One can account for the data by assuming that ISC is not rate determining for **1a,b**, but is rate determining for **8**:

$$^{3}[\mathbf{1a,b}] \xrightarrow{\text{fast}} {}^{1}[\mathbf{1a,b}] \xrightarrow{\text{slow}} \text{product}$$

$$^{3}[\mathbf{8}] \xrightarrow{\text{slow}} {}^{1}[\mathbf{8}] \xrightarrow{\text{fast}} \text{product}$$

This appears unlikely as no a priori reason for this change in mechanism is immediately apparent. Another interpretation of the data is that triplets **1a,b** cyclize to the excited triplet state of the acenaphthene.[13] This also appears unlikely as annealing a sample of **1a** in hexafluorobenzene from 77 K to room temperature, in a dark room, does not produce any visible emission.

Wirz has observed dramatic rate accelerations of the decay of **8** in the presence of heavy atoms.[15b] However, the effect of the matrix on the reactivity of **1a** is quite modest. At 110 K the rate constants of decay of **1a** in 2-methyltetrahydrofuran, hexafluorobenzene, and iodobenzene are 4.8 ± 0.3, 6.1 ± 0.3, and $7.1 \pm 0.3 \times 10^{-3}\ \text{s}^{-1}$, respectively. The lifetime of **1a** is not changed by the addition of styrene to 2MTHF. In biradical **8** the internal spin orbit coupling is efficient and ISC can be stimulated by an external heavy atom. When the internal spin orbit coupling is efficient, as in **1a**, the heavy-atom matrix provides little enhancement of ISC.

The relative lifetimes of **1a,b** at 118 K are $k_H/k_D = 6.7$. The isotope effect has its origin predominantly in the respective log A values. These results are reminiscent of isotope effects observed in photoexcited triplets, as perdeuteration substantially increases phosphorescent lifetimes (less efficient $T_1 \rightarrow S_0$ ISC).[16] Similar kinetic analyses of heteroatomic derivatives of **1a,b** are in progress.

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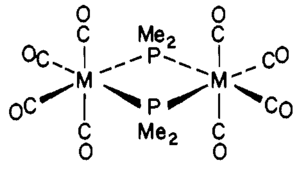
Why Some Binuclear Complexes Bridge, While Others, Even Though They Might Have a Quadruple Bond Available to Them, Do Not

Sir:

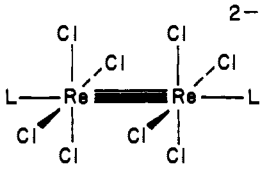
In 1978 Vahrenkamp reported a series of binuclear complexes $(CO)_4M(\mu\text{-}PMe_2)_2M(CO)_4$ (M = Mn, Cr, V) with edge-sharing bioctahedral structures, **1**.[1] A good structural case for an MM bond order of 0, 1, 2, respectively, was made. If the phosphido group is counted as PR_2^- one is led to oxidation state I for the metal, and the V complex is d^4–d^4.



1

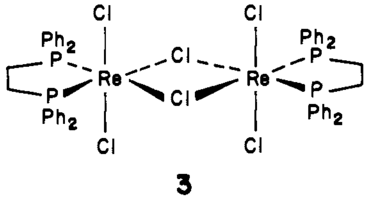
M	Mn	Cr	V
MM(Å)	3.76	2.90	2.73
MPM(°)	103.1	77.7	70.5

However, there are other d^4–d^4 dimers. These come from one of the most exciting chapters of modern inorganic chemistry, the work of Cotton and collaborators on metal quadruple bonding.[2] The classical example is $Re_2Cl_8^{2-}$; however, we know that two further weak axial ligands may add, giving a $Re_2Cl_8L_2^{2-}$ (**2**), which retains a short and strong bond.



2

Re–Re 2.22 Å



3

Re–Re 3.81 Å

The set of M_2L_{10} structures is not exhausted by these. There exist d^4–d^4 Re(III) dimers which have two bridging groups and *no* metal-metal bond. An example is the paramagnetic Walton complex **3**, $Re_2Cl_6(dppe)_2$,[3] whose Re–Re separation is nearly 1.6 Å longer than that in $Re_2Cl_8^{2-}$.

Thus there are three classes, at least, of d^4–d^4 M_2L_{10} complexes: (a) the Vahrenkamp compounds, bridged, diamagnetic, with medium-length MM bonds; (b) the Cotton structures, diamagnetic, short Re–Re distances, unbridged; (c) the Walton complexes, paramagnetic, long M–M distances, bridged. The basic structural question thrusts itself before our eyes. *What factor in the metal and ligand set makes a given M_2L_{10} d^4–d^4 complex assume one structure over another?* In particular, given the enticing prospect of a quadruple bond, why do the Vahrenkamp and Walton complexes not undo their bridging? Simply—*why do these complexes have the structures that they do?*

As part of a comprehensive study of M_2L_{10} dimers[4] we have

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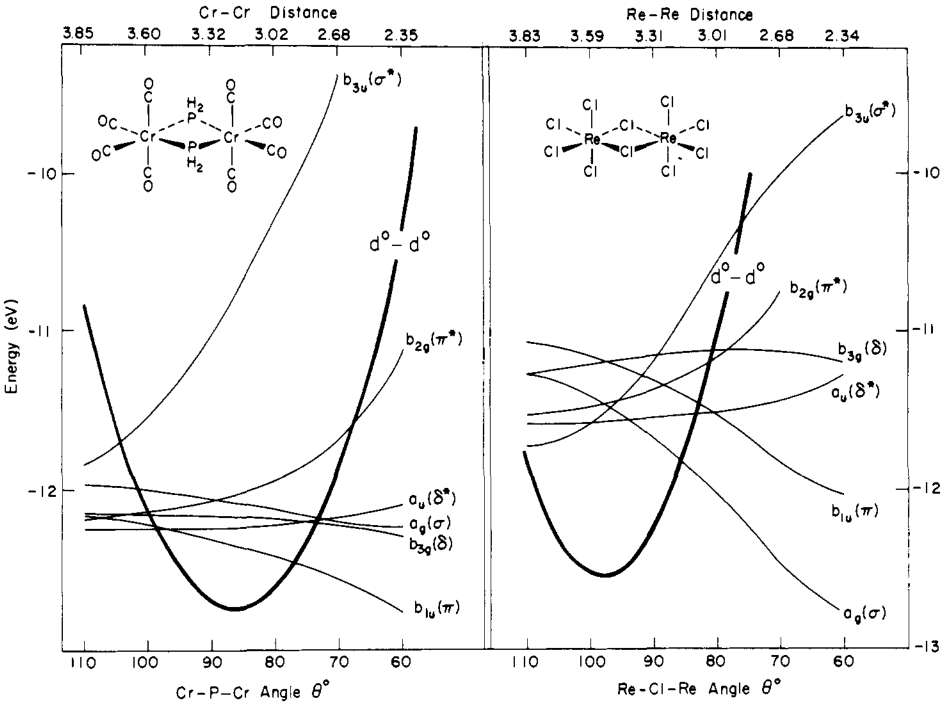
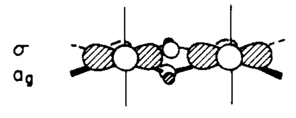


Figure 1. d-block energy levels of $Cr_2(CO)_8(PH)_2^{q}$ and $Re_2Cl_{10}^{q'}$ as a function of M-L-M angle. A nonlinear MM distance scale is at top. Superimposed on each diagram is the total energy of all the occupied levels below those shown, i.e. for a d^0-d^0 configuration.

carried out extended Hückel calculations on $Cr_2(CO)_8(\mu\text{-}PH_2)_2^{q}$ and $Re_2Cl_{10}^{q'}$, q, q′ = a variable charge. The bridged structures optimize at MPM = 98, 85, and 80° for the Vahrenkamp models, $q = 2+$ ("V"), $q = 0$ (Cr), and $q = 2-$ ("Mn"), respectively, while the d^4-d^4 $Re_2Cl_{10}^{4-}$ wants to have a ReClRe angle of 101°. The μ-PH_2 complexes are closed shell at their respective minima; the model for the d^4-d^4 compound has a small LUMO-HOMO gap at its calculated minimum of $\theta = 80°$, a larger one at the observed θ value of 70.5°. In contrast, in a bridged geometry of $Re_2Cl_{10}^{4-}$ six orbitals competing for eight electrons lie within 0.5 eV of each other. A high-spin ground state is certain.

Figure 1 is a Walsh diagram for the d-block levels of the two complexes. The six levels are shown schematically in **4–9**. In both $Cr_2(CO)_8(\mu\text{-}PH_2)_2$ and $Re_2Cl_{10}^{4-}$ there is a regime of strong MM interactions at small M(μ-L)M angles, where the levels partition according to their MM bonding character, σ below σ^*, π below π^*, δ below δ^*. There is a large intermediate region where the metal-metal bonding is unimportant and the level ordering determined by through-bond coupling.[5] Thus π comes above π^* at some MPM angle simply because μ-Cl or $-PH_2$ have filled orbitals to destabilize π while nothing in the bridge can interact with π^*. Where the dominance of the through-bond coupling takes over is a function of the bridging ligand—for instance in the π,π^* case the pertinent interacting Cl lone pair is a better donor than the corresponding PH_2 level, which is a bonding orbital.



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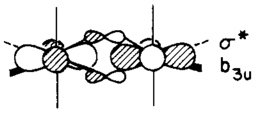

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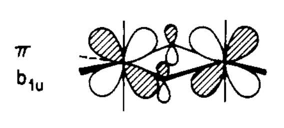

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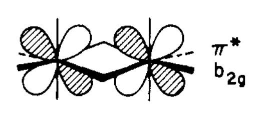

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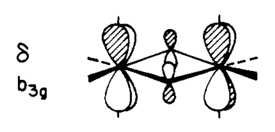

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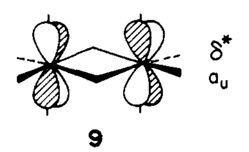


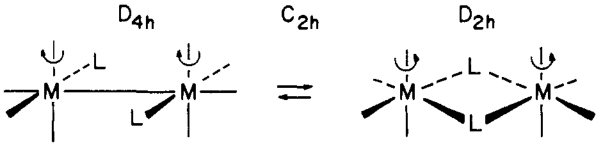
9

More striking than their differences are the similarities of the two level schemes. In both there is a region of MM double bonding for a d^4-d^4 electron count. This occurs at a small MLM angle, where σ, π, δ, and δ^* are occupied, π^* and σ^* empty. Why then does the PR_2 complex optimize in that region, while $Re_2Cl_{10}^{4-}$ does not? The phenomenological answer is in the d^0-d^0 energy curves superimposed on Figure 1. Into the total energy enter not only the d-block levels but also the levels below, the d^0-d^0 core. In that core energy will be found steric problems, if any, bridge bonding propensities, etc. The d^0-d^0 curve has a minimum at MPM = 86° for $Cr_2(CO)_8(PH_2)_2^{10+}$, a much sharper minimum at 97° for $Re_2Cl_{10}^{4+}$. In the μ-PR_2 case the d block can "tune" the minimum as the electron count changes from Mn to Cr to V. For μ-Cl the double-bonded region at a small MCM angle is simply inaccessible—the Walton complexes are forced into the region of no MM bonding and paramagnetism by the shape of the d^0-d^0 curve.

The difference between the d^0-d^0 curves may be traced in part to interactions between the axial ligands—much more repulsive for donors (Cl in $Re_2Cl_{10}^{4+}$) than for acceptors (CO in $Cr_2(CO)_8(PH_2)_2^{10+}$). Another part of the effect is to be found in the bridge bonding region, the electrons bonding the $M(\mu\text{-}L)_2M$ rhomboid. Details will be found in the full paper.[4]

Given that we have learned why the double-bonded bridged alternative is not available to the Cotton complexes, we must deal with the converse question—why don't the Vahrenkamp compounds open up? To this end we examined unbridged alternatives $(CO)_5ReRe(CO)_5^{6+}$ and $Cl_5ReReCl_5^{4-}$, both calculated at short and long Re-Re separations based on known $Re_2(CO)_{10}$ and $Re_2Cl_8L_2^{2-}$ structures. For $Re_2Cl_{10}^{4-}$ a classical quadruple-bonding pattern obtains—σ, π, and δ filled. For $Re_2(CO)_{10}^{6+}$ one observes a very different level scheme—π, δ, δ^*, and π^* are below σ. A similar pattern is already in the literature for $Mn_2(CO)_{10}$[6a] and $Re_2(CO)_{10}$[6b] and is supported by spectroscopic evidence.[6,7] Behind the high energy of the σ level are two factors: (a) the greater σ, π, and δ splitting in the acceptor-substituted monomer fragment and (b) the greater localization of the orbitals on the metal when the substituents are donors. If the level ordering of $Re_2(CO)_{10}$ can be extrapolated back to a similarly substituted d^4-d^4 dimer, as we think it can, then we believe there is no chance of a quadruple bond in a d^4-d^4 L_5MML_5 dimer with acceptor substituents.

Thus the Vahrenkamp compounds do not open up because there is nothing especially good waiting for them in the unbridged alternative. The Cotton complexes do not go into the bridged double-bonded structure because core steric effects make inaccessible the region where a double bond could exist. Interestingly the concerted conversion of a Cotton complex into a Vahrenkamp type structure, **10** ⇄ **11**, is a forbidden reaction.



10 **11**

If the steric troubles of the bridged alternative could be relieved, perhaps by bidentate bonding across axial sites, it is conceivable that bridged, double-bonded and unbridged, quadruple-bonded d^4-d^4 isomers might coexist.[8]

The forbiddenness of the interconversion is specific to a d^4-d^4 electron count and donor substituents. It is allowed for d^7-d^7, an important class of molecules including the well-studied $[CpFe(CO)_2]_2$.

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(9) Our work was generously supported by the National Science Foundation through Research Grant CHE 7828048.

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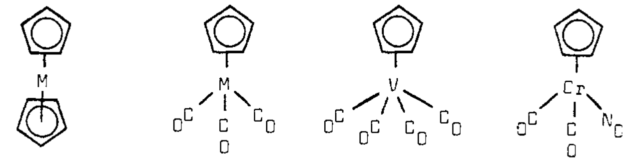
A New, General Route to Functionally Substituted η^5-Cyclopentadienyl Metal Compounds

Sir:

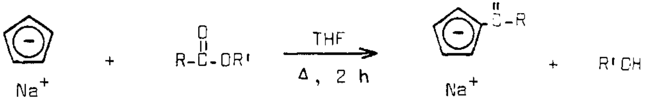
The very extensive chemistry associated with bis(η^5-cyclopentadienyl)iron (ferrocene) (**1**) has been due in large measure to the fact that this remarkable organometallic compound undergoes certain aromatic-type electrophilic substitution reactions,[1] resulting in products which often possess unique chemical and physical properties.[2] In spite of considerable additional research efforts along these lines, however, only a very few other η^5-cyclopentadienyl metal compounds have ever been found to undergo analogous aromatic-type substitutions. These include the related sandwich compounds bis(η^5-cyclopentadienyl)ruthenium (ruthenocene, **2**),[3] bis(η^5-cyclopentadienyl)osmium (osmocene, **3**),[3] (η^5-cyclopentadienyl)tricarbonylmanganese (cymantrene, **4**)[4] and its technetium (**5**)[5] and rhenium (**6**)[5,6] analogues, (η^5-cyclopentadienyl)tetracarbonylvanadium (**7**),[7] and (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene, **8**).[8,9] The failure of most η^5-cyclopentadienyl metal compounds to undergo ring substitution may be ascribed either to their inherent lack of aromatic character or to more facile reaction pathways under the reaction conditions involved. In any event, the inability of most η^5-cyclopentadienyl metal compounds to form functionally substituted derivatives by ring-substitution routes has severely impeded the development of η^5-cyclopentadienyl metal chemistry of the type shown by compounds **1-8**.



1 M = Fe
2 M = Ru
3 M = Os
4 M = Mn
5 M = Tc
6 M = Re
7
8

We now report the development of a new and apparently general route for the formation of a wide variety of functionally substituted η^5-cyclopentadienyl metal compounds. The method provides a convenient means of introducing functional substituents on η^5-cyclopentadienyl rings in systems which are incapable of undergoing electrophilic aromatic substitution, and as such should greatly stimulate research in this branch of chemistry.

We find that the reactions of cyclopentadienylsodium with either ethyl formate, methyl acetate, or dimethyl carbonate in refluxing tetrahydrofuran solution for 2 h produces 60-90% yields of the respective compounds formyl- (**9**), acetyl- (**10**), or methoxycarbonylcyclopentadienylsodium (**11**).[10] The solid products **9-11** are moisture sensitive but are generally stable in air for short periods of time, in contrast to cyclopentadienylsodium itself. The generation of **9-11** likely proceeds via intermediate formation of the corresponding 1-substituted cyclopentadienes, the latter being rapidly metalated by the sodium alkoxide produced concurrently in the reaction. The ^1H NMR spectra of **9-11**[11] are of interest in that resonances for the substituted cyclopentadienyl hydrogens occur as unresolved multiplets rather than as apparent triplets as in the case of most η^5-cyclopentadienyl transition metal compounds substituted with analogous electron-withdrawing substituents.[12] Additional NMR investigations as well as X-ray diffraction studies on **9-11** are underway in order to elucidate the nature of the ring-metal bonding in solution and in the crystal state, respectively.[13]



9 R = H
10 R = CH_3
11 R = OCH_3

The utility of these organosodium reagents in organometallic chemistry is aptly demonstrated by their reactions with cobalt or nickel salts to form functionally substituted sandwich