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# Electronic Structure of $M_4(CO)_{12}H_n$ and $M_4Cp_4H_n$ Complexes

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**Abstract:** The electronic structure of tetranuclear hydrido clusters $M_4(CO)_{12}H_n$ and $M_4Cp_4H_n$, $n = 3, 4, 6$, is analyzed with the aid of symmetry arguments and molecular orbital calculations. The orbitals of the clusters are derived by protonating $M_4(CO)_{12}$ and $M_4Cp_4$ tetrahedra. The important levels of these are the inward and surface-like higher occupied orbitals of $a_1 + e + t_2$ symmetry (plus a low-lying unfilled $t_1$ orbital occupied by three electrons in the electron-rich $Ni_4Cp_4H_3$ cluster). The electron distribution in the surface orbitals e and $t_2$ is studied as a function of staggered or eclipsed carbonyl orientation and along the edges or faces of the tetrahedron. The results of this study provide an understanding of the variable location of hydrogens in these clusters.

This paper is concerned with the electronic structure of tetranuclear hydrido clusters of the type $M_4(CO)_{12}H_n$ and $M_4Cp_4H_n$, Cp = cyclopentadienyl, M = a transition metal, and $n$ = 3, 4, or 6. The well-characterized molecules in this series share the basic feature of a near-tetrahedral disposition of the metal centers, but then diverge to exhibit staggered, **1**, or eclipsed, **2**, orientations of the carbonyl groups (relative to



1          2
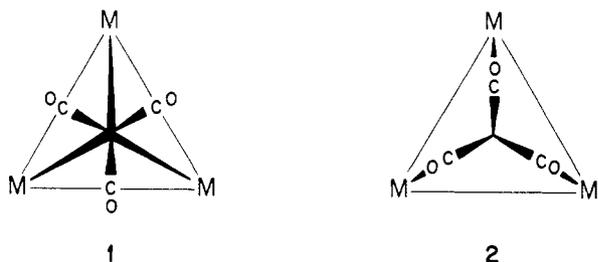
the metal–metal edges), and edge- or face-bridging hydrogens. They may also possess varying spin states and propensities to hydrogen mobility. This choice of geometrical and electronic structure is of interest to us.

Let us review what is known about these molecules, making reference only to well-established geometrical facts, and keeping in mind the problems associated with accurately locating hydride positions in X-ray crystallographic structures. $Re_4(CO)_{12}H_4$[2a] has four face-bridging hydrides and eclipsed carbonyl groups.[2b] $Re_4(CO)_{12}H_6^{2-}$ has staggered carbonyls, and the hydrides are presumably edge-bridging,[3] though this has not been definitely established. $Ru_4(CO)_{12}H_4$ has been synthesized[4] and a $D_{2d}$ geometry with edge-bridging hydrides (**3**) established through X-ray diffraction.[5] In addition crystallographic studies on the derivatives $Ru_4(CO)_{11}$-$H_4P(OCH_3)_3$,[2b] $Ru_4(CO)_{10}H_4(PPh_3)_2$,[5] and $Ru_4(CO)_{10}$-$H_4(diphos)$[6] all show staggered carbonyls and four edge-bridging hydrides, though the disposition of the edges bearing hydrides differs: $Ru_4(CO)_{12}H_4$, $Ru_4(CO)_{11}H_4P(OCH_3)_3$, and $Ru_4(CO)_{10}H_4(PPh_3)_2$ have configuration **3**,[5] while



3          4
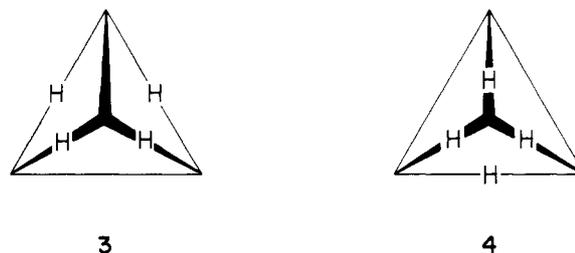
$Ru_4(CO)_{10}H_4(diphos)$ has configuration **4**. Hydride motions are complex and interesting in these Ru compounds.[4,6]
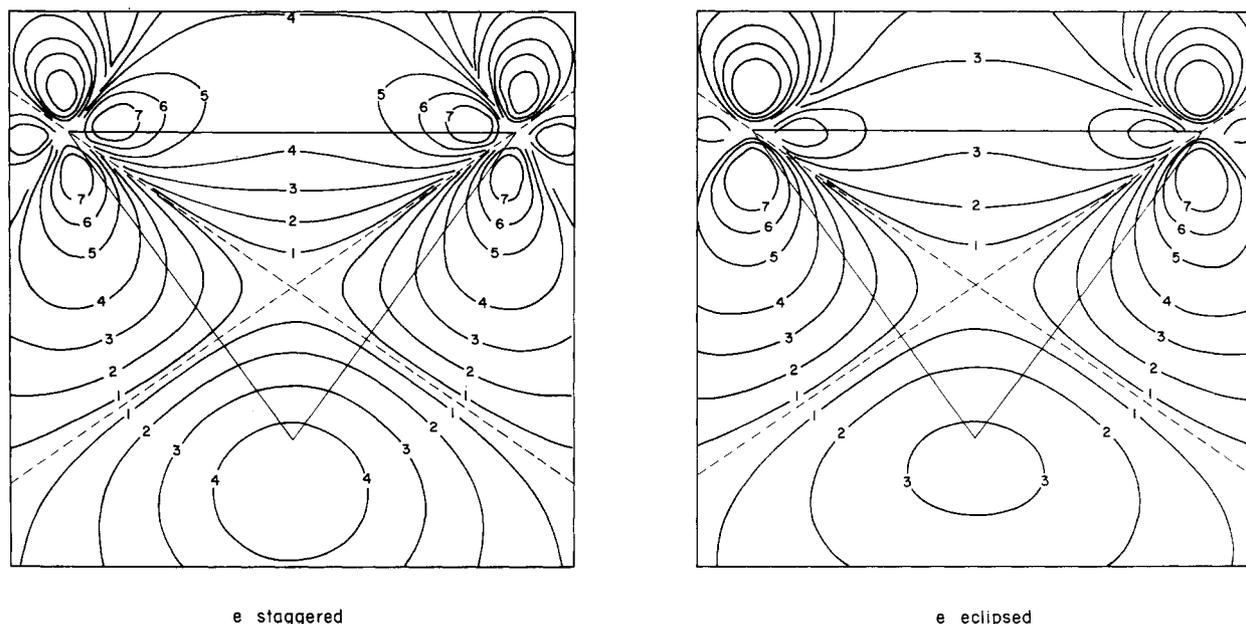
In the cyclopentadienyl complexes the question of eclipsing or staggering is a moot one, since the barrier of rotation of a fivefold rotor such as an $\eta^5$-cyclopentadienyl ring against the pseudo-threefold rotor presented to it by a metal vertex of the tetrahedron is expected to be small. $Co_4Cp_4H_4$ is known[7] and face-bridging hydrogens have been inferred from the crystal structure.[8] $Ni_4Cp_4H_3$ has also been synthesized[9] and has been studied by X-ray[10] and neutron[11] diffraction. Both methods concur in showing three face-bridging hydrogens. This compound is especially interesting because, in contrast to all molecules mentioned above, it is paramagnetic, with three unpaired electrons.[9]

## The Orbitals of $M_4(CO)_{12}$

The natural construction of the electronic structure of the molecules is from the orbitals of tetrahedral $M_4(CO)_{12}$, **5**, or $M_4Cp_4$, **6**, interacting with three to six hydrogen atoms. In the real molecule the hydrogens may exhibit extremes of hydridic or protonic character, or some behavior in between—this will not affect our analysis which finds it convenient to begin with the formalism of an "electron-precise" or "saturated" cluster $Ir_4(CO)_{12}$ or $Ni_4Cp_4$ and to think of protonating that cluster or removing some electrons from it.

The electronic structure of these saturated clusters is well understood.[12-15] The $Ir(CO)_3$ and NiCp fragments are isolo-

**5**                **6**

bal[16] with each other, and with CH or BH$^-$. The transition metal fragments are characterized by six frontier orbitals, as shown in **7**. Three are low lying, the descendants of the octa-



**7**

hedral $t_{2g}$ set. These low-lying orbitals are primarily d in character and interact little with neighboring metal atoms. Whatever directionality they have comes to the fore in the $M(CO)_3$ fragment where they are so disposed in space that they eclipse the three carbonyls.[17]

More important are the three higher orbitals. These have significant admixtures of metal s and p, making for greater overlaps with neighboring metal atoms and bridging ligands.[18] The three delocalized orbitals, $a_1 + e$, are the equivalent of three localized hybrids completing an octahedron around the metal atom. This quasi-octahedral directionality is pronounced in $M(CO)_3$ and will figure importantly in setting the orientation of the carbonyls in the cluster as staggered or eclipsed. In MCp the directionality is suppressed.[16,17]

In $Ir_4(CO)_{12}$ and $Ni_4Cp_4$ each metal carries nine d electrons. Six of these are lone-pair-like, in the lower "$t_{2g}$" set, three in the upper set of valence orbitals. One has one electron per hybrid, with the consequence that localized electron pairing can occur along the edges of the tetrahedron. This is the reason for calling these clusters saturated and analogous to tetrahedrane (or $P_4$).[12-15]

The 12 orbitals formed by the four sets of three high-lying hybrids at each $M(CO)_3$ or MCp fragment transform as $a_1 + e + t_1 + 2t_2$. These may be partitioned further in two ways. The $a_1$ combination of the individual fragment points inward, toward the center of the cluster, while the e combinations are more surface-like, tangential, peripheral. The inward orbitals generate $a_1 + t_2$, the surface set $e + t_1 + t_2$.[19] The presence of $t_2$ in both sets is a sign that the inward-surface partitioning is not clean. The other partitioning focuses on the localized bonding model of six electron pairs along tetrahedral edges.[12-15,19-22] It leads to six bonding molecular orbitals (MOs) of $a_1 + e + t_2$ symmetry and six antibonding combinations, $t_1 + t_2$.

The detailed ordering of the valence orbitals of the saturated cluster was obtained from a calculation on a model $Fe_4(CO)_{12}{}^{4-}$, using the extended Hückel method, with parameters listed in the Appendix. Since the hydrido clusters show both staggered and eclipsed carbonyl orientations, **1** and **2**, the calculation was done for both cases. The frontier orbitals are shown in Figure 1. In each geometry the $a_1 + e + t_2$ occupied set of cluster orbitals is at high energy, fairly well separated from other orbitals. This supports the general picture of bonding in these clusters that has been assembled previously[12-17] and gives us some confidence that the primary effects of protonation may be gleaned by focusing on these orbitals alone.



**Figure 1.** Frontier orbitals of $Fe_4(CO)_{12}{}^{4-}$ with staggered and eclipsed carbonyl groups, and $Fe_4Cp_4{}^{8-}$.

The staggered geometry of the saturated cluster is preferred to the eclipsed one by 2.0 eV in our calculations. Most, but not all, of that bias is in the $a_1 + e + t_2$ set of higher occupied MOs. The $a_1$ orbital is oriented inward and is not sensitive to carbonyl orientation. The e orbital is considerably lower in energy in the staggered geometry, and the $t_2$ somewhat higher in the same conformation. Since these orbitals are crucial in our further discussion of protonation, we pause here to explain these energy trends.

Let us begin with a basis set of three hybrid orbitals per metal center in the staggered geometry, **8**, and the eclipsed, **9**. One line of reasoning is to simply say that **8** is better set up



**8**                **9**

for edge bonding, while **9** is prepared for face bonding. Edge bonding implies six bonding orbitals, $a_1 + e + t_2$, as mentioned above. Analyzed in a primitive manner, face bonding means that from the three orbitals pointing into a face in **9** one forms three MOs, locally of a + e symmetry. Of these only one is bonding, the in-phase a combination. Combining four such faces, one will get in the full tetrahedron really only four bonding combinations, of $a_1 + t_2$ symmetry. In the eclipsed or face-bonded structure the e combination is descended from an antibonding orbital, and so lies at high energy. Conversely, the $t_2$ orbital is more bonding in the eclipsed structure than in the staggered one.

Another line of reasoning begins with the construction of the proper symmetry-adapted linear combinations for the two

e staggered                                                    e eclipsed

**Figure 2.** Density plots of the metal part of the e set of $Fe_4(CO)_{12}$. The wave function has been squared and summed over the two degenerate levels. The occupation is thus formally one electron per level. The plots are in one of the mirror planes of the molecule, with the horizontal line representing a metal–metal bond. The values shown on the contours indicate the variation in $\Psi^2$, and the relationship to the actual values of the contours is as follows: $1 = 0.000\ 05$, $2 = 0.0005$, $3 = 0.002$, $4 = 0.005$, $5 = 0.0125$, $6 = 0.025$, $7 = 0.05$. The dashed lines show nodes.

geometries. Given the degeneracy, there is no unique way to do this for the e and $t_2$ wave functions. One choice is given below, unnormalized.

$$e \begin{cases} 2(\varphi_1 + \varphi_4) + 2(\varphi_9 + \varphi_{10}) - (\varphi_2 + \varphi_8) - (\varphi_3 + \varphi_{11}) \\ \quad - (\varphi_5 + \varphi_7) - (\varphi_6 + \varphi_{12}) \\ (\varphi_2 + \varphi_8) - (\varphi_3 + \varphi_{11}) + (\varphi_5 + \varphi_7) - (\varphi_6 + \varphi_{12}) \end{cases} \quad (1)$$

$$t_2 \begin{cases} (\varphi_1 + \varphi_4) - (\varphi_9 + \varphi_{10}) \\ (\varphi_2 + \varphi_8) - (\varphi_6 + \varphi_{12}) \\ (\varphi_3 + \varphi_{11}) - (\varphi_5 + \varphi_7) \end{cases} \quad (2)$$

$\varphi_i$ is a hybrid orbital as numbered in **8** or **9**. The orbitals are grouped to emphasize bonding pairs in the staggered conformation.

The tetrahedral symmetry imposes certain constraints on the electron density of various orbitals. Thus the $t_2$ orbital must have zero density at the center of the tetrahedron and the e orbital vanishes everywhere along the four threefold axes. The latter condition implies zero electron density in the tetrahedral face centers. Whatever bonding characteristics the e orbital has are concentrated along the edges. One of the e combinations in eq 1 is shown schematically in **10** and **11**. The point that
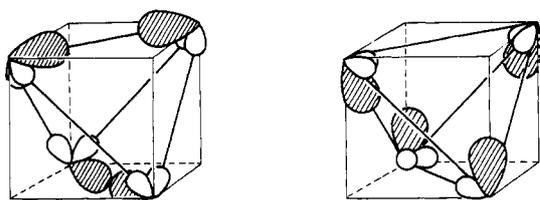


10                                                    11

emerges is that edge bonding in the e orbital is significantly better in **10**, the staggered conformation, than in **11**. This is reinforced by Figure 2, an actual contour plot of the total

electron density in the e orbital in one mirror plane of the tetrahedron.

The $t_2$ orbital has electron density over the edges and face centers. One of its components is shown in **12** and **13**. It is
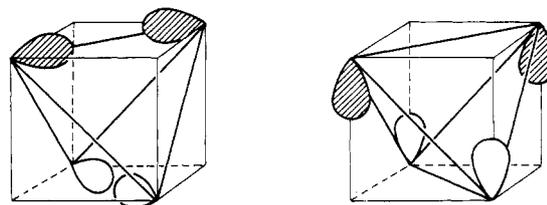


12                                                    13

clearly more edge concentrated in **12**, face-like in **13**. The differential is less than it might seem from **12** and **13**, owing to the admixture of the higher $t_2$ set. Contour diagrams of the total electron density in the $t_2$ orbital for both the staggered conformation, somewhat bovine, and the eclipsed form, perhaps more porcine (or tigrine to one referee) in appearance, are presented in Figure 3. The basic point persists, namely, that $t_2$ is more bonding along the edges in the staggered geometry, more bonding along the faces in the eclipsed conformation. The face bonding turns out to be somewhat more important as far as the orbital energy is concerned.

To summarize, the e orbital is at higher energy in the eclipsed geometry, the $t_2$ at somewhat lower energy in the same geometry. As Figure 1 shows, the e orbital trend dominates. The staggered geometry is also favored by some lower orbital interactions. These are linear combinations of the set of three descended from the $t_{2g}$ orbital of the octahedron, the bottom three orbitals in **7**. These orbitals are filled, so that interactions between them are repulsive. They also possess some directional character, though not as much as the upper set of three, and point to directions that complete a trigonal prism with the three carbonyls.[17] This is shown schematically in **14**. Four-electron destabilizations from these orbitals, while not large, are greater in the eclipsed geometry.

We have not discussed in any detail the $M_4Cp_4$ orbitals, though these are also shown in Figure 1. The fivefold axis of

$t_2$ staggered                       $t_2$ eclipsed
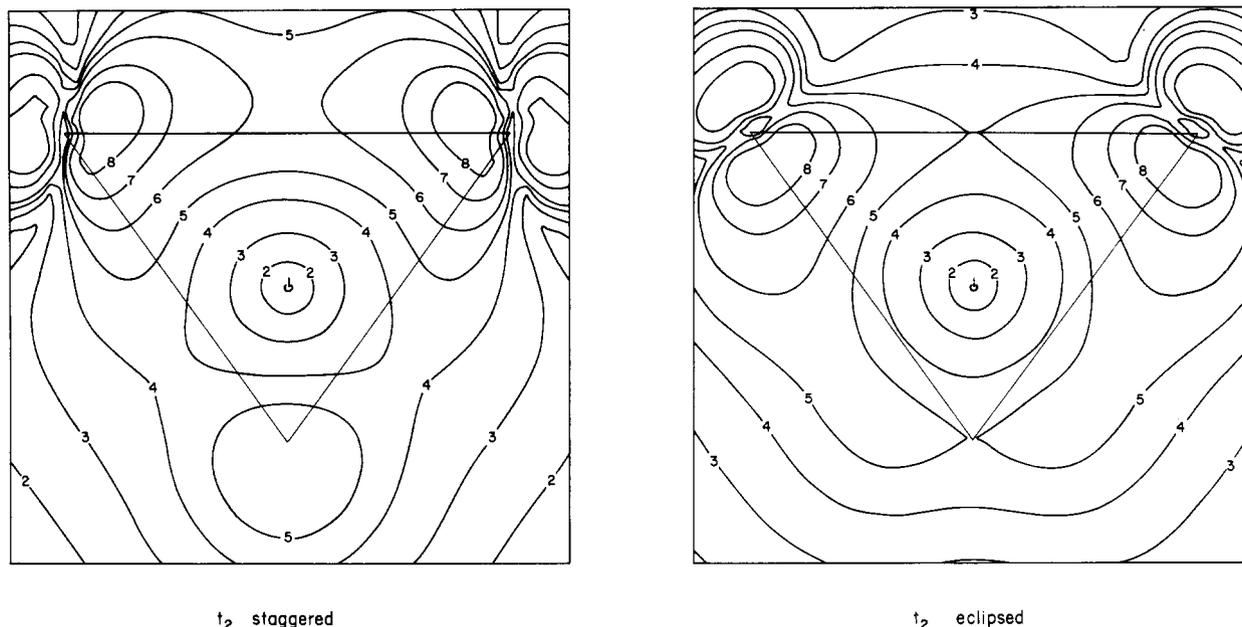
**Figure 3.** Density plots of the metal part of the $t_2$ set of $Fe_4(CO)_{12}$. The wave function has been squared and summed over the three degenerate levels. The occupation is thus formally one electron per level. The plots are in one of the mirror planes of the molecule, with the horizontal line representing a metal–metal bond. The values shown on the contours indicate the variation in $\Psi^2$, and the relationship to the actual values of the contours is as follows: $1 = 0.000\,05$, $2 = 0.0005$, $3 = 0.002$, $4 = 0.005$, $5 = 0.008$, $6 = 0.0125$, $7 = 0.025$, $8 = 0.05$.



empty

filled

**14**

**Table I.** Interactions of Tetrahedral Framework Orbitals with a Probe Hydrogen

| | face | edge |
|---|---|---|
| e | 0 | staggered > eclipsed |
| $t_2$ | eclipsed > staggered | staggered > eclipsed |
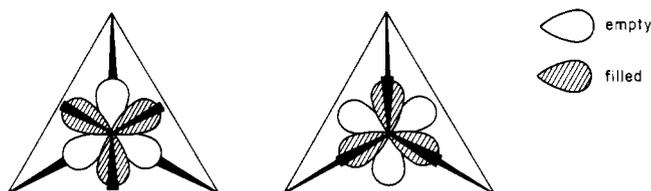
the Cp group is incommensurate with the threefold axis of the tetrahedron, so that the actual symmetry of any $M_4Cp_4$ geometry is lower than $T_d$. Of course the pseudotetrahedral nature of the complex is retained, so that splittings of the e and $t_2$ level as shown in Figure 1 are small. The basic pattern of high-lying $a_1 + e + t_2$ is preserved. The position of the "e" level in $M_4Cp_4$ is intermediate between the two $M(CO)_3$ cases discussed above, just about at the same energy as the $a_1$ level.

## Construction of the Hydride Complexes

As we approach a number of protons to the edges or faces of $M_4(CO)_{12}$ or $M_4Cp_4$, the extent of interaction will be governed by the usual perturbation theoretic expression:

$$\Delta E = \frac{|H_{ij}|^2}{E_i - E_j} \qquad (3)$$

We will have to watch carefully the electron count to determine if the net interactions are stabilizing two-electron or destabilizing four-electron ones. But in either case the most important factor will be the overlap of an incoming proton with the framework orbitals of the tetrahedron. That overlap depends on the electron density and the arguments of the previous section may be summarized qualitatively in Table I. The inward pointing $a_1$ orbital has been omitted because it provides no differentiation between the various sites.

Six protons coming in along the edges, each bearing a 1s orbital, transform as $a_1 + e + t_2$. They interact beautifully with the high-lying MOs of a saturated cluster. Carbonyl staggering is preferred. The compound that we calculated is $Fe_4$-

$(CO)_{12}H_6{}^{2+}$, a model for the known isoelectronic species $Re_4(CO)_{12}H_6{}^{2-}$.[3]

Four protons coming in on face centers transform as $a_1 + t_2$. In $Fe_4(CO)_{12}H_4$ they would add a factor favoring the eclipsed carbonyl orientation, but that would be superimposed on the natural tendency for staggering. With four electrons less the e orbital which is unaffected by face protonation would be vacated. This is the orbital largely responsible for the staggered conformation of the saturated cluster $[Fe_4(CO)_{12}{}^{4-}$ or $Ir_4(CO)_{12}]$, so that in the electron-deficient system, e.g., $Re_4(CO)_{12}H_4$, there should be no ambiguity about eclipsing being preferred.

There are of course alternative edge-protonation patterns to be considered, of the type illustrated in **3** and **4** and found in various substituted $Ru_4$ clusters. If we retain 12 carbonyl groups, the protonated geometry analogous to **3** has $D_{2d}$ symmetry, while that similar to **4** is reduced to a single mirror plane. We have analyzed only the $D_{2d}$ structure in detail.

In $D_{2d}$ four edge-bridging protons transform as $a_1 + b_1 + e$. The $t_2$ level reduces to $e + b_2$ and e to $a_1 + b_1$. Thus nearly all levels of the cluster are affected. It is clear that staggering of the carbonyls should be even better in the protonated cluster.

This is about as far as a qualitative analysis based on symmetry arguments can be pushed. The important question not answered is whether face protonation is better than edge protonation for four hydrogens. This involves a weighing of various interactions, and we resorted to a detailed calculation. Table II summarizes the results, the energies in each case referred to an arbitrary energy zero for the most stable calculated geometry.

First note that the computed energies support the qualitative
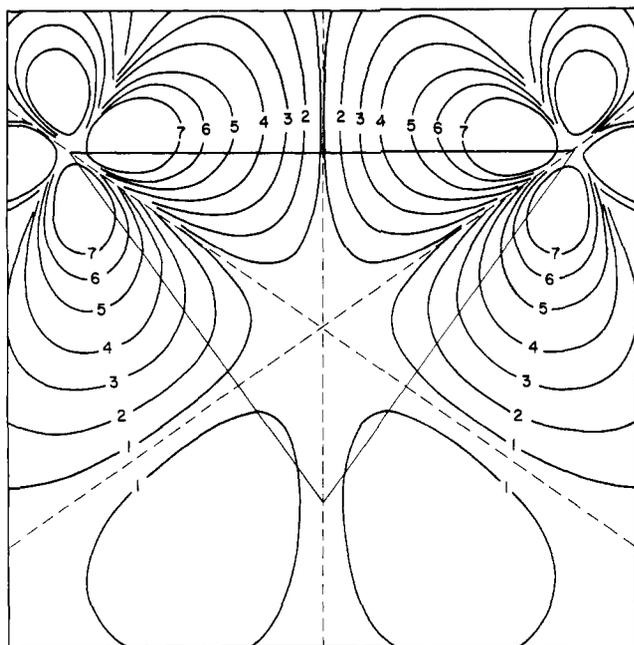
Fe₄Cp₄   " t₁ "

**Figure 4.** A density plot of the metal part of the "$t_1$" orbital of Fe₄Cp₄. As before, the wave function has been squared and the formal occupation is one electron per level. The plot is in one mirror plane of the molecule with the metal–metal bond horizontal. The relationship between the shown numbers and values of $\Psi^2$ is as follows: 1 = 0.000 05, 2 = 0.0005, 3 = 0.002, 4 = 0.005, 5 = 0.0125, 6 = 0.025, 7 = 0.05. The dashed lines show nodes.

**Table II.** Calculated Energies for M₄(CO)₁₂H₄ Clusters (eV)

| | carbonyls staggered | | carbonyls eclipsed | |
|---|---|---|---|---|
| | edge | face | edge | face |
| Fe₄(CO)₁₂H₄ | 0.4 | [0] | 2.9 | 1.3 |
| Fe₄(CO)₁₂H₄⁴⁺ | 1.8 | 1.4 | 2.8 | [0] |

conclusions reached above: Face protonation reduces the barrier to eclipsing (it was 2.0 eV in unprotonated Fe₄-(CO)₁₂⁴⁻) in Fe₄(CO)₁₂H₄ and still more so in the electron-deficient cluster with four electrons less. The minimum energy conformation for the latter case is well defined—it is a face-bridging structure with eclipsed carbonyls, in agreement with the known structure of Re₄(CO)₁₂H₄.[2]

The equilibrium structure of M₄(CO)₁₂H₄, M = Fe, Ru, is less well defined by the calculations. The face-bridging geometry is preferred by 0.4 eV, which does not agree with the observed structures, all edge bridging.[4-6] We are not overly concerned with this disagreement, because the energy difference in our approximate calculation is not large, and also because we know that the related Co₄Cp₄H₄ structure has face-bridging hydrogens.[8] Our calculations for a model Fe₄Cp₄H₄⁴⁻ indeed indicate a large preference of 2.4 eV for face protonation. The detailed rationale for this preference is involved. The energy difference is spread out over a number of orbitals, and is not easy to analyze. However, we can trace part of the extra stabilization of the face sites in the Cp compound over the CO to additional interaction with a second t₂ set. This lies below the framework orbitals shown in Figure 1, and is descended from the t₂g set (see **7**) of each fragment. This second t₂ orbital is at higher energy in M₄Cp₄ than M₄(CO)₁₂ because there is less back-bonding or stabilization by unfilled terminal ligand orbitals than in the carbonyl case. Though the

calculations were actually carried out for a Fe₄Cp₄H₄⁴⁻ model, the results should be valid for M₄Cp₄H₄, M = Co, Rh, Ir.

Only one entry appears for the edge-bridged hydrides in Table I. Actually we have calculated models for the two structural types found, **3** and **4**. These are essentially indistinguishable in energy, within 0.02 eV of each other.

Our general conclusion is that the parent Ru₄(CO)₁₂H₄ system and its substituted derivatives should be characterized by relatively low barriers to movement of hydrogens between edge and face positions. Mobility of hydrogens in H₄Ru₄(CO)₁₂₋ₓLₓ ($x$ = 1–4, L = P(OMe)₃) has been observed;[4] however, no information is yet available on the pathway traversed by the hydrogen atoms. For the Ru₄-(CO)₁₀H₄(diphos) case studied by Shapley and co-workers[6] a dynamic process is implicated which involves as waypoints terminal hydrides. These have not as yet been considered in our theoretical studies. The Re₄(CO)₁₂H₄ system should have significantly higher barriers to intramolecular tautomerism, which is in accord with experimental findings.[23]

For trihydrides we have studied Fe₄(CO)₁₂H₃⁻ and Fe₄Cp₄H₃⁸⁻ as models for the known Ru₄(CO)₁₂H₃⁻ and Ni₄Cp₄H₃ structures.[9-11,24] Four alternative structures were computed for Fe₄(CO)₁₂H₃⁻, shown in **15–18**, all with



15          16          17          18
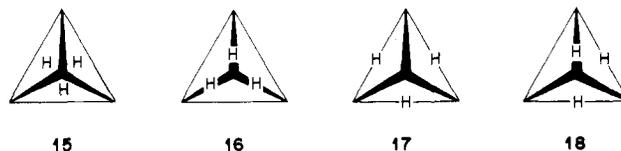
staggered carbonyls. The face-bridged structure **15** comes out 0.3 eV more stable than the three edge-bridged geometries **16–18**, all of which have nearly identical energies. This parallels the results for Fe₄(CO)₁₂H₄ mentioned above and is subject to the same reservations. The preference for face bridging in Fe₄Cp₄H₃⁸⁻ stems from interactions similar to the ones discussed for the four proton system.

The Ni₄Cp₄H₃ structure is of special interest because it is so electron rich, exceeding the normal electron count for a tetrahedral cluster by three electrons. In Figure 1 it will be seen that the Ni₄Cp₄ cluster has a low-lying empty t₁ orbital which is split only very slightly in the true reduced symmetry of the cluster. Its contours are shown in Figure 4. By symmetry this orbital has nodes along all C₃ and C₂ axes of the tetrahedron. The orbital is totally unaffected by the addition of three face-bridging hydrogens. For that matter it would be equally unaffected if the hydrogens were edge bridging. As mentioned above, the preference for face bridging over edge bridging is set by other, lower orbitals. The three extra electrons in Ni₄Cp₄H₃ populate the (nearly) triply degenerate metal-centered t₁ orbital, explaining the observed paramagnetism of the compound.[9]

00360, and receipt of an NIH Research Career Development Award (CA-00015).

## Appendix

The calculations were performed using the extended Hückel method.[25] The $H_{ii}$'s and orbital exponents for Fe were taken from previous work.[17] The hydrogen $H_{ii}$ was set at $-10.0$ eV. This places the hydrogens energywise above the valence orbitals of the cluster, giving the H's the character of protons. Calculations with hydrogen $H_{ii}$'s at $-13.6$ eV, our normal value, result in a slight change in the magnitude of the calculated energy differences, but do not alter the conclusions reached. The parameters are given in Table III.

The metal–metal distance was kept at 2.54 Å and the cluster geometry tetrahedral. The Fe–C distance in the carbonyl cluster was 1.8 Å, and the distance from the metal to the center of the cyclopentadiene ring in $Fe_4Cp_4$ was 1.7 Å. The hydrogens were placed 0.86 Å above the cluster face and 1.14 Å from the edge in the face- and edge-protonated systems, respectively.

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# The Band Structure of the Tetracyanoplatinate Chain

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**Abstract:** The band structure of the tetracyanoplatinate chain is examined in the tight-binding approximation based on the extended Hückel method. The unit cell contains a staggered $[Pt(CN)_4]_2^{4-}$, and the calculation is repeated at various Pt–Pt separations. The free electron nature of the bands is probed by computing effective masses. From the band structure and the density of states one derives an expression for the total energy per unit cell as a function of partial oxidation of the polymer. The equilibrium Pt–Pt separation so estimated decreases to less than 3 Å for a loss of 0.3 electron per platinum, in reasonable agreement with structural studies. Details of the band structure are supported by explicit and simple molecular orbital arguments.

A class of partially oxidized one-dimensional conducting salts of tetracyanoplatinate, $Pt(CN)_4^{2-}$, has been one of the most extensively studied low-dimensional conducting materials.[1] The crystal structures of these compounds contain the planar platinum complex, $Pt(CN)_4^{2-}$, stacked together to form parallel linear or nearly linear chains of Pt atoms.[2] Structural and chemical observations on these compounds reveal that the Pt atoms are all equivalent, and thus they are in a single partial oxidation state, and that the Pt–Pt distance ($r_{Pt-Pt}$) becomes shorter with increase in the partial oxidation number of Pt.[2] In a band picture the fractional oxidation state of Pt corresponds to a partially filled band. Experiments on $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ (KCP) indicate that except for the Peierls instability the conduction electrons in KCP behave as nearly free electrons along the Pt chain.[3] Further, this free electron character persists among the analogues of KCP despite a large variation of $r_{Pt-Pt}$ in these compounds.

Calculations of the band structure of the $Pt(CN)_4^{2-}$ chain reported so far have considered in general only a linear chain of Pt atoms.[4,5] A three-band model (i.e., inclusion of $5d_{z^2}$, $6s$ and $6p_z$ of Pt, where $z$ refers to the Pt-chain axis) was found inadequate for the description of the electronic structure of KCP.[4a] Under the assumption that the $CN^-$ ligands force the Pt atom to adopt a wave vector independent s–d hybridization, a two-band model (i.e., inclusion of s–d hybrid and $p_z$ orbitals) produces a free-electron-like band.[4a] An important recent calculation by Bullett considers the full $Pt(CN)_4^{2-}$ chain.[5b]

In the present work the band structure of the $Pt(CN)_4^{2-}$ chain was examined within the tight-binding scheme[6] based upon the extended Hückel method.[7] Our calculations included all the valence atomic orbitals of the Pt, C, and N atoms of a unit cell in the $Pt(CN)_4^{2-}$ chain. Questions of theoretical importance in the electronic structure of the $Pt(CN)_4^{2-}$ chain are (a) the free-electron behavior of the conduction electrons

    