*, 6088. (e) Whangbo, M.-H.; Hoffmann, R. *Ibid.* **1978**, *100*, 6093. (f) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187. (g) Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7736. (h) Schilling, B. E. R.; Hoffmann, R. *Ibid.* **1979**, *101*, 3456. (i) Dedieu, A.; Albright, T. A.; Hoffmann, R. *Ibid.* **1979**, *101*, 3141. (j) Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* **1979**, *18*, 654.

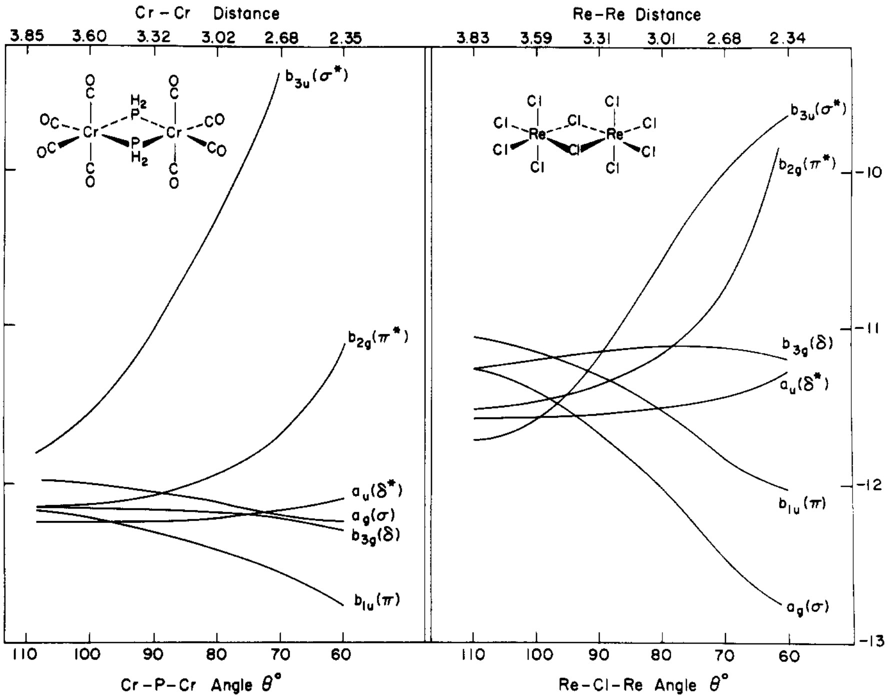


Figure 2. Computed energy of d-block orbitals of $Cr_2(CO)_8(PH_2)_2$ and Re_2Cl_{10} as a function of MLM bridging angle. At the extremes of small and large θ there are some additional levels in this energy range, arising from ligand–ligand interactions. These have been omitted from the drawing.

a model for the Vahrenkamp complexes, $z = 2+$ corresponding to d^4–d^4, V; $z = 0$ to d^5–d^5, Cr; $z = 2-$ to d^6–d^6, Mn. The charge on the Re complex, meant to model the Walton compounds and related systems, spans electron configurations from d^0–d^0 to d^4–d^4.

Let us first consider the frontier d-block orbitals. The site symmetry at each metal is pretty close to octahedral, even for substantial departures of θ from 90°. The familiar three below two splitting follows, becoming six below four in the dimer. The nest of six low-lying d orbitals that will characterize any of our dimers is shown schematically in Figure 1. No energy ordering is yet implied. In the coordinate system we use, the t_{2g} set is made up of xz, xy, and $z^2 - y^2$. The nonstandard nomenclature for the last orbital is a consequence of the fact that in a dimer the natural choice of z axis is along the metal–metal axis, not along one of the octahedral axes. Thus instead of z^2, $x^2 - y^2$, xy, xz, yz we have x^2, $z^2 - y^2$, yz, xz, xy. The axes change; the orbitals are of course the same.[18a] The orbitals in Figure 1 are labeled according to D_{2h} symmetry, and also by their cylindrical pseudosymmetry which summarizes so neatly their bonding characteristics.[18b]

The orbitals are well described as bonding and antibonding combinations of metal d functions. There is a variable degree of delocalization to the terminal ligands and some admixture of metal s and p orbitals, which is omitted from the schematic drawing. There is also some symmetry-conditioned mixing in of bridging ligand orbitals, and that is drawn in.

Next we draw the variation of the six energy levels as a function of θ (Figure 2). A nonlinear metal–metal separation scale is included at the top. Note the following general features.

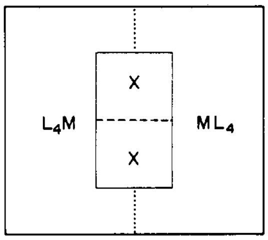
1. At large θ all the levels for $Cr_2(CO)_8(PH_2)_2$ start out at lower energy than those of Re_2Cl_{10}. The d-orbital parameters in the Appendix actually have Re(5d) at lower energy than Cr(3d). The reversed order in the molecule is a direct consequence of the terminal ligands—they stabilize the d orbitals when they are acceptor carbonyls, destabilize them when they are donor chlorides.

2. At small θ, small MM distance all the bonding levels decrease in energy with decreasing θ; all antibonding levels increase. Clearly this is metal–metal bonding at work.

3. At large θ the ordering of levels departs widely from any preconceived metal–metal bonding order. π* drops below π, δ* below δ. This occurs at a smaller θ for L_b = Cl than PH_2. It is quite clear that other effects are at work here in setting the orbital ordering. We will analyze them in detail soon, but even here we can say that these perturbations are caused by interaction with bridging ligand orbitals,[16,17a] a phenomenon which in the organic context is well-known as "through-bond coupling".[19]

Fragment Analysis

Let us try to understand these orbital patterns. A natural construction is from two ML_4 fragments and the bridging groups, a building-up process indicated schematically in **12**. The orbitals of an ML_4 fragment, L = donor or acceptor, are well-known.[20] Their pattern, **13**, has in each case a set of three orbitals, descended from the octahedral t_{2g} set, below two hybrids directed toward the octahedral sites. The important difference between L = CO and Cl is that π and δ are in the former below σ, in the latter above. This is a consequence of the better π-bonding capability of π and δ relative to σ. The π bonding is stabilizing in the acceptor case, destabilizing for the donor. A second effect, not visible in **13**, is that the carbonyl π* levels interact more with the metal orbitals than do the chlorine lone pairs. The result is that the t_{2g} set in $M(CO)_4$ is more delocalized away from the metal than in MCl_4.



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Now we allow the two ML_4 fragments to interact, removing the dotted barrier in **12**. The metal–metal distance is that cor-

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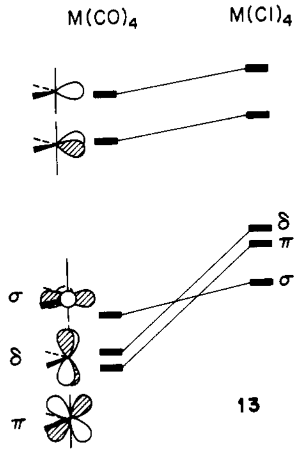
(18) (a) The situation is further complicated by the fact that in the dimer the in- and out-of-phase combinations of $z^2 - y^2$ mix with the corresponding combinations of x^2. Thus none of the a_g or b_{3u} orbitals is pure $z^2 - y^2$ or x^2. (b) Because of the mixing alluded to in (a) the a_g and b_{3u} orbitals have some δ and δ* character as well, but it is small.

(19) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(20) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599. (c) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801-3812. (d) Burdett, J. K. *Ibid.* **1979**, *101*, 5217.



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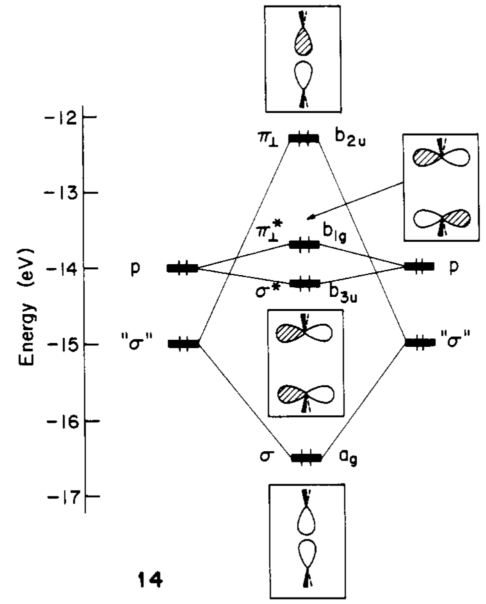
responding to an idealized octahedral dimer, $\theta = 90°$. Figure 3 shows the obvious through-space splitting, pairwise interaction with the bonding combination coming below the antibonding one. There are two understandable differences between Re_2Cl_8 and $Cr_2(CO)_8$. First, the splitting is smaller for Cr, simply because the orbitals are more delocalized, as mentioned above. Second, the $\pi,\delta-\sigma$ grouping of the monomer fragment is preserved, simply because the direct through-space interaction is as yet weak.

The two bridging ligands are coupled next (remove dashed barrier in **12**). **14** shows the four top $(PH_2)_2$ orbitals, those derived



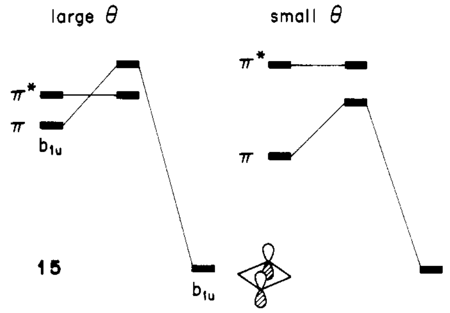
14

from σ and p combinations of a phosphido group. A similar pattern, less spread out in energy, appears for two chlorides. Finally we can interact the two components of the molecule, M_2L_8 and X_2, to form the composite. This is carried out in Figure 4. A similar construction has been published recently by Burdett.[20d]

Four out of the six d block orbitals of M_2L_8 find a symmetry match with the orbitals of the coupling unit. These are $b_{1u}(\pi)$, $b_{3g}(\delta)$, $a_g(\sigma)$, and $b_{3u}(\sigma^*)$. The other two d orbitals, $a_u(\delta^*)$ and $b_{2g}(\pi^*)$, have no such match and, hence, they will be left untouched by coupling. This accounts for the reversal of the $\pi-\pi^*$ and the $\delta-\delta^*$ ordering in the region of large θ in Figure 2. There the through-space splitting is small, whereas the through-bond coupling is large, leading to π and δ being above π^* and δ^*, respectively. As θ decreases, through-space coupling takes over and the bonding below antibonding ordering is retained even after through-bond coupling. This is shown in **15** for the $\pi-\pi^*$ set.

This effect on the $\delta-\delta^*$ ordering will take place at much smaller θ than for the $\pi-\pi^*$ pair because of the smaller through-space coupling.

These considerations are common to both Re_2Cl_{10} and $Cr_2(CO)_8(PH_2)_2$. The reason for the later occurrence of these or-



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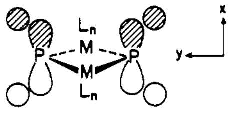
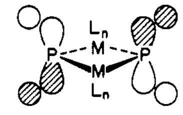
dering reversals in Re_2Cl_{10} is to be found in the difference between the coupling units $(Cl)_2$ vs. $(PH_2)_2$. The $b_{1u}(\pi)$ and $b_{3g}(\delta)$ type orbitals of $(Cl)_2$ are pure p lone pairs, whereas the analogous $(PH_2)_2$ orbitals are the PH bonding orbitals **16a** and **16b**. The



16a

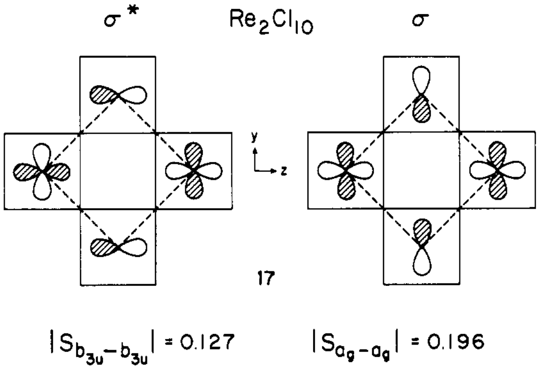


16b

coupling b_{1u} and b_{3g} orbitals of $(Cl)_2$ are less delocalized and higher in energy than the corresponding $(PH_2)_2$ orbitals (-14.15 and -14.25 eV vs. -17.20 and -17.35 eV). This leads to a stronger through-bond coupling of $(Cl)_2$ with Re_2Cl_8 throughout the range of θ, impeding the dropping of π and δ below π^* and δ^*, respectively.

Two further details of orbital trends of Figure 2 merit explanation. In Re_2Cl_{10} the σ orbital, a_g, is the lowest energy one at small θ, while in $Cr_2(CO)_8(PH_2)_2$ it remains above π and δ. This is a consequence of the initial ordering in the ML_4 unit (**13**). The remaining difference between the two molecules is in the ordering of σ and σ^* at θ = 110–100°.

Both $\sigma(a_g)$ and $\sigma^*(b_{3u})$ fragment orbitals of M_2L_8 find a symmetry match in a_g and b_{3u} orbitals of the coupling unit. Why then does σ lie above σ^* in Re_2Cl_{10} but not in $Cr_2(CO)_8(PH_2)_2$? This can be understood by considering the overlaps of the fragment orbitals at some θ, as shown in **17** and **18** for 90°.



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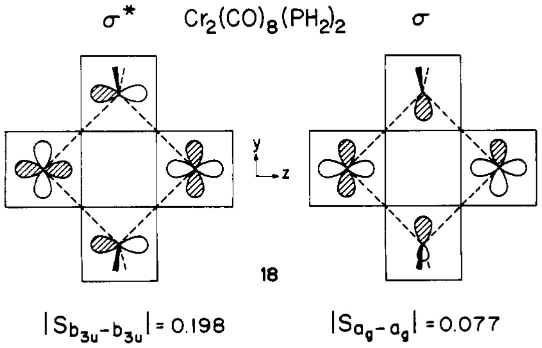

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This is through-bond coupling in action. The overlap of the σ^*-type fragment orbitals is smaller than the overlap of the σ-type fragment orbitals for Re_2Cl_{10}. This, together with the small through-space coupling, raises σ above σ^*. On the other hand,

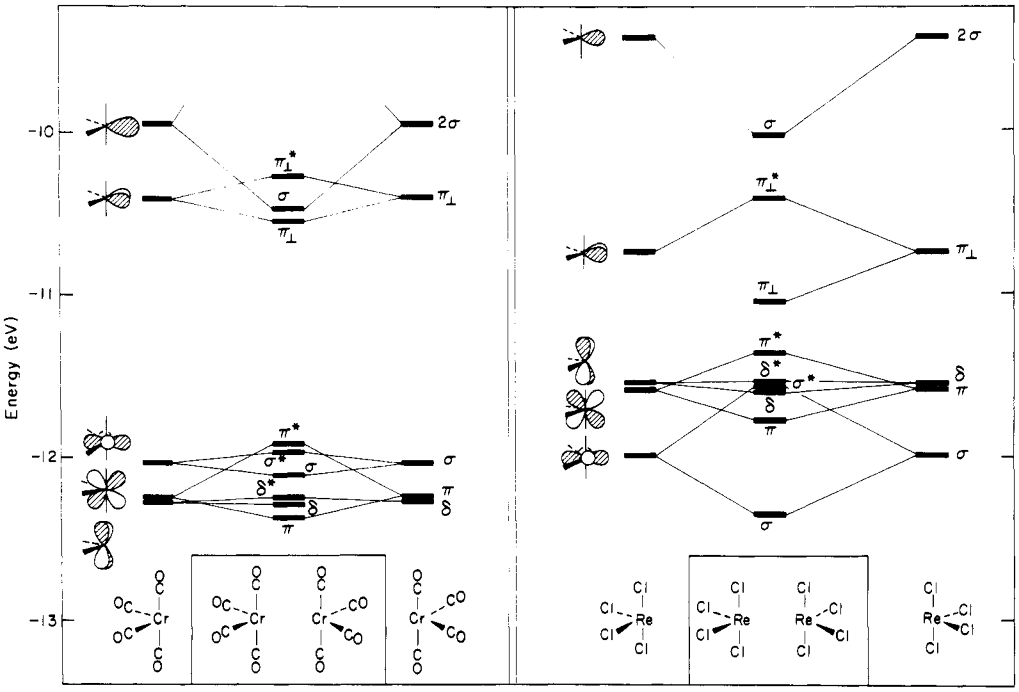


Figure 3. The interaction of two ML_4 fragments in a geometry corresponding to the M_2L_{10} dimers with MLM 90°.

the reverse situation obtains for $Cr_2(CO)_8(PH_2)_2$; there the σ*-type overlap is larger leading to a σ below σ* ordering.

The process we have just gone through, a detailed examination of the ordering and slope of each level in the Walsh diagram, may have seemed tedious. But in fact it was both absolutely necessary as a qualitative check on an approximate calculation and psychologically satisfying as a measure of the degree of understanding that we can attain with rather simple symmetry-based ideas. We have no doubt that these trends will be observed in much better calculations than ours.

The Core Must Not Be Neglected

What is the role of the orbitals we have so laboriously examined in the last section in determining the geometry of the molecule? If these d block orbitals were all that mattered, a rather similar picture, with minor differences, would emerge for a given d-electron configuration of $Re_2Cl_{10}{}^z$ and $Cr(CO)_8(PH_2)_2{}^z$. Referring back to Figure 2 we see that for d^6–d^6 all levels would be filled. The occupied σ* and π* levels rise sharply with decreasing θ so the equilibrium geometry is expected to lie on the side of high θ. The orbitals that are filled are (not in order of energy) σ, σ*, π, π*, δ, δ*, i.e., no net bond, if one simply counts bonding and antibonding combinations. For d^5–d^5 the σ* orbital will be vacated and the minimum should move to smaller θ; a formal MM bond results. For d^4–d^4 the equilibrium geometry should shift to still smaller θ, a shorter metal–metal bond. This is forced by occupation of σ, π, and δ easily overcoming the only orbital which rises in energy with decreasing θ, δ*. A formal double bond is present. All this is in accord with 18 electron rule considerations and strongly supports the picture of bonding in these molecules forwarded by Vahrenkamp.[1] The only differential so far perceptible for Re_2Cl_{10} is that its regions of substantial gaps between filled and unfilled levels for the d^4–d^4 and d^5–d^5 configurations set on at somewhat smaller θ than for the $Cr_2(CO)_8(PH_2)_2$ compounds.

Part of this simplistic picture is retained, part lost, when we actually compute the geometries of minimum energy for a given d-electron count (Table I). The Vahrenkamp compounds indeed have minima which are sensitive to the electron count. While the absolute values of the computed metal–metal bond lengths are not good (remember that these are all calculated for one set of parameters appropriate at best to Cr), the trend is precisely that found by Vahrenkamp, as is the d-electron configuration at the equilibrium geometry.

Table I. Optimum Geometries and Configurations for the Vahrenkamp and Walton Complexes

d-electron configuration	θ_{min}, deg	r_{min}, Å	closed shell configuration at θ_{min}
		$Cr_2(CO)_8(\mu\text{-}PH_2)_2{}^z$	
d^6–d^6	97.5	3.52	$\pi^2\,\delta^{*2}\,\delta^2\,\pi^{*2}\,\sigma^2\,\sigma^{*2}$
d^5–d^5	85.0	3.18	$\pi^2\,\delta^{*2}\,\delta^2\,\sigma^2\,\pi^{*2}$
d^4–d^4	80.0	3.04	$\pi^2\,\delta^{*2}\,\delta^2\,\sigma^2$
d^0–d^0	86.0	3.21	
		$Re_2Cl_8(\mu\text{-}Cl)_2{}^z$	
d^5–d^5	101.4	3.64	$\sigma^{*2}\,\delta^{*2}\,\pi^{*2}\,\pi^2\,\delta^2$
d^4–d^4	100.9	3.62	$\sigma^{*2}\,\delta^{*2}\,\pi^{*2}\,\pi^2$
d^3–d^3	103.4	3.69	$\sigma^{*2}\,\delta^{*2}\,\pi^{*2}$
d^2–d^2	102.5	3.67	$\sigma^{*2}\,\delta^{*2}$
d^1–d^1	102.6	3.67	σ^{*2}
d^0–d^0	97.3	3.53	

It is quite another story for the Walton compounds. No matter what the electron count the minima are all roughly in the same region, θ = 97–103°. The single compound whose structure we know well, **5**, has θ = 99°, in reasonable agreement with the d^4 result. Furthermore, if one examines the region near θ = 100° in Figure 2, one finds all six d levels bunched up within an interval of 0.5 eV. A high-spin ground state is expected for any electron count that allows it, i.e., from d^1–d^1 to d^5–d^5. And indeed, the Walton compound **5** is high spin.

How has it come about that similar Walsh diagrams such as those in Figure 2 have led to such disparate geometrical and magnetic end results for these two classes of molecules? Phenomenologically, it is easy to provide the answer. Figure 2 is a Walsh diagram. It shows the behavior of the individual d block levels. The extended Hückel total energy of course is not just the sum of the energies of the electrons in these orbitals, but also of the energies of the mass of electrons in lower levels. It is in these lower levels that bridge bonding and ligand steric repulsions are to be found, and as it will turn out these are determinative.

A graphic account of what happens is given in Figure 5. This shows the d^0–d^0 potential energy curve superimposed on the Walsh diagram of Figure 2. The total energy of any configuration is obtained by adding the energy of the appropriate number of d-block electrons to the d^0–d^0 energy. The $Cr_2(CO)_8(PH_2)_2$ and Re_2Cl_{10} d^0–d^0 curves are very different. The former has a minimum at θ = 86°, the latter a much sharper minimum at θ = 97°, a much larger distance. For the Vahrenkamp compounds the slope increments provided by the d-block levels are sufficient to shift

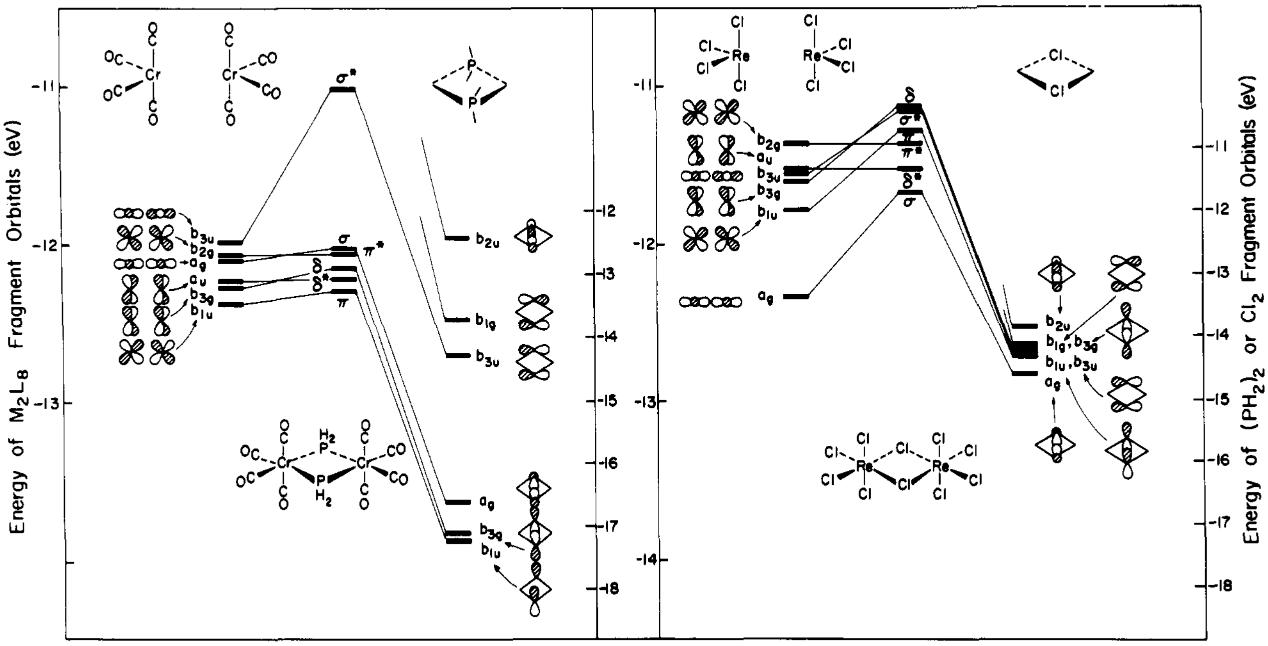
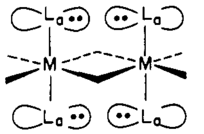


Figure 4. Interaction diagram for M_2L_8 and $(\mu\text{-}L)_2$ segments of the M_2L_{10} dimers. Note that the M_2L_8 and the bridging fragments have different energy scales.

the minima for d^6–d^6 to large θ, a longer metal–metal bond, and for d^4–d^4 to smaller θ, a shorter bond. For the Walton compounds the situation is very different. The d^0–d^0 curve has its minimum at a long metal–metal distance, and it has *very* steep walls. Even though "single bond" d^5–d^5 and "double bond" d^4–d^4 regions are available, with substantial stabilization for the ten or eight d electrons involved, these regions occur at θ values so small, so far away from the minimum of the d^0–d^0 curve, that they have no chance of overcoming the repulsive part of the d^0–d^0 potential. To put it another way, whatever makes the d^0–d^0 curve have its minimum at $\theta \sim 100°$ and of great depth, that factor overcomes any d-block propensities and forces all d-electron configurations of Re_2Cl_{10} to have a geometry near $\theta = 100°$.

Steric Effects in the Core

We must penetrate behind the phenomenology and ask why the d^0–d^0 curves are so different. The question may be split into two parts: (1) What is the reason for the location of the minimum in the two curves? (2) What is the reason for the rising walls of varying steepness flanking the minimum? We shall start with the second part of the question. Within the extended Hückel method any strongly destabilizing effect must originate in overlap repulsion. In other words, the destabilization arises from interactions of doubly occupied MOs among themselves. This repulsion is proportional to the overlap between the orbitals and it falls off very rapidly with increasing distance. The distance dependence brings us naturally to a consideration of the cross interaction of axial ligands attached to different metal atoms. The overlap factor further propels us to single out the L_a orbitals pointing toward each other, **19**.



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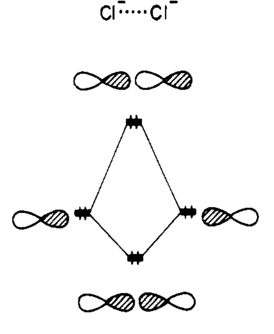
To probe the difference between L_a = Cl and L_a = CO we have computed the potential-energy curves for the approach of $Cl^-\cdots Cl^-$ and CO···CO. As can be seen from Figure 6, the curve for $(CO)_2$ is only mildly repulsive, whereas that for $(Cl_2)^{2-}$ is highly repulsive. If one focuses on the orbitals pointing toward each other, one can trace the effect to the vacant π* orbitals on CO. These act as electronic guards, stabilizing the upper combination of the π orbitals and preventing it from rising too steeply in energy. This is illustrated below by **20** and **21**.



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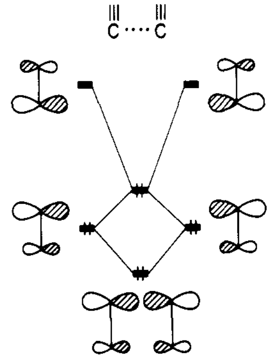

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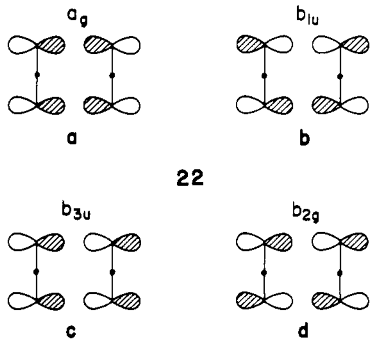
Let us now carry over this model into the actual systems under consideration. In the case of X = Cl, there are four relevant combinations of lone-pair orbitals of the apical substituents (**22**).



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b_{3u} (**22c**) and b_{2g} (**22d**) are the orbitals among these which are antibonding between the apical chlorines. As the Cl···Cl distance decreases both climb up in energy, causing a large destabilization of the d^0–d^0 system. This is in fact what one observes in the calculations at $\theta = 70°$ (r_{MM} = 3.0 Å). At this separation these

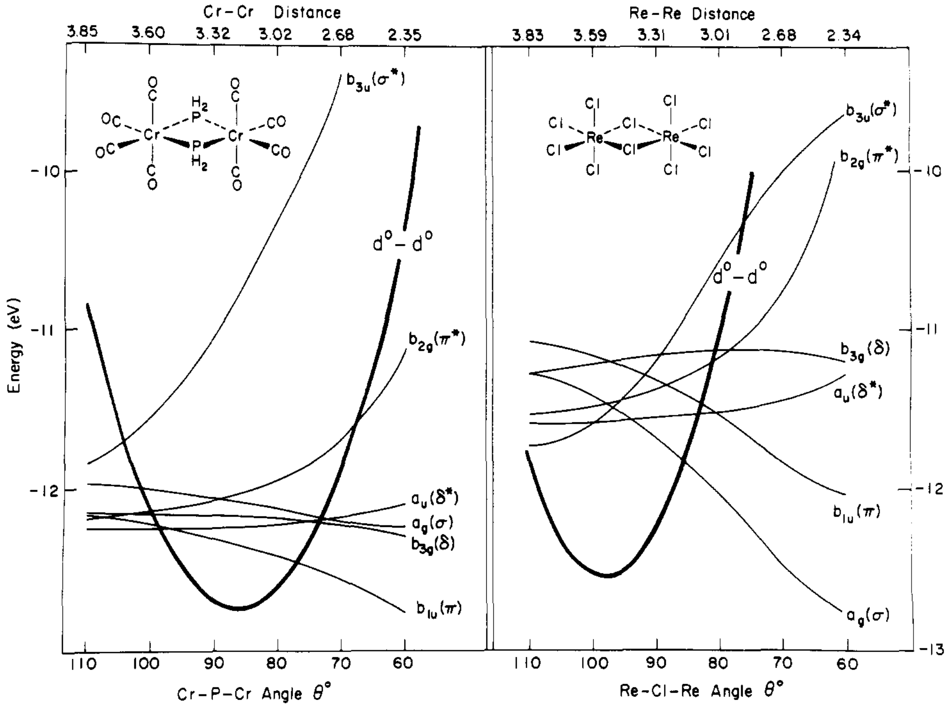


Figure 5. Computed energies of d-block orbitals, as in Figure 2, but with superimposed d^0–d^0 energy curves. The energy zero for the latter is arbitrary, but the energy scale is the same as for the orbital energies.

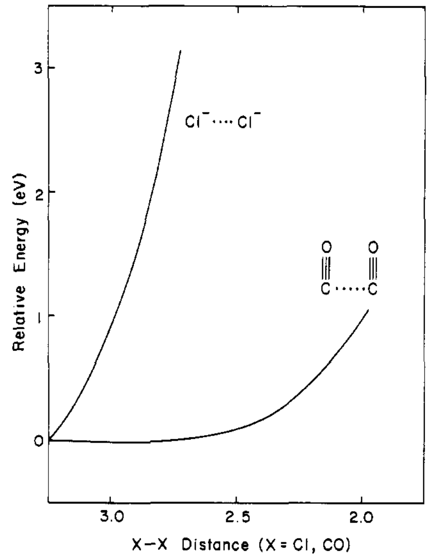
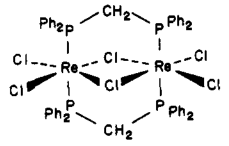


Figure 6. Energy of two COs and two Cl^- in a parallel approach.

orbitals infiltrate among the d-block orbitals and one of them, b_{2g}, rises all the way above the d-block orbitals. For X = CO, there are also four such combinations of the π orbitals. However, here, the b_{2g} and b_{3u} combinations are not allowed to rise sharply in energy, owing to the aforementioned tempering effect of the π^*_{CO} orbitals. This leads to the difference observed in the steepness of the energy walls on the low θ side of the d^0–d^0 energy curves (Figure 5).

One way of tempering the low θ wall of the $E(d^0)$ curve for the Walton compounds is to tie the apical groups together so that the mutually repelling lone pairs are eliminated and the approach of apical substituents is prevented. In this way, the d-block levels may be allowed to shift θ_{min} into the region where metal–metal bonding can be turned on. Interestingly, we find one case in the literature which may conform to this description. The Walton compound $Re_2Cl_6(dppe)_2$ (d^4–d^4) (**5**), which has four apical chlorines, is paramagnetic,[5a,b] whereas $Re_2Cl_6(dppm)_2$ (d^4–d^4) is diamagnetic.[5d] The structure of the diphosphino methane complex is not completely established. But it is thought to be **23**, with characteristically bridging dppm units. In that case it would fit our criteria for bypassing the steric problems of the general class



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of Walton compounds, and could have a Re–Re bond of intermediate length. A crystal structure of this molecule and a synthetic effort directed toward other representatives in which a similar steric strategy is applied would be of the greatest interest.

The strategy we have in mind has already been implemented in an elegant manner in two compounds containing W–W bonds of orders 1 and 2.[21a] These are $W_2(\mu\text{-}S)_2(Et_2NCS_2)_4$ and $W_2(\mu\text{-}S)_2(Et_2NCS_2)_2(CH_3O)_4$. Both have bidentate Et_2NCS_2 units bridging two axial sites. In the second, W(V), compound the metal separation is 2.79 Å, much shorter than that in W_2Cl_{10} (3.814 Å).[21b] In the first compound, which is W(IV), the metal–metal separation is still shorter, 2.53 Å.

Another way to escape the steric problems of the bridged structure yet maintain multiple bonding is by aggregation into larger polyhedra. This is in fact realized, in the lovely Re_3Cl_9 and $Re_3Cl_9L_3$ structures.[22]

If we return for a moment to the Vahrenkamp compounds, we can see even in the carbonyl case an effect of ligand–ligand repulsions. The full potential of the double bonding in the d block is not realized in the equilibrium geometry, as may be seen from

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[21] (a) Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2946–2950. (b) Cotton, F. A.; Rice, C. E. *Acta Crystallogr., Sect. B* **1978**, *34*, 2833–2834.

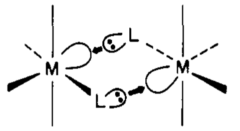
[22] (a) Cotton, F. A.; Lippard, S. J.; Mague, J. T. *Inorg. Chem.* **1965**, *4*, 508. (b) Bennett, M. J.; Cotton, F. A.; Foxman, B. M. *Ibid.* **1968**, *7*, 1563. (c) Cotton, F. A.; Mague, J. *Ibid.* **1964**, *3*, 1094. (d) Bertrand, J. A.; Cotton, F. A.; Dollase, W. A. *Ibid.* **1963**, *2*, 1166. (e) Tisley, D. G.; Walton, R. A. *Ibid.* **1973**, *12*, 373.

Figure 5. The calculated minimum is at $\theta = 80°$, the observed one at 70.5°. At either of these values the total d-electron energy is still heading down, but the ligands run into a figurative steric wall if the VV distance is decreased. Vahrenkamp aptly subtitled his paper "An Impossible Metal-Metal Bond" and in one neat figure graphically shows the way the carbonyls begin to bend away from each other as one progresses from Mn to Cr to V.

The argument in this section has stressed the repulsions between axial chlorines. There are numerous M_2L_{10} structures in which the distance between axial chlorines is actually smaller than that between the metals. The axial ligands appear to bend toward each other. The phenomenon is clearly exhibited in W_2Cl_{10}[21b] and in many extended structures, which will be surveyed below, with low d-electron counts. This effect is the result of metal tempering of ligand–ligand repulsions and will be reported on separately.

Bridge Bonding in the Core

Molecular-orbital theory forces one into thinking of molecules in ways which stress symmetry adaptation and delocalization. But we should not forget the donor–acceptor modality explicit in the coordination bond formed in these complexes, and summarized in structure **24**. Ligands such as halide or phosphido, if monodentate, bear free electron pairs available for dative bonding with an acceptor orbital on the metal. The donor–acceptor idea is fleshed out by the actual existence, especially in the d^0–d^0 series, of monomer–oligomer equilibria. For instance, $NbCl_5$ is dimeric in the solid, monomeric in the gas phase.[23a] $ZrCl_4$ is also monomeric in the gas phase but condenses into a polymeric solid.[23b]



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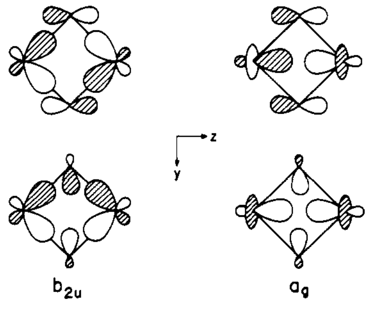
What is the relationship of this point of view to the problem of defining the d^0–d^0 energy minima? Well, having the donor–acceptor model in mind one would be led to think quite simplistically that, as the prospective bridging ligand becomes a better electron donor and the metal orbital a better acceptor, the bridging bonds will be stronger and the d^0–d^0 dimer more stable. A corollary to that hypothesis is that the bridging site will always be occupied by donor ligands, whereas the terminal sites will be preferred by acceptors. This is almost always so.

Given this supposition, how is one to separate in the observed curves the effect of axial ligands discussed in the last section from some bridge bonding preference created by the difference between Cl^- and PR_2^-? We have attempted to do so by replacing the terminal ligands, all eight of them, by sterically undemanding hydrides. The d^0–d^0 curves for $Cr_2H_8(PH_2)_2$ and $Re_2H_8Cl_2$ are shown in the solid lines of Figure 7. The minimum for bridging chloride is at larger θ and shallower than that for bridging phosphido, as observed for the original Walton and Vahrenkamp models.

Still one is not sure if this difference is attributable specifically to the bridging region and how exactly it comes about. We were forced to examine in detail the bonding in the bridge region, not the d orbitals, but the $M_2(\mu\text{-}X)_2$ bonding orbitals. Qualitatively, one expects four bridge MOs which arise from the interaction of the lone-pair combinations of the bridging unit with the M_2L_8 orbitals of the same symmetry (see Figure 4 and the discussion preceding it). These are shown in **25**–**28**.



25 **26** **27** **28**

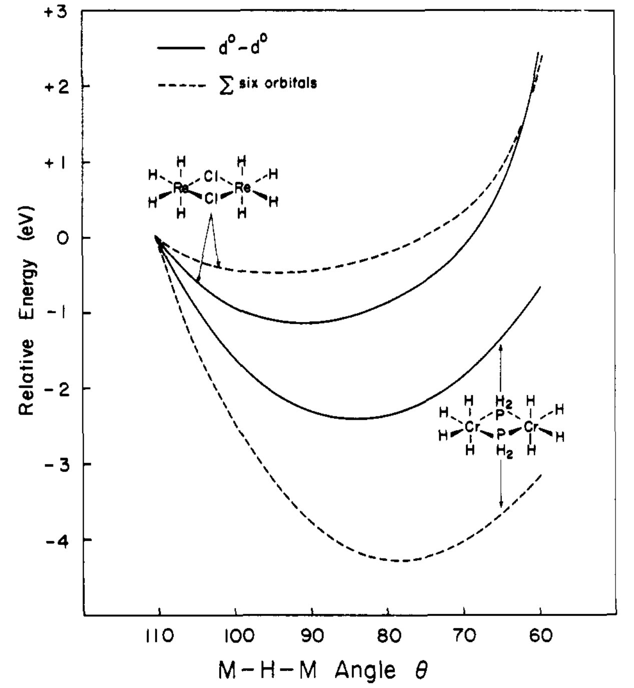
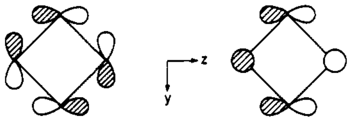


Figure 7. d^0–d^0 energy curves for $Re_2H_8Cl_2$ and $Cr_2H_8(PH)_2$ (solid lines) and an energy sum for the same molecules including those levels identified as being primarily involved in bridge bonding (dashed lines).

The connection of these delocalized MOs to the localized picture can be made by taking sums and differences. Eventually four equivalent bond orbitals result.

Following our line of reasoning, if the relative location and the depth of the minimum of the $E(d^0)$ curves reflect the strength of the bridging bonds for different bridging groups, then the summed energy of the four bridging orbitals **25**–**28** should resemble the $E(d^0)$ curve. To check that we have tried to identify the bridging orbitals of $Cr_2H_8(\mu\text{-}Cl)_2$ and $Cr_2H_8(\mu\text{-}PH_2)_2$. In addition to the four MOs, **25**–**28**, we have found two more orbitals of b_{1g} and b_{3u} symmetries, **29** and **30**, which have high electron density on the bridge atoms. This is somewhat discouraging since a great simplification was made in going from, say, $Cr_2(CO)_8(P(CH_3)_2)_2$ to $Cr_2H_8(PH_2)_2$. But there is no way of preventing the delocalization of the bridge bonding, and instead of four orbitals we must minimally consider a total of six. The orbital sum of the energies of the 12 electrons in these six orbitals is also plotted in Figure 7, with dashed lines. It can be seen that the six orbital minima mimic nicely the complete d^0 curves. We conclude that the better electron donor, PH_2^-, forms stronger bridging bonds than Cl^-. But why are those stronger bonds formed at a smaller θ?



29 **30**

We saw earlier in structure **14** and Figure 4 that the inherent interaction of two phosphido groups with each other, no metal present, was stronger than that of two chlorides. That interaction between the bridging ligands is a four-electron destabilizing one.

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[23] (a) Zalkin, A.; Sands, D. E. *Acta Crystallogr.* **1958**, *11*, 615. Reference 11a, p 938. Smith, G. S.; Johnson, C. L.; Elson, R. E. *Acta Crystallogr.* **1967**, *22*, 300. (b) Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 146.

Table II. Experimental Geometry and Magnetic Properties of the Walton-Type Compounds $[M_2D_8(\mu\text{-}D)_2]$

compd	d-electron configuration	θ, deg	r_{MM}, Å	magnetic properties	ref
Mo_2Cl_{10}	d^1–d^1	98.6	3.84	$\mu = 1.67\ (1.52)\ \mu_B$/Mo	25a,b
Re_2Cl_{10}	d^2–d^2	98.1	3.739	$\mu = 1.79\ \mu_B$/Re	25b–d
$Cr_2(H_2O)_2$(2,6-carboxylatopyridine)$(\mu\text{-}OH)_2$	d^3–d^3	99.5	2.981	$J = -8.6\ cm^{-1}$	25e,f
$(Cr_2O_{10})^{14-}$	d^3–d^3	101.2	3.101	$\mu = 3.5\ \mu_B$/Cr	25g,h
$Re_2Cl_6(dppe)_2$ [b]	d^4–d^4	99.2	3.809	$\mu = 2.05\ \mu_B$/Re	5a–c
$[Mn_2Cl_4(H_2O)_4(\mu\text{-}Cl)_2]^{2-}$	d^5–d^5	94.6	3.828	$J = -0.015\ cm^{-1}$	25i

[a] $J < 0$ indicates singlet below triplet; $2J$ is the singlet–triplet separation. [b] dppe = $Ph_2PCH_2CH_2PPh_2$.

It has two consequences. The greater that interaction, the higher are the antibonding combinations pushed up, and the better a donor are these bridging ligands. So PR_2^- will form stronger bridge bonds than Cl^-. But the bonding with the metal fragments, while it, so to speak, relieves some of the overlap repulsion, does not remove it entirely. The traces of the overlap repulsion remain: phosphido groups wish to remain farther apart than the chlorides. For a given MM separation this leads to a greater θ for bridging Cl^- than for PR_2^-. Steric and electronic effects are difficult to sort out in any theory. Our explanation, depending as it does on four-electron repulsions, merges into the steric influence of L_b–L_b interactions stressed by Ross and Stucky.[14]

At this point we are satisfied that our questions regarding the shape of the $E(d^0)$ curve have been adequately answered. The energy wall at low θ is dominated by the repulsion of the axial substituents, as analyzed in the preceding section. The location of the minima is governed by the nature of the bridging atoms. Superimposed on the d^0–d^0 energy of the bridging region there is a variable contribution due to metal–metal interaction. This may be attractive or repulsive and depends on the electron count. In the bridged complexes, the potential for some metal–metal bonding should be optimally realized when the terminal ligands are acceptors (the Vahrenkamp complexes) and less so when they are donors (the Walton compounds).

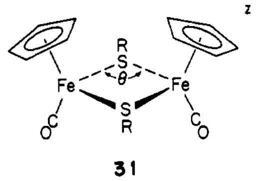
A Survey of $M_2L_8(\mu\text{-}D)_2$ Structures

At this point we wish to step back from the theoretical discussion, review the experimental evidence, and compare it with our conclusions. There is a wealth of experimental data available, which we have collected and summarized, part here, mostly in the supplementary material deposited with this paper.

Structures are known for many donor bridging $M_2A_8(\mu\text{-}D)_2$ complexes,[1,3] though the Vahrenkamp series is the most complete since it includes a rare d^4–d^4 complex. In the d^5–d^5 structures θ ranges between 69 and 78° and increases to 92–103° for d^6–d^6. The ranges of metal–metal bond lengths in these diamagnetic complexes overlap: d^5–d^5, 2.90–3.15 Å; d^6–d^6, 2.94–3.89 Å.

In addition to the octacarbonyls one finds a host of diamagnetic complexes of the type $Cp_2(CO)_2M_2(\mu\text{-}X)_2$, related to the previous group by the common isolobal replacement of a Cp^- by three carbonyls. The d^5–d^5 complexes have smaller angles at the bridge, 79–85°[24a–c], except for *cis*-$Cr_2Cp_2(NO)_2(\mu\text{-}OMe)_2$, which has θ = 95°, Cr–Cr 2.88 Å.[24f]

The only d^6–d^6 complex we have found, *trans*-$Fe_2Cp_2(CO)_2(\mu\text{-}SPh)_2$, has a larger θ, 98°, and a longer MM distance of 3.39 Å.[24d] In one of his many elegant studies directed toward exploiting the nature of metal–metal bonding Dahl reported the crystal structure of a closely related derivative, the mercapto phenyl replaced by methyl, and the entire molecule oxidized by one electron, cationic.[24e] The structures are compared in **31**. Dahl and Connelly concluded that the electron is removed from a metal–metal antibonding orbital, and our calculations (see Figure 2, it is the b_{3u} σ^*) certainly agree.

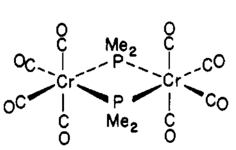


31

z = 0 +1
R = Ph CH_3
r_{Fe-Fe} = 3.39 2.925
θ = 98° 82°

Quite a different situation is displayed by the Walton-type complexes. The few which are listed in Table II range from d^1–d^1 to d^5–d^5 but display a remarkably narrow range of θ, 95–101°. In all the cases, the compounds are either paramagnetic or have a triplet state lying as little as 0.03 cm^{-1} above the closed-shell singlet.

There are many structures not included in Table II, dimeric and polymeric high-spin (where applicable, i.e., d^2–d^4) edge-sharing bioctahedral structures. The interested reader is referred to the supplementary material deposited with this paper. Angles at the bridge of 100 ± 5° are typical of these. We terminate the discussion here by noting that the single d^5–d^5 complex in Table II, $Mn_2Cl_4(H_2O)_4(\mu\text{-}Cl)_2^{2-}$ (**32**), forms a contrast with the Vahrenkamp compound $Cr_2(CO)_8(\mu\text{-}PR_2)_2$ (**2**) as sharp as the one between **3** and **5**, which was the impetus to this study. Here are two d^5–d^5 M_2L_{10} complexes with a difference of 0.93 Å in metal–metal bond length, 17° in θ, and entirely different magnetic behavior!



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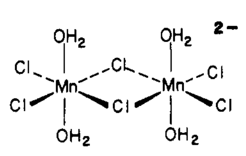

32

	2	32
MM	2.90Å	3.83Å
θ	77.7°	94.6°
	diamagnetic	1 = −0.015 cm^{-1}

Acceptor Bridges

The complexes we plan to study are $M_2D_8(\mu\text{-}A)_2$ and $M_2A_8(\mu\text{-}A)_2$. The bridging acceptors may be CO, NO, CNR, CR_2, SiR_2, GeR_2, or SnR_2, and as prototypes of these we will choose the carbonyl and carbene bridges. With the experience of the previous sections the analysis should and will be straightforward, but perhaps it is worthwhile to anticipate the critical differences.

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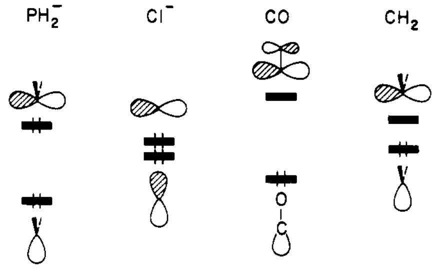
(24) (a) Bush, M. A.; Sim, G. A.; Knox, G. R.; Ahmad, M.; Robertson, C. G. *Chem. Commun.* **1969**, 74–75. (b) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1970**, 611–616. (c) McPhail, A. T.; Sim, G. A. *Ibid.* **1968**, 1858–1865. (d) Ferguson, G.; Hannaway, C.; Islam, K. M. S. *Chem. Commun.* **1968**, 1165–1166. (e) Connelly, J. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7472–7474. (f) Hardy, A. D. U.; Sim, G. A. *Acta Crystallogr., Sect. B* **1979**, *35*, 1463–1465.

(25) (a) Sands, D. E.; Zalkin, A. *Acta Crystallogr.* **1959**, *12*, 723. (b) Knox, K.; Coffey, C. E. *J. Am. Chem. Soc.* **1959**, *81*, 5. (c) Mucker, K.; Smith, G. S.; Johnson, Q. *Acta Crystallogr., Sect. B* **1968**, *24*, 874. (d) Schüth, W.; Klemm, W. *Z. Anorg. Allg. Chem.* **1934**, *220*, 193. (e) Ou, C. C.; Borowski, W. J.; Potenza, J. A.; Schugar, H. J. *Acta Crystallogr., Sect. B* **1977**, *33*, 3246. (f) Cline, S. J.; Kallesøe, S.; Pedersen, E.; Hodgson, D. J. *Inorg. Chem.* **1979**, *18*, 796. (g) Meunier, G.; Frit, B.; Galy, J. *Acta Crystallogr., Sect. B* **1976**, *32*, 175. (h) Kahn, O.; Briat, B.; Galy, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1453. (i) Willett, R. D. *Acta Crystallogr., Sect. B* **1979**, *35*, 178.

They are tied up in the electron-counting convention and the bridge-region bonding.

Each of the bridging ligands we have studied or will study has a σ- and a π-type orbital available for bonding, as shown in **33**.



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We have omitted the third Cl^- lone pair and the second π^* of the carbonyl, focusing only on the orbital which interacts in the plane of the $M_2(\mu\text{-}X)_2$ rhomboid. The electron occupations shown are those corresponding to the electron-counting conventions given in the introduction. Note how they make the structurally similar PH_2^- and CH_2 electronically very different, one a π donor, the other a π acceptor.

Once bridge bonding is established we know that there should be four occupied orbitals in the bridge region. One can think of these as four localized equivalent shown above in **25**–**28**. For the donor bridges the eight electrons in the four bridge bonding orbitals **25**–**28** may be derived (the symmetry is right) from the four donor electron pairs of $(PR_2)_2^{2-}$ or Cl_2^{2-}. The metal, while it does contribute some d-orbital character to **25**–**28**, can be thought of as saving its d-block orbitals and electrons. **25**–**28** are not frontier orbitals; they are in the core, at lower energy.

Not so for the acceptors. CO and CH_2 enter into bonding as two-electron bases, not four-electron ones. Their σ orbitals can give rise only to **27** and **28**. Orbitals **25** and **26** are of course still there, but they are at higher energy. They arise from the interaction of metal d orbitals and the acceptor π functions. In the normal electron counting bookkeeping the four electrons in these two orbitals are counted as being the metals'.

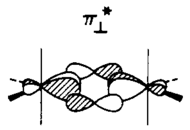
One could try to evade this problem by transforming the acceptors into donors by transferring two metal electrons to each, making them CO^{2-} and CH_2^{2-}. That is an especially attractive process for the group 4 ER_2 bridges, structurally so similar to PR_2. Yet the problem is not really solved by this maneuver. No matter where one places the electrons the fact will remain that two of the bridge bonding combinations, **25** and **26**, by virtue of their contribution of high-lying bridging ligand π orbitals, are not to be found at low energy, but interspersed in the metal d block. To put the problem in another way: for the acceptor bridges it is going to be hard to distinguish clearly between bridge core and d-block orbitals. This is a problem we will have to live with, and as long as we keep our conventions internally consistent, and try to understand another person's convention rather than argue with it, no loss of information will result.

The actual calculations we have done are for $Re_2Cl_8(\mu\text{-}A)_2$ and $Re_2(CO)_8(\mu\text{-}A)_2$, A = CO, CH_2. The geometrical parameters are in the Appendix. Figure 8 is the Walsh diagram for the carbonyl bridges. It shows the dense block of frontier orbitals, rich in d character.

1. The general features of the Walsh diagram are similar to the donor case, in that the levels are bunched together at large θ. They spread apart, sorting themselves according to metal–metal bonding or antibonding character at smaller θ. All the levels are at higher energy in the case of Re_2Cl_8—this is the terminal donor vs. acceptor effect.

2. Compared to the bridging donor case the region of θ in which MM bonding levels are below antibonding ones is greater. Recall, for instance, how in Figure 2 δ^* was below δ almost over the entire diagram. Here δ is below δ^* everywhere.

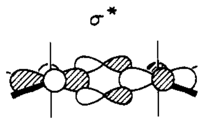
3. There is an additional low-energy MO in the d block. We designate it $\pi_\perp^*$ (**34**). It, together with σ^*, has distinctly lower



34

d character than the other five orbitals. The presence of this orbital allows d^7–d^7 molecules to exist.

4. If we focus on the orbital slopes, the most striking difference between the μ-D and μ-A case is in σ^*, **35**. That orbital rose



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sharply in the donor case, while here it just slouches at nearly constant energy in the middle of the diagram. One has the feeling that it is quite a different oribtal in the two cases, and indeed it has significantly less metal d character, as in the case of $\pi_\perp^*$.

The interaction diagram of Figure 9 provides the information to explain the differences between μ-D and μ-A. (Only that for terminal carbonyls is shown, the one for terminal halides being quite similar.) σ^* and $\pi_\perp^*$ are very different. $\pi_\perp^*$ is descended from an out-of-phase combination of carbonyl π^* orbitals. σ^* begins as one of the metal d functions, but the rise in energy which it showed so dramatically in the μ-D case is now inhibited by another carbonyl π^* combination of matching symmetry. For most θ σ^* has a substantial μ-CO contribution. So, in fact, $\pi_\perp^*$ and σ^* are the orbitals we have been talking about in the beginning of this section—they are as much core bridge orbitals as they are d orbitals.

As in the case of μ-D,π^* and δ^* are left untouched by interactions with the bridge. π and δ are affected by through-bond coupling. But whereas in the donor case they were pushed up in energy by mixing with occupied donor orbitals, and so crossed π^* and δ^*, here they are depressed in energy by similar mixing with carbonyl π^* acceptor levels. Thus the through-bond coupling here operates to support the through-space interaction in keeping σ, π, and δ below σ^*, π^*, and δ^* throughout almost all of the Walsh diagram.

What d-electron counts should be stable and at which geometries? Figure 8 indicates that for $M_2(CO)_8(\mu\text{-}CO)_2$ d^1–d^1 to d^4–d^4 are likely to be open-shell configurations, high spin. For $M_2Cl_8(\mu\text{-}CO)_2$ there is a chance of a closed shell for d^4–d^4 at low θ. From the μ-D discussion we have learned to be cautious concerning drawing any firm conclusions about the bonding until we have seen what region of θ is allowed by repulsions and bonding in the core. We will look at this soon, but let us digress for a moment on metal–metal bonding in the more obvious closed-shell configurations.

In the d^6–d^6 complexes the configuration is (not in precise order of energy) $\sigma^2\pi^2\delta^2\sigma^{*2}\delta^{*2}$ and either π^{*2} or $\pi_\perp^{*2}$. In d^7–d^7 it would be $\sigma^2\pi^2\delta^2\sigma^{*2}\delta^{*2}\pi^{*2}\pi_\perp^{*2}$. Thus in d^6–d^6 the net number of filled MM antibonding orbitals equals that of bonding ones, while in d^7–d^7 it exceeds the bonding ones by one. Should one conclude that there is no bond in the d^6–d^6, an antibond in d^7–d^7? Yes and no. The $Re_2(CO)_{10}^{2+}$, d^6–d^6, overlap population is slightly positive for all θ, whereas the $Mn_2(CO)_8(PH_2)_2$ overlap population is slightly negative. The difference is in the σ^* level, and $\pi_\perp^*$, if it is occupied. Both of these are really more involved in bridge bonding than in metal–metal bonding. If we exclude them from the configuration count, then the d-block orbitals that remain filled in the d^7–d^7 complex are $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2}$, for a net single bond.

The interesting conclusion is that the d^7–d^7 $M_2(CO)_8(\mu\text{-}CO)_2$ complexes are like the d^5–d^5 $M_2(CO)_8(\mu\text{-}PH_2)_2$, which connects up to our previous discussion of the ambiguity of electron counting and bonding in the bridge region: the μ-CO complex would revert to d^5–d^5 if the carbonyls were artificially counted as CO^{2-}. The

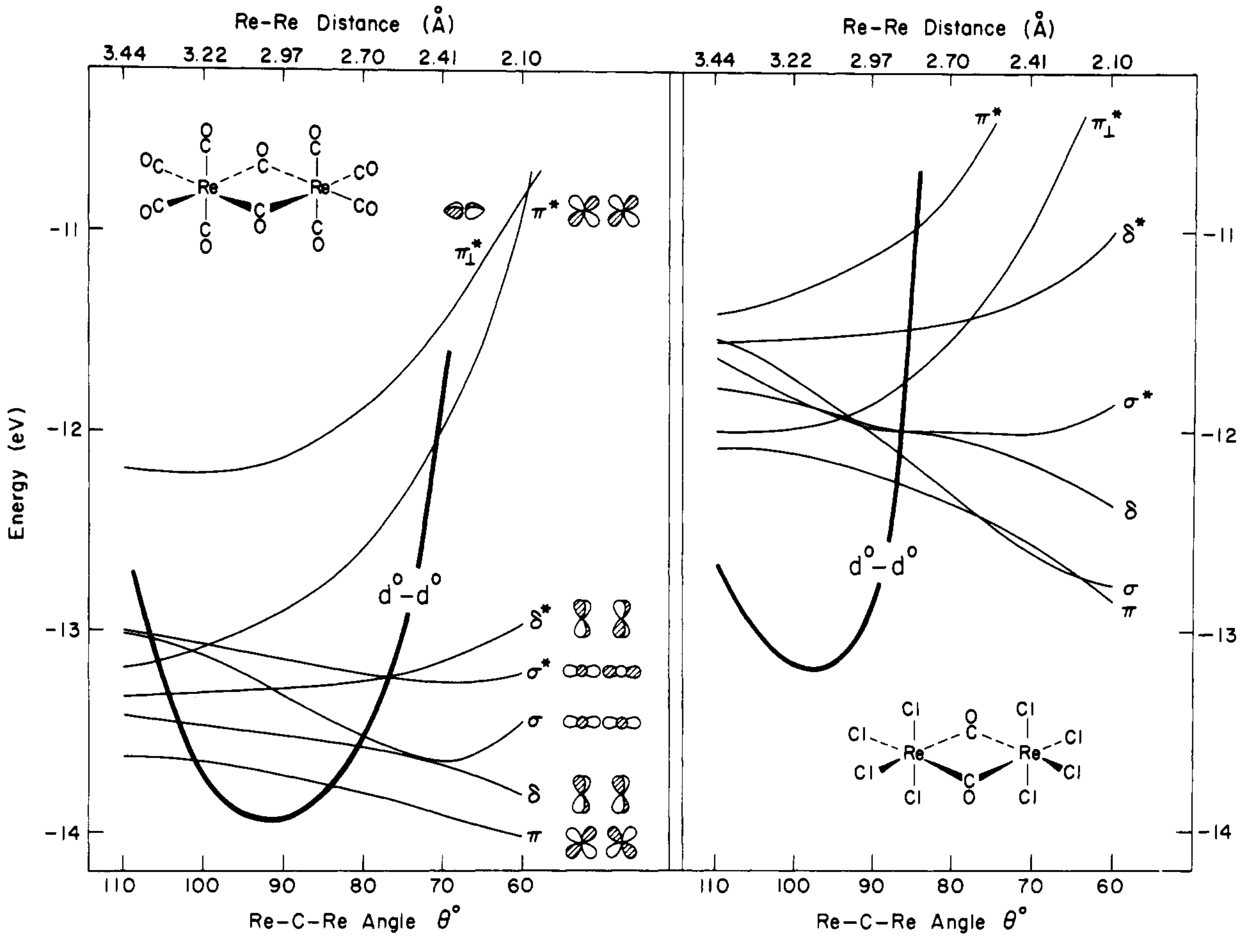


Figure 8. Computed energy of d-block orbitals of $Re_2(CO)_{10}$ and $Re_2Cl_8(CO)_2$ as a function of MLM bridging angle. d^0–d^0 energy curves are superimposed. For these the energy zero is arbitrary and the energy scale is the same as for the orbital energies.

similarity of d^7–d^7 $M_2(CO)_8(\mu\text{-}CO)_2$ and d^5–d^5 $M_2(CO)_8(PH_2)_2$ would not at all surprise anyone using classical 18 electron rule considerations, for in either case, no matter how one counts electrons, a metal–metal single bond would be forced.

The d^9–d^9 energies are superimposed on the Walsh diagram of Figure 8; the actual computed minima for various electron counts are listed in Table III. Keep in mind the ambiguity mentioned above, that two orbitals in the d block perhaps should be considered to be part of the bridge bonding core. In $Re_2(CO)_{10}$ the d^9 curve has a broad minimum near $\theta = 90°$. The onset of the repulsive wall occurs only for $\theta < 70°$, so the d orbitals are able to shift the minimum according to their occupation. For terminal chlorides the d^0 curve is very steep for $\theta < 90°$. It dominates all configurations, which optimize at θ 92–95°.

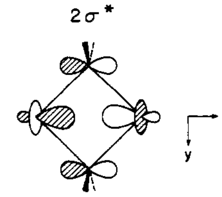
The lowest unfilled level in the d^7–d^7 carbonyl bridging complexes is a $2\sigma^*$, strongly metal–metal antibonding. It will be discussed in detail in the next section, but it is interesting to note here that the photochemistry of $Cp_2M_2(CO)_4$ complexes is dominated by M–M bond cleavage, in accord with population of this orbital in the excited state.[26]

Bridging Methylenes

Carbonyl and carbene are similar in our calculations, except that CH_2 is both a better σ donor and a better π acceptor. The mixing that provided an ambiguity as to the nature of σ^* and $\pi_\perp^*$ is thus accentuated. The calculated Walsh diagrams (Figure 10 shows one) are generally similar to Figure 8, with one additional feature. This is the presence at high θ of another low-lying orbital. It is σ^* in symmetry, shown in **36**.

Table III. Optimum Geometries for CO Bridged Complexes

d-electron configuration	θ_{min}, deg	r_{min}, Å	closed shell configuration
		$Re_2(CO)_8(\mu\text{-}CO)_2^z$	
d^7–d^7	92.0	3.018	$\pi^2\ \delta^2\ \delta^{*2}\ \sigma^2\ \sigma^{*2}\ \pi^{*2}\ \pi_\perp^{*2}$
d^6–d^6	85.5	2.852	$\pi^2\ \delta^2\ \sigma^2\ \delta^{*2}\ \sigma^{*2}\ \pi^{*2}$
d^5–d^5	73.7	2.520	$\pi^2\ \delta^2\ \sigma^2\ \sigma^{*2}\ \delta^{*2}$
d^0–d^0	90.0	2.970	
		$Re_2Cl_8(\mu\text{-}CO)_2^z$	
d^7–d^7	94.9	3.094	$\pi^2\ \pi_\perp^{*2}\ \sigma^{*2}\ \delta^2\ \sigma^2\ \delta^{*2}\ \pi^{*2}$
d^6–d^6	92.7	3.040	$\pi^2\ \sigma^{*2}\ \delta^2\ \sigma^2\ \pi_\perp^{*2}\ \delta^{*2}$
d^5–d^5	92.3	3.029	$\pi^2\ \sigma^{*2}\ \sigma^2\ \delta^2\ \pi_\perp^{*2}$
d^4–d^4	91.9	3.018	$\pi^2\ \sigma^{*2}\ \delta^2\ \sigma^2$
d^0–d^0	98.0	3.170	



36

The parentage of this level may be traced as follows. Referring back to the $M_2(CO)_8$ fragment (i.e., no bridging group) of Figure 3, one sees two b_{3u} or σ^* levels. One is from the d block, the out-of-phase mixture of $z^2 - y^2$. The other is from the out-of-phase mixture of the $M(CO)_4$ fragment orbitals, and lies very high in energy. The two methylenes contribute a b_{3u} combination which

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[26] (a) Abrahamson, H. B.; Palazzotto, M. C.; Reichel, C. L.; Wrighton, M. S. J. Am. Chem. Soc. 1979, 101, 4123–4127. (b) Calderon, J. L.; Fontana, S.; Frauendorfer, E. J. Organomet. Chem. 1974, 64, C10.

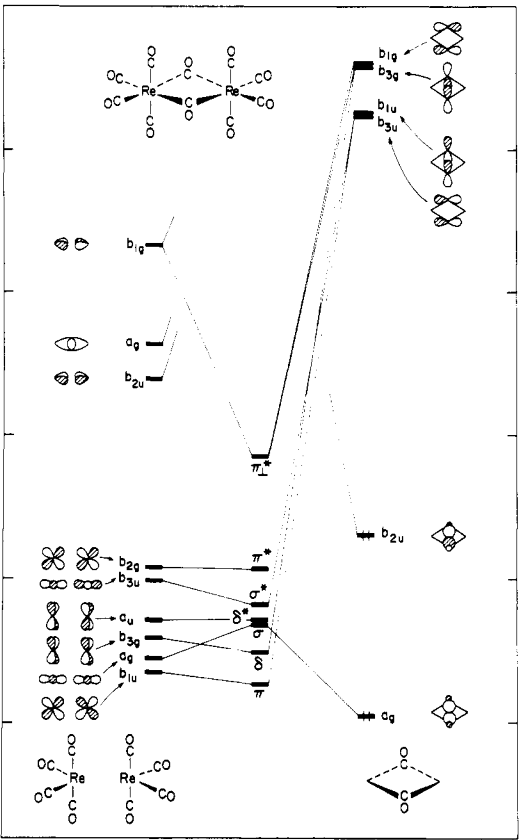

Figure 9. Interaction diagram for $Re_2(CO)_8$ with two bridging carbonyls, in a geometry corresponding to the $Re_2(CO)_8$ dimer with Re–C–Re 90°. The $2\sigma^*$ orbital is omitted.

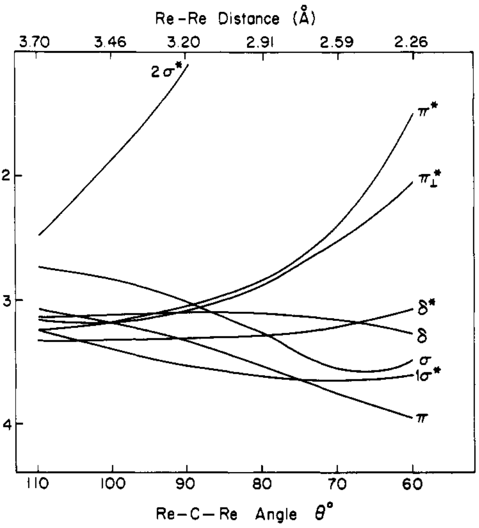

Figure 10. Walsh diagram for $Re_2(CO)_8(\mu\text{-}CH_2)_2$ as a function of Re–C–Re angle. Some levels belonging to the core are omitted from the diagram.

is 2 eV above the d block. It is sandwiched between the two $M_2(CO)_8$ σ^* levels and this is what becomes **36**. The presence of this eighth low-lying orbital is important, because it allows the existence of d^8–d^8 complexes. A similar orbital is present in the carbonyl case, but it is substantially higher in energy.

The optimized geometries are listed in Table IV. d^7–d^7 and d^8–d^8 configurations are nice closed shells. The d^0–d^0 curve is shallow, allowing a tuning of the geometries by the d-electron count. The equilibrium geometries, e.g., for d^7–d^7, emerge some 10° smaller than in the carbonyl case.

Table IV. Geometries of Methylene Bridged Complexes $Re_2(CO)_8(CH_2)_2^z$

d-electron configuration	θ_{min}, deg	r_{min}, Å	closed shell configuration at θ_{min}
d^8–d^8	102.1	3.515	$1\sigma^{*2}\ \delta^{*2}\ \pi_\perp^{*2}\ \pi^2\ \pi^{*2}\ \delta^2\ \sigma^2\ 2\sigma^{*2}$
d^7–d^7	81.9	2.962	$1\sigma^{*2}\ \pi^2\ \sigma^2\ \delta^{*2}\ \delta^2\ \pi_\perp^{*2}\ \pi^{*2}$
d^6–d^6	77.6	2.832	$\pi^2\ 1\sigma^{*2}\ \sigma^2\ \delta^{*2}\ \delta^2\ \pi_\perp^{*2}$
d^5–d^5	<60	<2.26	$\pi^2\ 1\sigma^{*2}\ \sigma^2\ \delta^2\ \delta^{*2}$
d^0–d^0	80.0	2.905	

As in the carbonyl case the simple counting up of the occupied orbitals labeled as MM bonding or antibonding does not reflect properly the nature of the MM interaction; $1\sigma^*$ and $2\sigma^*$ between themselves carry a mixture of metal–metal nonbonding and slight antibonding, barely enough to cancel out σ. $\pi_\perp^*$ is mainly involved in bridge bonding. The net effect is close to no bond in d^8–d^8, a single bond in d^7–d^7. Again this is pretty much what one would expect had one counted the bridging groups as CH_2^{2-}.

A highly interesting feature of Figure 10 is the existence of a substantial energy gap between δ^* and $\pi_\perp^*$ at low θ, coupled with a shallow d^0–d^0 curve. A low-spin d^5–d^5 complex with a very short metal–metal bond is an intriguing possibility.

Comparison with Experiment for Bridging Acceptors

The known carbonyl-bridged M_2L_{10} structures to our knowledge all have a Cp ring on each metal and a formal d^7–d^7 electron count. A summary of these structures, as well as of the methylene-bridged ones, is given in the supplementary material deposited with this paper. All the known carbonyl-bridged d^7–d^7 complexes have 83° $\leq \theta \leq$ 87°, which is a slightly smaller value than we compute for the somewhat different d^7–d^7 $M_2(CO)_{10}$ system.

Typical of the carbene and other group 4 ER_2 structures are the d^8–d^8 $Fe_2(CO)_8(\mu\text{-}SnMe_2)_2$, θ = 103.7°, Fe–Fe 4.139 Å,[27] and $Mn_2(CO)_8(\mu\text{-}SnPh_2)_2$, θ = 73.4°, Mn–Mn 2.871 Å.[8] Carbene bridging indeed diverts θ to smaller values by ~10° and allows the existence of d^8–d^8 compounds, as expected.

A very interesting structure has recently been determined, that of $Re_2(NCS)_{10}^{3-}$. It has typical bioctahedral geometry, θ = 77°, Re–Re 2.61 Å.[28] This is a d^3–d^4 system. If the level scheme of $Re_2(CO)_{10}$, Figure 8, can be used for the thiocyanate ligand as well, we would conclude that in this molecule there are five energy levels, π, δ, σ, σ^*, and δ^*, available for the seven electrons. It is difficult to predict the ground spin state, because the levels in question are not much separated from each other. But, as the slopes of the orbitals in Figure 8 show, *any* assignment of the electrons within the block of five should lead to a short metal–metal bond and small θ. This is what is observed.

Bridge Bonding and Acceptor Bridging

We explicitly noted above the dichotomy in electron counting between bridging acceptors (normally counted as two-electron donors) and bridging donors (four-electron donors). We also showed that if this convention is followed two of the orbitals in what is normally considered the d block are equally bridge and d orbitals. A consequence of this observation is that there is a correlation between the d^8, d^7, and d^6 acceptor bridging cases and the d^6, d^5, and d^4 Vahrenkamp compounds. Let us try to resolve some of the ambiguity remaining in this story, and delineate a simple picture of bridge bonding for μ-A.

It takes eight electrons to bond the bridging region. The picture we have had before, for bridging donors, is symbolized by **24a**. In this resonance structure there are two localized donor–acceptor

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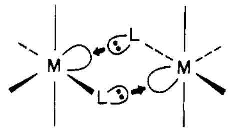
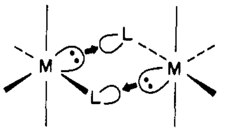
[27] Gilmore, C. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1972**, 1387.

[28] Cotton, F. A.; Davison, A.; Ilsley, W. H.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 2719.



24a



24b

dative bonds between a lone pair on L of one ML_5 unit and an empty orbital of the other ML_5 unit. The complete delocalized picture of bridge bonding has been given before—the four delocalized orbitals of **25–28** are equivalent to four localized bonds (**30–33**), two of which are explicitly shown as dative in **24a**.

When the bridging position is occupied by an acceptor, the roles of the metal and ligand reverse from those indicated in **24a**. Now the M centers are required to be electron rich to take part in dative bonding with the acceptor orbitals on L, as shown in **24b**. The bridge bonds form. They use up four electrons, which in this convention are assigned originally to the metal.

Here is the important difference and the connection, between the μ-A and μ-D cases. In the d^n–d^n μ-D case all $2n$ metal electrons are available for occupying the six MM bonding and antibonding orbitals (the d-block MOs, the ones made up of the three low-lying t_{2g}-like orbitals of each ML_5 moiety). In the d^n–d^n μ-A case four of those electrons are used up in completing the bridge bonding, and only $2n - 4$ are available for the real d block. Thus:

1. The d^8–d^8 μ-A complexes will have two bridging bonds, and then a sufficient number of electrons to fill up all six MM orbitals. The result is no M–M bond, the same as the d^6–d^6 Vahrenkamp case.

2. The d^7–d^7 μ-A case will have only ten electrons to occupy the six MM orbitals, resulting in a formal single MM bond. Again this is analogous to the d^5–d^5 Vahrenkamp compounds. Here also the μ-CR_2 compounds will be more stable than the μ-CO. This is likely to be the reason why all the μ-CO d^7–d^7 cases we found are of the $M_2Cp_2(CO)_2(\mu\text{-}CO)_2$ variety, whereas, the μ-CR_2 cases are of the $M_2(CO)_8(\mu\text{-}CR_2)_2$ type. Replacement of three COs by Cp makes the metal center a better electron donor and this is needed in order to form strong bridging bonds with the inferior (relative to CR_2) acceptor CO. Continuing this line of thought, one may expect d^7–d^7 $M_2Cp_2(CO)_2(\mu\text{-}CR_2)_2$-type compounds to be even more stable than the $M_2(CO)_8(\mu\text{-}CR_2)_2$ type. We think that some of these will be made soon.

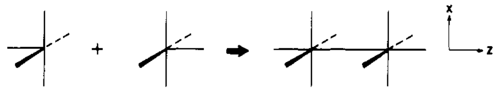
3. The d^6–d^6 case will have eight electrons which will occupy four out of the six MM orbitals. This leads to compounds having two bridge bonds plus two formal MM bonds, much like the d^4–d^4 Vahrenkamp compounds. As we mentioned before, we have not been able to find any such acceptor bridged complexes. A synthetic challenge arises.

4. As the bridging ligand becomes a better acceptor and the metal orbital a better donor, the bonding in the bridge region will be strengthened. Thus, for each d count the CR_2-type ligands will form stronger bridging bonds than does CO or its analogues. Moreover, substitution of 3 CO on the metal by Cp will raise the orbitals of the metal, making the metal a better donor. Thus, bridging should be favored in the $Cp_2M_2(CO)_2(\mu\text{-}CO)_2$ family more than in $(CO)_8M_2(\mu\text{-}CO)_2$, as is indeed observed.[10–13] In general, CO bridging will require a better electron donor metal orbital than does CR_2.

Now that we have settled some of the bothersome questions regarding the bridge region, and we have understood what holds the bridged compounds together, we can turn to the next question. What about alternative L_5MML_5 compounds?

Metal–Metal Bonded Dimers

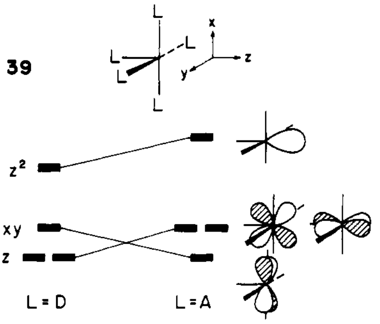
M_2L_{10} complexes in which the metal–metal bond is not supported by bridges form a fascinating group of complexes, from quadruply bonded $Re_2Cl_8L_2^{2-}$ to singly bonded $Mn_2(CO)_{10}$. That we have not, and will not, devote much attention to them is not a reflection of their unimportance. On the contrary, the story of the quadruple bond, as elegantly developed by Cotton and co-workers,[4] is a most fascinating one. The reason we will not spend much time on these lovely molecules is because they have already been subjected to extensive theoretical scrutiny. Even if there is no unanimity, much is known about their electronic structure.[29] Let us quickly construct the orbitals of M_2L_{10}, from those of two ML_5 fragments, **37** and **38**.



37 **38**

The orbitals of a C_{4v} ML_5 fragment are well-known.[20a,b] Above a set of three orbitals descended from t_{2g} of an octahedron there is a lone hybrid, made up of *s*, *z*, and z^2, and pointing toward the missing octahedral site, **39**. The position of *xz*, *yz* relative to *xy* depends in an obvious way on the π-donor or -acceptor character of the ligands. The energy and shape of the z^2 hybrid are sensitive to the distance and electronic properties of the unique axial ligand and to the apical to basal ligand angle.

39



The four valence orbitals of ML_5 partition nicely into $\sigma(z^2)$, $\pi(xz,yz)$, and $\delta(xy)$ symmetries. These are preserved when the D_{4h} dimer is formed. Figure 11 shows the interaction that follows upon building up $Re_2Cl_{10}^{4-}$ from two $ReCl_5^{2-}$ and $Re_2(CO)_{10}$ from two $Re(CO)_5$ units. The pairwise splitting of ML_5, σ, π, and δ into M_2L_{10} σ, σ^*, π, π^*, δ, and δ^* in each case is obvious. There are, however, crucial differences in detail, which we now describe.

The splitting between σ and σ^*, π and π^*, and δ and δ^* is much greater for Re_2Cl_{10} than for $Re_2(CO)_{10}$. There are two factors responsible for this. First, there is a greater localization of the orbitals of σ, π, and δ symmetry on the metal in the case of the chloride, leading to a greater overlap of the fragments in dimer formation. The numbers next to the ML_5 orbitals in Figure 11 indicate the percent localization of a given orbital on the metal. Second, the distance between the metal atoms is much greater in $Re_2(CO)_{10}$.

The level pattern for Re_2Cl_{10} is π below σ below δ below δ^*. The position of σ in this level scheme may seem strange—one might think that σ would be below π. That is in fact what we obtain if the axial chloride is removed, to form Re_2Cl_8. The axial ligation pushes σ up.

There is no question that there is a quadruple bond in $Re_2Cl_{10}^{4-}$, d^4–d^4. The overlap population for this configuration is 1.133. Two

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(29) (a) Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1967**, *6*, 924. (b) Mortola, A. P.; Moskowitz, J. W.; Rösch, N. *Int. J. Quantum Chem., Symp.* **1974**, *8*, 161. (c) Norman, J. G., Jr.; Kolari, H. J. *J. Chem. Soc., Chem. Commun.* **1974**, 303. *J. Am. Chem. Soc.* **1975**, *97*, 33; **1978**, *100*, 791. (d) Biagini Cinoli, M.; Tondello, E. *Inorg. Chim. Acta* **1974**, *11*, L3. (e) Cotton, F. A.; Kalbacher, B. J. *Inorg. Chem.* **1977**, *16*, 2386. Cotton, F. A.; Stanley, G. G. *Ibid.* **1977**, *16*, 2668. (f) Benard, M.; Veillard, A. *Nouveau J. Chim.* **1977**, *1*, 97. Benard, M. *J. Am. Chem. Soc.* **1978**, *100*, 2354. (g) Gardner, C. D.; Hillier, I. H.; Guest, M. F.; Green, J. C.; Coleman, A. W. *Chem. Phys. Lett.* **1976**, *41*, 91. Guest, M. F.; Hillier, I. H.; Gardner, C. D. *Ibid.* **1977**, *48*, 587. (h) Reingeverts, M. D.; Korol'kov, D. V. *Teor. Eksp. Khim.* **1974**, *10*, 596. (i) Hay, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 2897. Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.

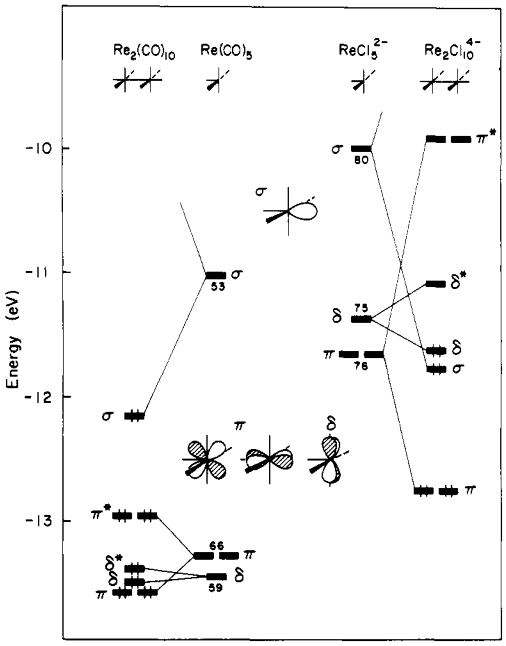
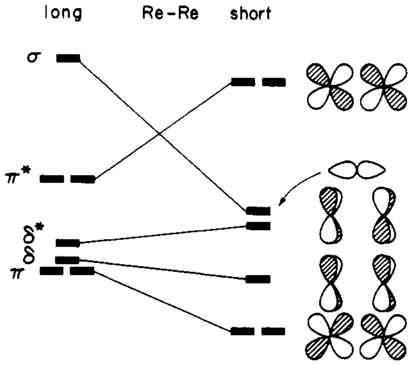


Figure 11. Dimerization of $Re(CO)_5$ (left) and $ReCl_5$ (right). The numbers next to the monomer levels indicate the percentage of the electron density in that MO that is on the metal.

electrons more occupy δ*, two electrons fewer empty δ, either case leading to a triple bond.

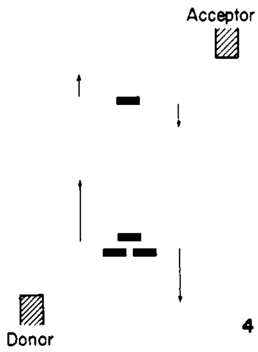
The level ordering in $Re_2(CO)_{10}$ is quite different. Though the same orbitals are there as in Re_2Cl_{10}, the ordering in Figure 11 is $\pi < \delta < \delta^* < \pi^* < \sigma$. Filling all seven levels gives a formal single bond: the Re–Re overlap population for d^7–d^7 is 0.266. It seems that no other electron count would give a nice closed-shell species, and the position of σ appears at first sight anomalously high. In fact the actual position of the levels is quite sensitive to the metal–metal distance. The trend, indicated in **40**, is perfectly consistent with the shorter distance being responsible for stronger metal–metal interaction.



40

The level pattern for short Re–Re distances in $Re_2(CO)_{10}$, shown in **60**, is unusual in that it indicates a triple bond with no σ component for d^3–d^3, only a double bond for d^4–d^4, a triple bond for d^5–d^5, an open-shell double bond for d^6–d^6, and finally the single bond for d^7–d^7. The d^5–d^5 case is interesting. While $V_2(CO)_{10}$ is not known, we do have a set of isolobal $Cp_2M_2(CO)_4$ complexes, M = Cr, Mo, W, with very short metal–metal bonds.[30] The electronic structure of these is discussed elsewhere.[31]

Why is there such a different level pattern for $Re_2(CO)_{10}$ and Re_2Cl_{10}, specifically in the position of the σ level relative to δ and δ*? In $Re_2(Cl)_{10}$ σ is below δ and δ*, a necessary condition for obtaining a quadruple bond in the d^4–d^4 configuration. In $Re_2(CO)_{10}$ σ remains above the δ, δ* pair, no matter what the Re–Re distance. In particular this is so even if the Re–Re distances are made the same in the two complexes. Part of the effect is the aforementioned enhanced interaction due to greater d-electron localization in the halide complex. But most of the effect is traced to the monomer fragment itself. Compare $ReCl_5$ and $Re(CO)_5$ in Figure 11. The general shift upward of the donor substituted levels, relative to those of the acceptor, is obvious, and understandable. But note also that σ is shifted less by the donor–acceptor effect than π or δ. This is because σ is a hybrid of s, z, and z^2, and to a first approximation only the z part feels the π donor or acceptor effect. The phenomenon may be understood from the schematic drawing **41**.



41

In $Re_2(CO)_{10}$ the stabilization of σ upon dimerization of two $Re(CO)_5$ units is not sufficient to bring it below the δ, δ* pair. The crucial positioning of the σ level above the d block is entirely consistent with other computations[32a,b,f] and the experimental evidence.[32] The work of Miessner and Korol'kov[32f] contains a clear analysis of the sensitivity of the level ordering to M–M separation.

While we think that our picture is a consistent one, the reader should be warned that there are many ways in which it could go wrong. First, an approximate MO procedure, the extended Hückel method, is behind our conclusions. Second, in this field MO calculations much better than ours are faced by the limitations of a single-configuration model.[29] Third, a global approach, extrapolating to all molecules from a single model calculation, an approximate one at that, may lead to results that do not hold for every case, or for every d-electron configuration.[33]

Interconversion of Bridged and Metal–Metal Bonded Structures

At the beginning of this paper we stated the basic question that served as the impetus to this study. How does it come about that three sets of d^4–d^4 complexes coexist side by side: the quadruply bonded Cotton compounds $Re_2Cl_8L_2^{2-}$, the bridged, metal–metal

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(30) (a) Potenza, J.; Giordano, P.; Mastropaolo, D.; Efraty, A.; King, R. B. *J. Chem. Soc., Chem. Commun.* **1972**, 1333–1334. Potenza, J.; Giordano, P.; Mastropaolo, D.; Efraty, A. *Inorg. Chem.* **1974**, *13*, 2540. (b) Klingler, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034–5039; **1975**, *97*, 3535–3536. (c) Curtis, M. D.; Butler, W. M. *J. Organomet. Chem.* **1978**, *155*, 131. (d) Chisholm, M. H.; Rankel, L. A.; Bailey, W. I., Jr.; Cotton, F. A.; Murillo, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 1261–1262. Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Rankel, L. A. *Ibid.* **1978**, *100*, 802–807. Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rankel, L. A. *Ibid.* **1978**, *100*, 807–811. Bailey, W. I., Jr.; Cotton, F. A.; Jamerson, J. D.; Kolb, J. B. *J. Organomet. Chem.* **1976**, *121*, C23–C26. Bailey, W. I., Jr.; Collins, D. M.; Cotton, F. A. *Ibid.* **1977**, *135*, C53–C56. (e) Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 3533–3535. Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85–94. Ginley, D. S.; Bock, C. R.; Wrighton, M. S.; Fischer, B.; Tipton, D. L.; Bau, R. *J. Organomet. Chem.* **1978**, *157*, 41–50.

(31) (a) Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R., *J. Am. Chem. Soc.* **1980**, *102*, 2576–2585. (b) Hofmann, P., to be published.

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(33) A referee notes in this context the different d block level schemes for $Mo_2(O_2CCH_3)_4$ and $Rh_2(O_2CCH_3)_4$ (ref 29c).

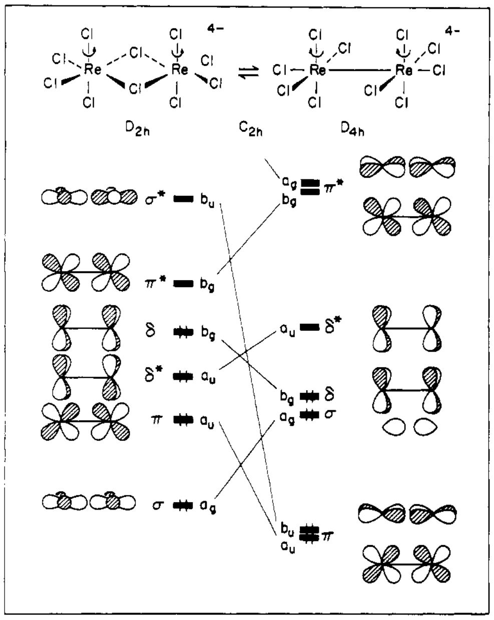
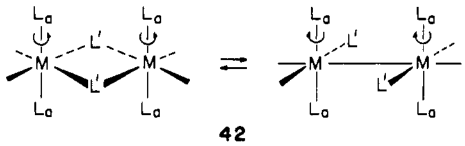


Figure 12. Correlation diagram between the levels of a bridged Re_2Cl_{10}, Re–Cl–Re 70°, and an unbridged, quadruply bonded structure.

unbonded, high-spin Walton complexes such as $Re_2Cl_6(dppe)_2$, and the still bridged but metal–metal bonded low-spin Vahrenkamp molecule $V_2(CO)_8(PR_2)_2$? A thorough investigation of the bridged complexes has laid bare the combination of steric factors, bridge bonding, and direct metal–metal interaction that makes one ligand set prefer the Vahrenkamp structure, another ligand the geometry and spin state of the Walton complexes.

Still to be explored is the interconversion of the bridged and unbridged alternatives. One way of relating these geometrical extremes of idealized D_{2h} and D_{4h} symmetry is through a C_{2h} path which may be described as a concerted rotation of the ML_5 moieties about the local vertical axes, **42**. We cannot trust the extended Hückel method to evaluate the energetics of this path, but we can inquire whether there are any symmetry-imposed barriers to these reactions.



42

A level correlation diagram is easy to construct but first we must worry about geometrical realities at each end of the correlation. In the metal–metal bonded $Re_2Cl_{10}^{4-}$ the axial bonds (now we use the label axial for the ligands along the MM axis) are likely to be stretched somewhat from 2.34 Å.[34a-g] We have studied this effect, of some interest also in connection with recent results on supershort quadruple bonds.[34h] It is a minor one in the present context, for only the metal–metal δ level (see Figure 11) is affected by it, shifting progressively to lower energy as M–L axial is stretched. At the bridged dimer end, the question is which part of the Walsh diagram of Figure 2 to correlate. Recall that steric effects limit access to the low θ region of the bridged dimers for terminal donors but not for terminal acceptors. The low θ region is the most interesting one, for in it exist the Vahrenkamp complexes. To avoid the construction of an excessive number of diagrams we show only one diagram, to the orbitals of a representative geometry in the double-bond region (θ = 70°). Then we can use the Walsh diagram to correlate over to the region of larger θ where the Walton compounds lie.

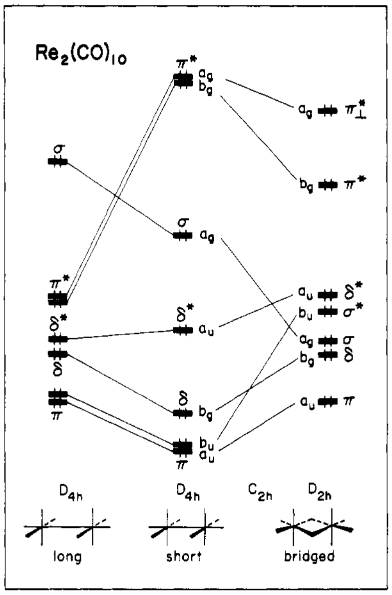
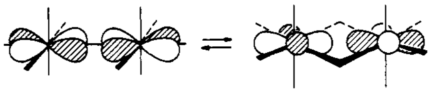


Figure 13. Correlation diagram between bridged and unbridged structures of $Re_2(CO)_{10}$. The correlation is simplified if, as at left, the Re–Re distance in the unbridged structure is reduced from 3.0 Å.

The intermediate symmetry is C_{2h}. The group theoretical reductions from D_{2h} and D_{4h} are simple to carry out. The resulting correlation diagram, Figure 12, clearly shows that the d^4–d^4 and d^5–d^5 reactions have a symmetry-imposed barrier due to a level crossing, if the bridged complex is at small θ. The villain of the piece is one of the π components of the quadruple bond, **43**, which clearly correlates with a σ^* level **44** in the bridged complex.



43 **44**

In the region of the large θ, where the Walton complex actually finds its equilibrium geometry, the σ^* level is at much lower energy (see Figure 2). The symmetry-imposed barrier does not exist, but this is not saying much because this is the region in which the levels are bunched up and the ground state should be and is a high-spin complex. The application of orbital symmetry conservation reasoning to reactions in which the spin state changes is ambiguous. In principle they should be forbidden. In practice they are facile: witness the familiar Ni(II) singlet–triplet equilibrium. One of us has worried much about the problem in the organic context.[35]

The correlation diagram shown above was for $Re_2Cl_{10}^{4-}$. We have also constructed a similar diagram connecting bridged and open structures of a model for the Vahrenkamp complexes, $Cr_2(CO)_8(PH_2)_2^z$, z = 2+, 0, 2–. Differing in some detail, it resembles in its essentials the diagram that interrelates the Walton and Cotton complexes. It is again a forbidden reaction for the d^4–d^4 (or d^5–d^5) molecules, allowed for d^6–d^6.

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The bridged complexes with μ-CO and μ-CH_2 have a fundamentally different orbital structure. Thus it is not surprising that the level correlation diagram which interrelates bridged and MM bonded structures of $Re_2(CO)_{10}$ (Figure 13) shows that the reaction is allowed for d^6–d^6 and the popular d^7–d^7 configuration.

There is a substantial amount of data[10n,g,r,s,y,36] on the facile interconversion of cis and trans isomers and terminal-bridge ligand exchange in $M_2Cp_2(CO)_2(\mu\text{-}CO)_2$ and related d^7–d^7 molecules. The mechanism which was established by the Cotton group[36n] involves the opening of the bridged structure to a MM bonded structure which can either close back allowing terminal–bridge ligand exchange or can undergo internal rotation leading to cis $\rightleftarrows$ trans interconversion.

A more detailed theoretical account of bridging alternatives in $(CpM(CO)_2)_2$ is given elsewhere.[31] The reader is also directed to a recent theoretical study of the bridging–nonbridging transformation by Burdett.[20d] It should also be said explicitly that the concerted mode of bridging–terminal ligand interconversion (**42**) is certainly not the only possibility. For a very nice consideration of alternative modes in the context of a multifaceted study of M_2L_{10}, M = Nb, Ta, L = OCH_3, the reader is directed to the work of Reiss and Hubert-Pfalzgraf.[37a]

Summary

Why do these M_2L_{10} complexes have the structures that they do? Our problem is inherently multidimensional, in electronic as well as Cartesian space. What we mean by this is that one has to worry not only about the geometrical degrees of freedom of the bridging and unsupported structures but also about the donor and acceptor capabilities of the ligands and the d-electron count. Let us summarize what we have learned about each structural type and then take a slice of the multidimensional surface along the d-electron count "coordinate".

$M_2A_8(\mu\text{-}D)_2$. The d^4–d^4 system *strives* to attain a double MM bond and the d^5–d^5 a single bond, and there is no bond in the d^6–d^6 case. For all of the d counts the bonding is augmented by bridge bonds whose strength depends on the electron-donating capability of μ-D and the acceptor ability of the ML_5 moiety. Higher d counts should be rare.

$M_2D_8(\mu\text{-}D)_2$. A high-spin complex with no metal-metal bonding is likely for any d count (except of course d^6–d^6 and d^0–d^0). MM bonding may materialize if the steric interaction of the apical ligands (e.g., **23**) is relieved. Once again, the structures are buttressed by bridging bonds and d counts higher than d^6–d^6 should be rare.

$M_2A_8(\mu\text{-}A)_2$. d^7–d^7 and even d^8–d^8 are now possible, with a formal single MM bond and no bond, respectively. In both cases there are bridge bonds whose strength depends on the acceptor strength of μ-A. Thus d^8–d^8 is more likely for μ-CR_2, μ-GeR_2, etc., than for μ-CO. Lower d counts, d^6–d^6 and d^5–d^5, with reasonably strong MM bonding are attractive possibilities. There exists an analogy between each d^n–d^n case and the d^{n-2}–d^{n-2} Vahrenkamp compounds.

$M_2D_8(\mu\text{-}A)_2$. As for the analogous μ-D case, these are likely to be high-spin complexes, except for d^7–d^7.

Now let us shift to another region of this space. This is the region where M_2L_{10} exists as L_5MML_5. What have we learned about the effect of the d-electron count?

D_5MMMD_5 (and by Inference D_4AMMAD_4). These metal–metal bonded species will be particularly stable for the d^4–d^4 Cotton compounds, where a quadruple bond exists. Two electrons more or less retains a triple bond.

A_5MMA_5 (and DA_4MMA_4D). For most acceptor ligands the maximum bonding capability is a triple MM bond. This will materialize for d^5–d^5 and for d^3–d^3. d^4–d^4 will have only a double MM bond, unlike the Cotton d^4–d^4 compounds. d^6–d^6 is a special case where a double-bonded species with a short bond and possibly open shell may exist. d^7–d^7 will be MM single bonded and closed shell.

After summarizing the events in each subspace let us now attempt to journey from one to the other asking the question: when do we expect bridging and when MM bonded structures? One could doubt whether an estimate of relative stability is forthcoming from an approximate MO study of the extended Hückel type, and indeed we do not trust our calculated total energies as a guide to thermodynamic stability. But there is a lot we have understood about those pieces of M_2L_{10} surface we have explored. Consequently, we are able to formulate some rules of thumb.

All the bridged structures have two bridge bonds (e.g., **24**) which are not present in the MM bonded analogues. These two bonds may or may not be augmented by formal MM bonds. The number of MM bonds in the L_5MML_5 was surveyed above. Thus, we can compare the total number of bonds for each structural alternative, a simplistic but useful protocol.

d^0–d^0, d^1–d^1, d^2-d^2. All geometrical alternatives examined show little distinction between high-spin and low-spin, donor or acceptor. Donors satisfy the electron deficiency of these systems, so kinetically such acceptor substituted complexes are unlikely. Bridging helps out no matter what the spin state.

d^3–d^3. Now begins a choice for donor substituted molecules—they may assume either the Cotton structure with a triple bond or that of a high-spin bridged complex. Acceptor substituted molecules find a single stable point: the triple bonded nonbridging structure.[30]

d^4–d^4. The M_2D_{10} compounds can have a quadruple bond in a D_5MMD_5 structure (the Cotton compounds). The bridged structures have at most two bridged bonds. Thus, in *most* cases M_2D_{10} will find a deeper minimum in the MM bonded structure. The high-spin Walton compounds are interesting alternatives. Most intriguing are the possibilities for doubly bridging, doubly bonded isomers of the Cotton compounds, separated by a symmetry-imposed barrier from their quadruply bonded unbridged analogues.

On the acceptor side the $M_2A_8D_2$ system can have at most a double MM bond in an L_5MML_5 structure. On the other hand, the bridged compounds have two formal MM bonds in addition to two bridge bonds, and will be the system of choice.

d^5–d^5. With many acceptor substituents, there is only an interesting multiply bonded minimum in a bridged structure. If several donors are present, compounds of the Vahrenkamp and Walton class are possible, and with many donors the compound should take on a triply bonded unbridged structure. There are many examples of this last structural type from the studies of Cotton and co-workers.[37b]

d^6–d^6. The L_5MML_5 structures will have at most a double MM bond and may be open shell. On the other hand, the Vahrenkamp and the Walton compounds are nice closed-shell molecules with two bridge bonds, and will be the structures chosen. A greater preference for bridging should exist for μ-A, where in addition to bridge bonds two formal MM bonds are expected.

d^7–d^7. Here in the case of M_2D_{10} there is a clear preference for D_5MMD_5, because d^7–d^7 is not stable in a bridged structure. However, when most of the ligands are acceptors, bridged geometries offer a real alternative. μ-A bridges should be strongly preferred for μ-CR_2, μ-GeR_2, etc., which are strong acceptors. This is not so for μ-CO (e.g., Mn_2CO_{10}) which requires Cp terminal ligands to buttress the donor–acceptor bridge bonds (e.g., $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$.

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Table V. Extended Hückel Parameters

atom	orbital	H_{ii}	orbital exponent[a] 1	2
Cr	4s	−8.66	1.700	
	4p	−5.24	1.700	
	3d	−11.20	4.95 (0.505 79)	1.800 (0.674 72)
Re	6s	−9.36	2.398	
	6p	−5.96	2.372	
	5d	−12.66	5.343 (0.635 91)	2.277 (0.567 71)
P	3s	−18.60	1.600	
	3p	−14.00	1.600	
Cl	3s	−26.30	2.033	
	3p	−14.20	2.033	
C	2s	−21.40	1.625	
	2p	−11.40	1.625	
O	2s	−32.30	2.275	
	2p	−14.80	2.275	
H	1s	−13.60	1.30	

[a] In parentheses, the coefficients in the double ζ expansion of the d orbitals.

d^8–d^8. Now a superlative bridging acceptor, such as a carbene, allows a structure in which there is no metal–metal bonding.

Stereochemical variety, isomerism, is what makes all of chemistry interesting. Inorganic molecules often provide isomeric richness by making choices between bridged and unbridged structures. We believe that we have achieved a certain degree of understanding of the factors that influence that choice.

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Appendix

Extended Hückel calculations[38a] were used, with a weighted H_{ij} formula.[38b] The parameters taken from previous calculations[16a,17i] are listed in Table V.

The geometric parameters of the model compounds were the following.

$Cr_2(CO)_8(\mu\text{-}PH_2)_2$. Cr···C = 1.85 Å, C···O = 1.15 Å, Cr–P = 2.35 Å, P···H = 1.438 Å, angle HPH = 100°, all CCrC angles were taken as 90 and 180°.

Re_2Cl_{10}. ReCl = 2.34 Å; all ClReCl angles were taken as 90 and 180° for the bridged structure. The ReRe bonded structure had optimized 160 and 70° ClReCl angles.

$Re_2(CO)_{10}$. Re–C(terminal) = 1.9 Å, Re–C(bridged) = 2.1 Å, C–O(terminal) = 1.15 Å, C–O(terminal) = 1.18 Å, all CReC angles were taken as 90 and 180° for the bridged and the MM bonded structure.

$Re_2(CO)_8(\mu\text{-}CH_2)_2$. Re–C(terminal) = 1.9 Å, Re–C(bridged) = 2.26 Å, HCH angle = 109.47°, C–H = 1.08 Å, all CReC angles for the terminal ligands were taken as 90 and 180°.

Supplementary Material Available: A summary of experimental data on donor and acceptor bridged M_2L_{10} complexes, with discussion (7 pages). Ordering information is given on any current masthead page.

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Effects of Basis Set and Configuration Interaction on the Electronic Structure of Methyllithium, with Comments on the Nature of the C–Li Bond

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Abstract: Ab inito calculations have been performed for methyllithium, employing a variety of Slater atomic orbitals in order to assess the basis set dependence of the wave functions of methyllithium and related molecules. Modifications to the electronic structure with changes in basis set are monitored through variations in the total energy, dipole moment, and total electron density, studied with the aid of electron density and density difference maps. The effects of electron correlation are examined by performing a large configuration interaction calculation starting from the most elaborate Hartree–Fock wave function. Previously used criteria for assessing the relative ionic or covalent character of chemical bonds are criticized, on the basis of a comparison of test calculations performed on a series of small molecules. The question of the amount of charge separation involved in C–Li bonding is reexamined by using our more complete wave function.

It has long been recognized that the accuracy of quantitative and even qualitative predictions formulated from the results of ab initio quantum mechanical calculations depends strongly upon the basis set employed. In light of this fact, it is surprising that relatively few studies of the variation in the description of molecular electron density with changes in basis set have been carried out. The majority of the reported investigations of the computational characteristics of various basis sets have tended to focus on the deployment of a limited range of sets of orbitals in the study of a wide collection of molecules.[2-4] The accuracy of the various

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