Electronic Structure of Piano-Stool Dimers. 6. Bimetallic Transition-Metal Hydrides of the Type $Cp_2M_2H_nL_{6-n}$[1]

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The electronic structures of a series of bimetallic transition metal hydrides of the formulation $Cp_2M_2H_{6-n}L_n$ (M = Re, W; L = NO, CO, I, $P(OPh)_3$; n = 0, 2, 4, 6) have been investigated via nonempirical Fenske–Hall molecular orbital calculations. Three basic geometries were probed for this system: $[CpML_3]_2$ (**1**), containing six terminal ligands; $[CpML_2]_2(\mu\text{-}L)_2$ (**2**), containing four terminal and two bridging ligands; and $[CpML]_2(\mu\text{-}L)_4$ (**3**), which contains two terminal and four bridging ligands. For complexes containing both hydride ligands and ancillary ligands L (where n = 2 or 4), the dimers were shown to preferentially bridge the hydride ligands. This is due to an unfavorable symmetry match between the π-type orbitals of bridging CO, NO, or I ligands and the frontier metal-based orbitals of the dimer framework. This is in direct contrast to the compounds of the piano-stool dimer class $Cp_2M_2L_4$, which, because of the absence of a second terminal ligand on each metal, have the appropriate metal-based orbitals needed to interact with the π-type orbitals of a bridging ligand. The bonding of the μ-H ligands in compounds of structure type **2** was found to be delocalized, electron-deficient, M–H–M interactions that are best described as an overall four-center, four-electron interaction.

The structure and bonding of transition-metal hydrides has been the subject of considerable debate, due, in large part, to the inaccuracy of hydride positions as determined by X-ray crystallography. This, coupled with the rapid fluxionality often observed in polyhydride complexes, has led to many questions regarding the bonding in these systems.[3]

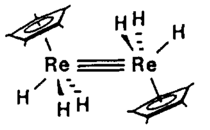
Our recent interest in the electronic structure and bonding in dimeric organometallic systems of the general formula $[CpM]_2L_n$ (Cp = η^5-C_5H_5), so-called piano-stool dimers, has led to our investigation of several bimetallic hydride systems within this expansive class. Previously our work has been concentrated on dimers containing ancillary ligands L that are π-acid ligands (CO, NO)[1,4] or hydrocarbyl fragments (CH, CH_2, CH_3, $C{=}CH_2$),[5] for which n = 3, 4, or 5. We have since expanded this investigation to include other related piano-stool geometries, as well as other types of ancillary ligands, in an effort to understand the role of the electronic structure on the conformation and reactivity within these systems.

In the preceding paper we examined piano-stool dimers of the formula $Cp_2M_2L_4$, where L = H, CO, or NO, and studied the effects on the orbital energetics within an isoelectronic series of replacing the σ-only hydride ligands with π-acid ligands such as CO and NO. Here we have extended this approach to include a series of dinuclear transition-metal hydrides of the general formula $Cp_2M_2H_{6-n}(L)_n$ where n = 0, 2, 4, or 6 and L = CO or NO. The analysis will begin by first considering the σ-only framework where n = 0 (in this case such a compound is known for M = Re and η^5-C_5Me_5).[6] From that point we will proceed by modeling the known systems $Cp_2W_2H_4(NO)_2$,[7] $Cp_2W_2H_2(CO)_4$,[8] and $Cp_2W_2(CO)_6$[9] wherein we have successively replaced two, four, and six hydride ligands with π-acid ligands. In each case we will examine various geometries possible for the bimetallic species. Finally we will conclude by considering the electronic effects of other ligands (e.g., I and $P(OPh)_3$) on the piano-stool dimer system.

The calculational procedure we have employed is the Fenske–Hall MO method, which has provided reliable results for similar monomeric and dimeric systems, and the details are given in the Appendix.

$Cp_2M_2H_6$: σ-Only Framework

Recently Herrmann et al. were able to isolate a bimetallic hydride of the formula $Cp^*{}_2Re_2H_6$ (Cp^* = η^5-C_5Me_5), by treatment of $Cp^*Re(O)Br_2$ with $LiAlH_4$ followed by MeOH workup.[6] Although little is known concerning the structure of this piano-stool dimer, it serves as a useful starting point for our analysis. We can visualize three possible arrangements of the hydride ligands based on the known structures of other $Cp_2M_2L_6$ compounds as well as related bimetallic polyhydrides. These are depicted below as structure types **1**, **2**, and **3**. In each structure type the Re atom is formally in the +4 oxidation state, resulting in a d^3–d^3 dimer. In order to satisfy the 18-electron rule, we must invoke a formal Re–Re triple bond for **1**, **2**, and



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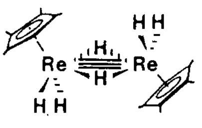

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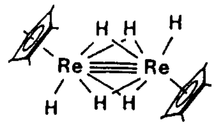

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[1] Part 5: Bursten, B. E.; Cayton, R. E.; Gatter, M. G. *Organometallics*, preceding paper in this issue.

[2] Camille and Henry Dreyfus Foundation Teacher-Scholar (1984–1989) and Fellow of the Alfred P. Sloan Foundation (1985–1987).

[3] See, for example: (a) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176–183. (b) Wei, C.-Y.; Marks, M. W.; Bau, R.; Kirtley, S. W.; Bisson, D. E.; Henderson, M. E.; Koetzle, T. F. *Inorg. Chem.* **1982**, *21*, 2556–2565. (c) Cotton, F. A.; Leung, P. C. W.; Roth, W. J.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 117–120.

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[5] (a) Bursten, B. E.; Cayton, R. H. *Organometallics* **1986**, *5*, 1051–1053. (b) Bursten, B. E.; Cayton, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 8241–8249. (c) Bursten, B. E.; Cayton, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 6053–6059.

[6] (a) Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111–137. (b) Herrmann, W. A.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1092–1093.

[7] (a) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 7971–7981. (b) Legzdins, P.; Martin, J. T.; Oxley, J. C. *Organometallics* **1985**, *4*, 1263–1271.

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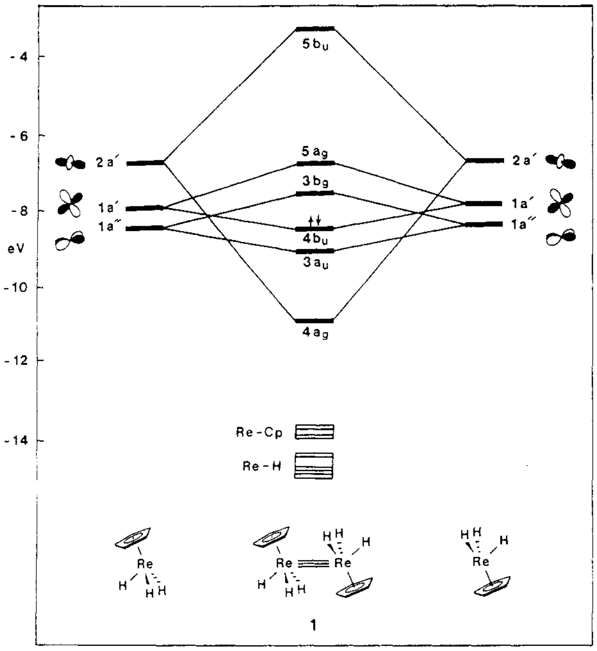


Figure 1. Molecular orbital diagram for the frontier orbital region of $[CpReH_3]_2$ (1). The arrows indicate the highest occupied MO.

3. We will begin by considering the bonding in the all-terminal structure type 1, followed by descriptions of the more complicated bridging ligand systems 2 and 3. We will address the validity of such a bond order for each conformation when we discuss their respective electronic structures.

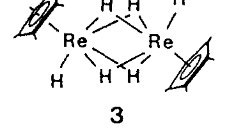
Figure 1 depicts the MO diagram of $[CpReH_3]_2$ (1),[10] built by joining two $CpReH_3$ units via a metal–metal bond to resemble two, four-legged piano-stool fragments.[11a] A set of six Re–H bonding orbitals are located slightly below the set of four Re–Cp(π) bonding interactions. Focussing on the metal-based orbitals ($4a_g$–$5b_u$), we find a "$\sigma^2\pi^4$" electron configuration resulting in a formal Re–Re triple bond. The four-legged geometry about each Re atom dictates that there is mixing between the orbitals that are of π and of δ symmetry with respect to the Re–Re axis. Therefore, as a result, the π-type interactions ($3a_u$, $4b_u$) show a considerable degree of δ^* mixing (ca. 65% π, 35% δ^*) that serves to significantly weaken the overall bonding picture. Furthermore, δ mixing into the Re–Re π^* virtual orbitals ($3b_g$, $5a_g$) lessens the destabilization of these empty orbitals to yield a HOMO – LUMO separation of only 0.77 eV, at the calculated Re–Re distance of 2.538 Å.

Turning our attention to the bridging hydrido isomers 2 and 3, we will construct their bonding descriptions by first assembling the terminal frameworks, followed by addition of the hydride bridges. Figure 2 shows the frontier orbital pictures of $[CpReH_2]_2$ and $[CpReH]_2$, each constructed from its respective monomeric fragments.[11b–d] The terminal framework $[CpReH_2]_2$ (left side) is qualitatively similar to that described for $[CpReH_3]_2$ in Figure 1, with one major difference: The removal of a terminal hydride ligand from each Re atom (in going from $[CpReH_3]_2$ to $[CpReH_2]_2$) frees up an additional metal-based orbital set ($4a_g$, $4b_u$) that is essentially Re–Re δ and δ^* in character. This effect is further demonstrated when we move to the framework $[CpReH]_2$ (right side of Figure 2). The removal of a second terminal hydride ligand from each Re atom yields yet another set of Re-based orbitals ($2b_g$, $3a_u$) which is also Re–Re δ and δ^* in character.

The MO diagram of 2 is completed in Figure 3 as the two bridging hydride ligands are added. The symmetric combination of μ-H 1s orbitals interacts with the $3a_g$ and $4a_g$ orbitals of the terminal framework to yield a three-orbital interaction resulting in the bonding $1a_g$ orbital, the nonbonding $4a_g$ orbital (Re–Re σ/δ), and the antibonding $6a_g$ orbital. The antisymmetric combination of μ-H 1s orbitals interacts strongly with one of the Re–Re π-type orbitals ($3a_u$). These two μ-H bonding orbitals are delocalized Re–H–Re interactions which will be discussed in greater detail later when we address the systems containing π-acid ligands. It is interesting to note here that the two Re–H–Re bonding interactions lie at lower energy than the four Re–(t-H) (t = terminal) orbitals. This increased stabilization indicates a stronger Re–H interaction in the bridging mode, due to both greater overlap of the H 1s orbital in the bridging site and a more favorable Re–Re interaction in the delocalized Re–H–Re interactions compared to the Re–(t-H) interactions. Focussing on the metal-based orbitals, we find an electron configuration of $(\sigma/\delta)^2\pi^2\delta^{*2}$, or approximately a *direct* Re–Re bond order of 1.

The bonding picture of the isomer $[CpReH]_2(\mu\text{-}H)_4$ (3) is completed in Figure 4 as the terminal framework is allowed to interact with four bridging hydride ligands. The hydrogen 1s orbitals split into the σ, π, and δ combinations shown on the right side of Figure 4. Once again, the totally symmetric μ-H combination interacts with two orbitals of the terminal framework ($3a_g$, $4a_g$) resulting in a three-orbital interaction and again generating the bonding $1a_g$ orbital, the essentially Re–H nonbonding metal-based $4a_g$ orbital (Re–Re σ/δ), and a higher lying antibonding level. The two H 1s π combinations interact strongly with both of the Re–Re π orbitals ($2a_u$, $3b_u$), and the H 1s δ combination exhibits a substantial interaction with a Re–Re δ orbial ($2b_g$). If we focus on the remaining occupied metal-based orbitals, an electron configuration of $(\sigma/\delta)^2\delta^{*2}\delta^{*2}$ emerges, resulting in no net *direct* Re–Re bonding. As such, the existence of a dimer in this quadruply bridged geometry would be completely dependent on the Re–(μ-H)–Re interactions to hold it together.

It should be noted that the μ-H ligands have been arranged in a staggered structure with respect to the terminal hydrides. This is in accord with the staggered arrangement found in the neutron diffraction study of $[Re(PEt_2Ph)_2H_2]_2(\mu\text{-}H)_4$.[12] Extended Hückel MO calculations performed on the model complex $[Re(PH_3)_2H_2]_2(\mu\text{-}H)_4$ by Hoffmann et al. indicate the staggered $(\mu\text{-}H)_4$ arrangement to be more stable than either the eclipsed configuration (45° rotation of the μ-H_4 set) or the half-eclipsed structure (45° rotation of one terminal metal unit).[13] In fact the overall electronic structure found for $[Re(PH_3)_2H_2]_2(\mu\text{-}H)_4$ is very similar to that calculated for 3. This is not surprising considering that each is a d^3–d^3 dimer, and struc-



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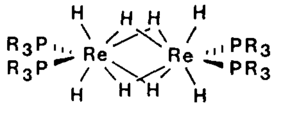

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[10] Cp was used to model Cp* in compounds 1, 2, and 3.

[11] (a) Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180–188. (b) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536. (c) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. *J. Am. Chem. Soc.* **1979**, *101*, 585–591. (d) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554–556.

[12] Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872–3874.

[13] Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141–3151.

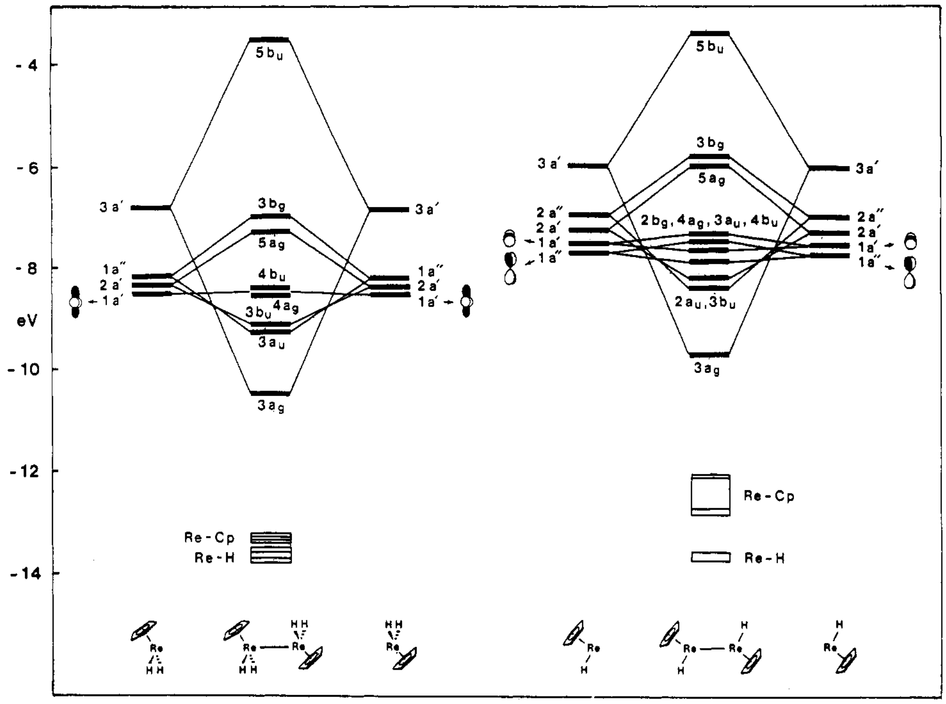

Figure 2. Molecular orbital diagram showing the frontier orbital region of the terminal frameworks: $[CpReH_2]_2$ (left) and $[CpReH]_2$ (right).

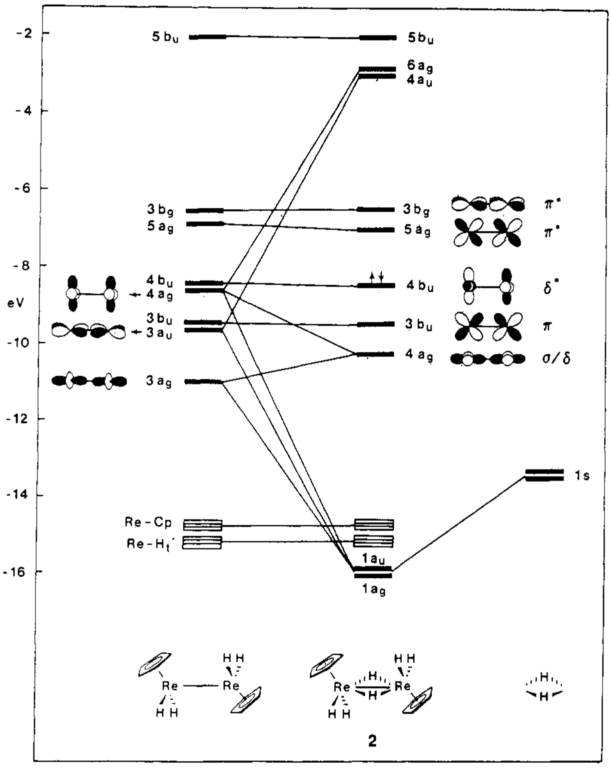

Figure 3. Interaction diagram for **2** constructed from the terminal framework, $[CpReH_2]_2$, and two hydride bridges. The arrows indicate the highest occupied MO.

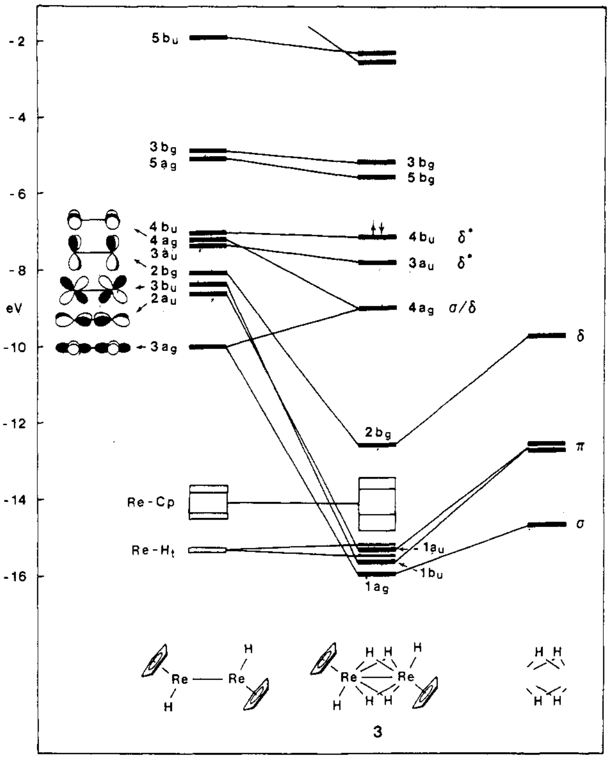

Figure 4. Interaction diagram for **3** constructed from the terminal framework, $[CpReH]_2$, and four hydride bridges. The arrows indicate the highest occupied MO.

turally the two complexes are similar if we view the cyclopentadienyl ligands as each occupying three coordination sites.

Comparing the electronic structures of the isomers **1**, **2**, and **3** (Figures 1, 3, and 4) reveals several interesting features:

(1) The net *direct* Re–Re bonding decreases as the number of bridging hydride ligands is increased. However, the *overall* Re–Re bonding may actually increase as the number of hydride bridges is increased. This is a difficult effect to decipher since the elimination of a *direct* Re–Re bond is accompanied with the formation of a *delocalized* Re–(μ-H)–Re bond, and the relative strengths of these interactions are difficult to gauge. We can get an idea of the relative strengths of these interactions from the work of Sattelberger et al. on a closely related bimetallic tantalum polyhydride system $[Ta(PR_3)_2Cl_2]_2(\mu\text{-}H)_2$.[14]

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[14] Scioly, A. J.; Luetkens, M. L., Jr.; Wilson, R. B., Jr.; Huffman, J. C.; Sattelberger, A. P. *Polyhedron* 1987, *6*, 741–757.

Structurally, this Ta dimer resembles **3** with two less hydride bridges (again assuming the Cp ligands of **3** to occupy three coordination sites). The electronic structure of the Ta dimer can easily be derived from that of **3** by eliminating the H 1s δ and one of the π interactions, thus generating metal-based π and δ orbitals in the frontier region. Occupation of the two lowest metal-based orbitals (d^2–d^2 dimer) yields a $\sigma^2\pi^2$ configuration and a *direct* Ta–Ta double bond. Xα–SW calculations performed on the Ta system also support this electronic description.[14] This species oxidatively adds H_2 to yield $[Ta(PR_3)_2Cl_2]_2(\mu\text{-}H)_4$, a d^1–d^1 dimer that is isostructural with **3**, with a concomitant reduction in the *direct* Ta–Ta bond order to one (σ^2). Interestingly, the crystal structures of these Ta dimers indicate that the Ta–Ta distance actually decreases by 0.03 Å in going from the Ta–Ta double-bonded $(\mu\text{-}H)_2$ dimer to the Ta–Ta single-bonded $(\mu\text{-}H)_4$ dimer.[14] Although this decrease may simply be due to the change in formal oxidation state (Ta(III) to Ta(IV)), it may indeed indicate that the two added delocalized Ta–(μ-H)–Ta interactions are as strong, or stronger, than the Ta–Ta π bond that they replaced.

(2) The calculated HOMO - LUMO separation increases in the series from **1** to **2** to **3** (cf. **1**, 0.77 eV; **2**, 1.43 eV; **3**, 1.59 eV) at identical Re–Re distances. If indeed a positive correlation exists between the magnitude of the HOMO - LUMO gap and stability, then geometry **3** would be slightly favored over either **1** or **2**.

(3) The summation of the energies of the Re–H bonding orbitals in each of the three isomers differs by only ~1.0 eV (ca. **1**, −89.9 eV; **2**, −91.0 eV; **3**, −90.5 eV). Therefore, in the absence of any symmetry-induced barriers, a relatively shallow potential surface would appear to exist in the rearrangement of the Re–H interactions from terminal to bridging modes.

From these conclusions, it is not possible to predict that one particular geometry will be favored. This is consistent with the likelihood that, as is the case for other bimetallic polyhydrides, the hydride ligands are fluxional in solution.[15] As we will see in the later sections, the lack of π-type interactions when dealing with hydride ligands allows a variety of energetically similar geometries to exist, a situation that will change when ligand π character is introduced. The actual solid-state and solution structures of $Cp^*_2Re_2H_6$ await further experimental results.

Although we cannot make a compelling case for the preference of any one of the previously discussed structures, the geometry of **2** provides a convenient starting point for moving into the π-acid systems. We will begin with the σ-only framework $[CpMH_2]_2(\mu\text{-}H)_2$, detailed earlier for **2**, and examine the electronic consequences associated with the successive replacement of hydride ligands with π-acid (NO or CO) ligands. We will concentrate on the metal-based orbitals $4a_g$–$3b_g$ (Figure 3) since the levels capable of efficient π interaction with these new ligands are located within this region.

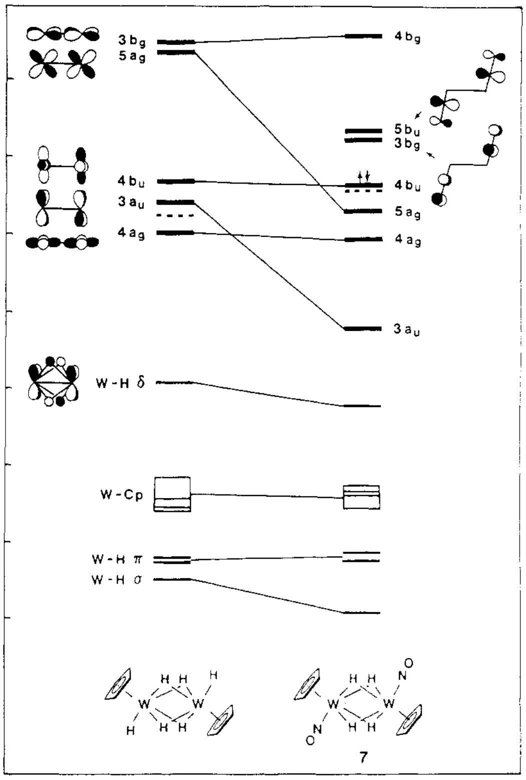
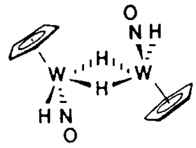


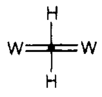
Figure 5. Comparative molecular orbital diagrams displaying the frontier orbital regions of **5** (left) and **6** (right), along with the correlation to the orbitals of **4** (center). The arrows indicate the highest occupied MO, and the dashed lines represent the energies of the W 5d Fock matrix elements.

$Cp_2W_2H_4(NO)_2$: π-Acid Effects

Recently Legzdins and co-workers have synthesized and characterized a tungsten hydride dimer of the formula $Cp_2W_2H_4(NO)_2$.[7] Through ^1H NMR (in particular the $J_{^1H-^{183}W}$ values) and X-ray crystallography, it has been shown that this compound exists with two bridging hydride ligands both in solution and in the solid state, as shown.



Furthermore, the bridging hydrides are static and do not interconvert with terminal ligands on the NMR time scale.[7a] The oxidation state of the W atoms is formally +2, resulting in a d^4–d^4 dimer. This compound poses some very interesting questions concerning its structure and bonding, questions which we fell are ideally suited to be answered through an examination of its electronic structure: (1) Why do the NO ligands choose to coordinate in a terminal rather than bridging mode? (2) The 18-electron rule would dictate a W–W double bond; how accurate is this description? (3) Is the static nature of the hydride ligands the result of energetically unfavorable alternative geometries? (4) Due to the static nature of the μ-H ligands, Legzdins et al. have proposed the "fused" four-center, six-electron representation shown below to describe the bonding within the dimetallacyclic core.[7a] Is such a formalism justified electronically?



To answer these questions we must refer to the MO diagrams provided in Figure 5. Looking first at the center MO diagram of the fictitious σ-only framework $[CpWH_2]_2(\mu\text{-}H)_2$ (**4**), we see that qualitatively it is nearly identical with its Re analogue. The metal-based d orbitals are labeled $4a_g$–$3b_g$ (C_{2h} symmetry) and are analogous to

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[15] (a) Okuda, J.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 1681–1690. (b) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319–2320 and references therein.

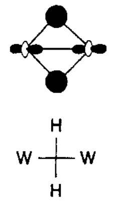
Table I. Percent NO and CO 2π Character in Selected Metal-Based Orbitals of Compounds 5, 6, and 8

5		6		9	
orbital	% NO	orbital	% NO	orbital	% CO
$4a_g$	0	$7a_g$	47	$3b_g$	28
$3b_g$	50	$7a_u$	34	$5a_g$	40
$4b_u$	50	$6a_u$	29	$4b_u$	34
$3b_u$	35	$6a_g$	25	$3b_u$	31
				$4a_g$	25

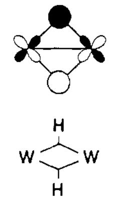
those illustrated for 2 in Figure 3. Let us first consider the reasons why the NO ligands prefer to coordinate in the terminal rather than bridging mode. The replacement of two μ-H ligands with two μ-NO ligands results in dimer **5**, the MO diagram of which is shown on the left side of Figure 5, along with the correlation of its orbitals to those of **4**. The μ-NO 2π orbitals are able to interact with, and consequently stabilize, three of the five metal-based orbitals. The $5a_g$ orbital, which is largely unperturbed by μ-NO ligation and remains at nearly the same energy as in the σ-only framework, becomes the LUMO of **5**. The $4a_g$ orbital is also unable to interact with the μ-NO 2π orbitals and is somewhat destabilized by NO 5σ interaction and ultimately becomes the HOMO. Since only three of the four μ-NO 2π combinations find symmetry matches in the W-based orbitals, the remaining nonbonding NO 2π orbital, the $4b_g$ orbital, resides at relatively low energy. If we now compare the electronic structure of **5** to that of its isomer **6** (where two terminal hydride ligands of **4** have been replaced by NO ligands), depicted on the right side of Figure 5, we can understand the reasons for a more favorable set of interactions in this isomer. Once again, correlation to the σ-only framework orbitals of **4** is shown. When both NO ligands occupy terminal coordination sites, all four NO 2π combinations find symmetry matches among the W-based set, such that the four occupied orbitals are all substantially stabilized. The empty $8a_g$ orbital ($3b_g$ orbital of framework **4**) cannot be stabilized, and it represents the LUMO of **6**. The symmetry has now been lowered to C_i; hence both the HOMO and LUMO of **6** are of a_g symmetry. The result of terminal NO bonding is a greater number of favorable W–NO back-bonding interactions, as compared to the bridging NO geometry. Interestingly, though, the total NO 2π contribution to the four highest occupied MO's is the same in both **5** and **6** (see Table I). Given the overall similarities in the bonding in **5** and **6**, why is the latter isomer preferred over the former? It is seen that the HOMO – LUMO separation in **6** (3.66 eV) is larger than that in **5** (3.02 eV). We have previously noted a good correlation between HOMO – LUMO gap and apparent thermodynamic stability for a large number of organometallic piano-stool monomers and dimers; this seems consistent with the notion of "absolute hardness" advanced by Pearson and Parr.[16] It is also noted, however, that the HOMO of **6** is higher in energy than that of **5**, and this might be used as support for the greater stability of **5** than **6**. This would be a misleading argument for these complexes in which the bonding mode of NO changes. In **5**, the bridging NO ligands are best considered as formally monoanionic ligands, whereas the terminal NO ligands in **6** are better considered to be NO^+ ligands. Thus, on proceeding from **5** to **6**, the *formal* oxidation state of W decreases from +4 to +2, and it would therefore be expected that the average energy of the W 5d based orbitals of **6** would be higher than that of **5**. Consistent with this, the average 5d energy, as best gauged by the diagonal 5d–5d Fock matrix elements ($F_{5d,5d}$), is lower in **5** than in **6**. In Figure 5, we have indicated the $F_{5d,5d}$ values as dashed lines, and it is seen that, in spite of its higher energy, the HOMO of **6** is more greatly stabilized, relative to the average 5d energy, than that of **5**. Finally, we have compared the total energies of these two isomers by using a new (and not yet completely tested) implementation of Fenske–Hall total energy.[17] The total energy of **6** is found to be ca. 23 eV lower than that of **5**. We have found that the total energy method generally predicts the most stable of a set of isomers, but the magnitudes of the energy differences are not that accurate.

To answer the question of the applicability of the 18-electron rule to this compound, or more specifically the W–W bond order, let us examine the MO diagram of **6** in more detail. Looking at the W-based orbitals, the electron configuration is $(\sigma/\delta)^2\pi^2\delta^{*2}\pi^{*2}$ (see Figure 3 for sketches of these orbitals) resulting in no formal *direct* W–W bond and a 16-electron count for each W atom. As is the case for many ligand-bridged transition-metal dimers, the metal–metal interaction appears to be delocalized through the bridging ligand orbitals.[18] This also helps answer the third question dealing with the bonding of the μ-H ligands.

As was mentioned earlier, the μ-H ligands of **2** (as a structure similar to **6**) form two delocalized, electron-deficient interactions with the metal atoms. The two W–(μ-H) bonding orbitals of **6** are shown



I



II

along with a more conventional "stick" designation. Representation I is a "fused" four-center, two-electron interaction, whereas II can be described as two "closed" three-center, one-electron interactions. Therefore, the combination of the bonding in the dimetallacyclic core is best represented as an overall four-center, four-electron interaction. In order to construct the delocalized W–H–W bonds, the μ-H ligands have utilized two W-based d orbitals that, without the presence of bridging ligands, would form W–W σ and π interactions.

The W–W distance in **6**, from its crystal structure, is 2.9032 Å, placing it the range of either a W–W single or double bond.[7a] This relatively short W–W distance must be the result of the strong delocalized W–(μ-H)–W interactions, illustrated above, since the metal-based orbitals indicate an absence of any *direct* W–W bonding.

As was mentioned earlier, the μ-H ligands in **6** were found to be static and not to interconvert with the terminal hydrogens in solution. This may be due to the presence of energetically unfavorable intermediates such as **5** along any fluxional pathway. We have considered two other viable intermediates, the geometric isomers $[CpW(NO)]_2(\mu\text{-}H)_4$ (**7**) and $[CpW(NO)H_2]_2$ (**8**). One of these two intermediates would be involved if the hydride ligands of **6** were to exchange by either of two likely pathways: (1) The terminal hydride ligands could move into a bridging position yielding the quadruply bridged intermediate **7**, followed by an unbridging of the opposite two hydride

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[16] (a) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516. (b) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561–567.

[17] Batt, R. H.; Bursten, B. E.; Luth, K. W., unpublished results.

[18] See, for example: Bino, A.; Bursten, B. E.; Cotton, F. A.; Fang, A. *Inorg. Chem.* **1982**, *21*, 3755–3759.

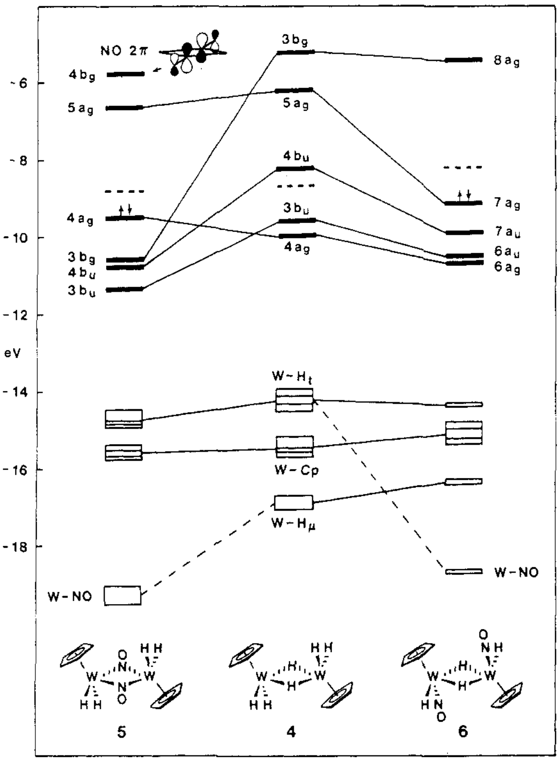
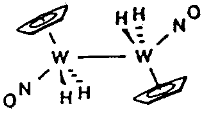


Figure 6. Molecular orbital diagram showing the frontier orbital region of 7 (right), along with its correlation to the orbitals of $[CpWH]_2(\mu\text{-}H)_4$ (left). The W–(t-H) (t = terminal) and W–NO σ orbitals are not shown. The arrows indicate the highest occupied MO, and the dashed lines represent the energies of the W 5d Fock matrix elements.

ligands. (2) The bridging hydride ligands could initially unbridge symmetrically to produce the all-terminal intermediate 8, followed by a bridging of the opposite two hydride ligands. Isomer 7 is structurally similar to the previously addressed 3, with the exception that the terminal hydrides have been replaced by nitrosyl ligands. The frontier orbital diagram of 7 is shown in Figure 6, along with its correlation to the orbitals of the fictitious framework $[CpWH]_2(\mu\text{-}H)_4$. From this diagram we can see that only two metal-based orbitals ($3a_u$, $5a_g$) interact significantly with, and are stabilized by, the NO 2π orbitals. This results in two nonbonding NO 2π combinations ($3b_g$, $5b_u$) that remain as the lowest unoccupied MO's, producing a HOMO – LUMO separation of only 1.21 eV. It is apparent that such a geometry is less favorable than that calculated for 6, wherein all four NO 2π combinations interact strongly with metal-based orbitals and a HOMO – LUMO separation of 3.66 eV results. In addition, total energy calculations indicate isomer 6 to be 92 eV more stable than 7. The other reasonable intermediate 8 contains all terminal ligands and as such resembles the geometry of the hydride complex 1.



In this geometry, the four W–W π and π* orbitals interact with the NO 2π orbitals and are stabilized close in energy to the W–W σ orbital. Only four of these five metal-based orbitals are occupied, resulting in a HOMO – LUMO separation of just 0.81 eV. Once again, the total energy of isomer 8 was found to be higher (8 eV) than that of 6. Thus we are not surprised by the lack of fluxionality exhibited by 6, based on the calculated instability of isomers 5, 7, and 8, likely intermediates for such a fluxional process.

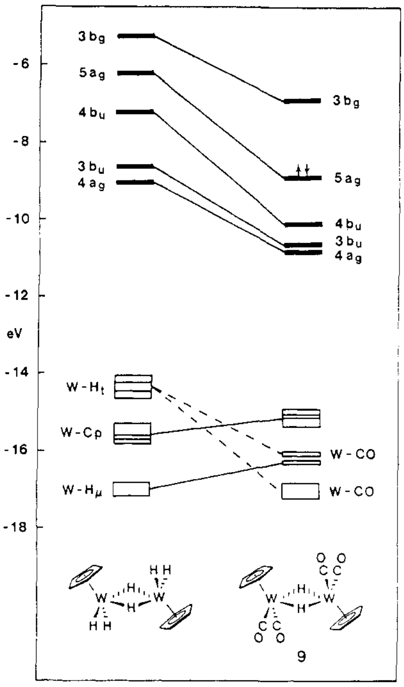


Figure 7. Molecular orbital diagram showing the frontier orbital region of 9 (right), along with its correlation to the orbitals of $[CpWH_2]_2(\mu\text{-}H)_2$ (left). The arrows indicate the highest occupied MO.

$Cp_2W_2H_2(CO)_4$: π-Acid Effects

In the previous section we replaced two hydride ligands of the σ-only model $[CpWH_2]_2(\mu\text{-}H)_2$ with two π-acid NO ligands. Here we proceed one step further and replace four hydride ligands with four π-acid CO ligands. The compound used to model this effect is $[CpW(CO)_2]_2(\mu\text{-}H)_2$ (9). This dimer was prepared by Alt and co-workers and was shown by ^1H NMR (again with the aid of $J_{^1H-^{183}W}$ values) to contain two hydride bridges.[8] As with the Legzdins nitrosyl hydride, the hydride bridges of 9 were also shown to be static in solution, and, again, the 18-electron rule would dictate a W–W double bond. It is of interest to note that, on proceeding from 6 to 9, the formal electron count for W does not change since a linear NO and H are replaced with two CO ligands on each metal atom.

The MO diagram for 9 is shown in Figure 7 along with its correlation to the orbitals of the corresponding σ-only framework. The coordination of four terminal π-acid ligands leads to the stabilization of all of the W-based d orbitals to a similar degree. The HOMO of 9 is the $5a_g$ orbital, thus resulting in a W-based orbital occupation of $(\sigma/\delta)^2\pi^2\delta^{*2}\pi^{*2}$ (see Figure 3 for sketches of these orbitals). This is the same electron configuration derived for the nitrosyl hydride 6; thus here also no formal *direct* W–W bond is present. The μ-H bonding is also similar to that described for 6, namely an overall four-center, four-electron interaction.

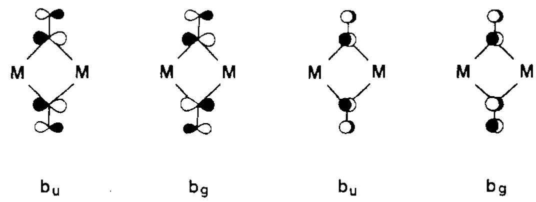
At this point it is instructive to comment further on the unfavorable bridging coordination mode of π-acid ligands in $Cp_2M_2L_6$ compounds. Both the nitrosyl hydride 6 and the carbonyl hydride 9 choose to bridge the σ-only hydride ligands rather than their π-acid ligands. Moreover, further replacement of the hydride ligands of 9 to formally yield the hexacarbonyl dimer $Cp_2W_2(CO)_6$ clearly demonstrates the desire for compounds within the $Cp_2M_2L_6$ system to avoid a π-acid bridge. It is well-known that $Cp_2W_2(CO)_6$ (as well as its Cr and Mo analogues) displays six terminally bound CO ligands.[19] This is in direct contrast to the

Scheme I

$$[CpW(NO)I]_2(\mu\text{-}I)_2 \xrightarrow{2H^-} \underset{\mathbf{10}}{[CpW(NO)I]_2(\mu\text{-}H)_2} \xrightarrow{2H^-}$$

$$\underset{\mathbf{6}}{[CpW(NO)H]_2(\mu\text{-}H)_2} \xrightarrow{2P(OPh)_3} \underset{\mathbf{11}}{[CpW(NO)(P(OPh)_3)]_2(\mu\text{-}H)_2}$$

$Cp_2M_2L_4$ species (addressed in the preceding paper) which readily bridge their π-acid ligands for fundamentally electronic reasons.[22] The reason for this difference is a basic one induced by the geometrical differences between the two piano-stool dimer systems $[CpML]_2(\mu\text{-}L)_2$ and $[CpML_2]_2(\mu\text{-}L)_2$. First let us consider the representations spanned by the various combinations of the 2π orbitals of two bridging EO (E = C, N) ligands under C_{2h} symmetry, which is the symmetry of the trans isomers of both of these piano-stool dimer systems. Shown below are the μ-EO 2π combinations, which transform as $2b_g + 2b_u$ in this point group.



In the $[CpML]_2(\mu\text{-}L)_2$ system the frontier metal-based orbitals transform as $2a_g + 1a_u + 2b_g + 2b_u$ such that each of the 2π combinations for the μ-EO ligands is able to find an orbital with which to interact. However, when two more terminal ligands are introduced to the dimer framework to yield the $[CpML_2]_2(\mu\text{-}L)_2$ system, these terminal ligands "steal" a b_g and an a_u orbital leaving a metal-based frontier orbital set of $2a_g + 1b_g + 2b_u$ symmetry. This causes one of the EO 2π representations (the b_g combination on the far right) to no longer have a symmetry match with this set of metal orbitals. Therefore $Cp_2W_2H_4(NO)_2$ and $Cp_2W_2H_2(CO)_4$ choose to bridge two hydride ligands to alleviate the aforementioned symmetry problem associated with two μ-EO ligands. It is interesting to note that this preference is lifted for ligands that lack a π orbital perpendicular to the $M_2(\mu\text{-}L)_2$ plane (e.g. CR_2, NR_2). Thus such ligands would represent potentially favorable bridging moieties for either the $[CpML]_2(\mu\text{-}L)_2$ or the $[CpML_2]_2(\mu\text{-}L)_2$ system.

$[CpW(NO)L]_2(\mu\text{-}H)_2$ (L = I, $P(OPh)_3$)

Thus far our attention has been focussed on the electronic effects resulting from successive replacement of hydride ligands with π-acid ligands. In this section we will examine the electronic implications associated with the replacement of hydride ligands with ligands of rather different electronic properties, namely, I and $P(OPh)_3$.

The specific compounds that we will address are $[CpW(NO)I]_2(\mu\text{-}H)_2$ (**10**) and $[CpW(NO)(P(OPh)_3)]_2(\mu\text{-}H)_2$ (**11**). These two dimers have both been synthesized by Legzdins and co-workers according to Scheme I.[7b] The structures of **10**, **6**, and **11** are all similar in that they each contain two static μ-H ligands, two terminal NO ligands, and trans Cp ligands. It can be seen, however, that the nature of the other terminal ligand on each W atom varies from an anionic, two-electron σ-donor (H^-) in **6**, to an anionic, two-electron weak π-donor (I^-) in **10**, to a neutral, two-electron σ-donor ($P(OPh)_3$) in **11**. It is of interest to understand the electronic perturbations involved with varying the nature of this terminal ligand.

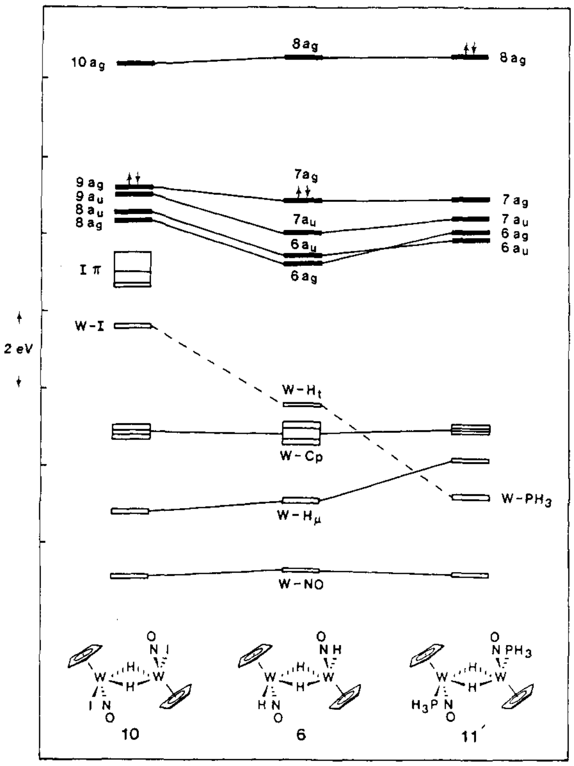


Figure 8. Comparative molecular orbital diagrams displaying the frontier orbital regions of **10** (left) and **11′** (right), along with the correlation to the orbitals of **6** (center). The arrows indicate the highest occupied MO.

The MO diagrams of **10**, **6**, and **11′** are shown in Figure 8. **11′** represents the model compound for **11**, where the $P(OPh)_3$ ligands have been replaced with PH_3 ligands. Let us begin by considering the iodide complex **10** on the left side of Figure 8. The molecular orbitals of **10** are shown as they correlate to the orbitals of the previously addressed nitrosyl hydride **6**. The major difference between the iodide ligand and the hydride ligand is the presence of a filled set of the 5p orbitals on the I ligand. The $5p_x$ and $5p_y$ orbitals interact weakly with the metal-based orbitals, in a filled–filled fashion, to slightly destabilize the W-based orbitals. The compound is formally a d^4–d^4 dimer, therefore the HOMO is the $9a_g$ orbital, and the LUMO is the $10a_g$ orbital, similar to those found for **6**. Other geometries for **10** were also considered. For example, we have already shown that $Cp_2M_2L_6$ systems prefer to bridge σ-only donor ligands rather than π-acid ligands, but we have not yet considered π-donor ligands as bridging moieties. It was found that when the I ligands were allowed to adopt a bridging site, their π-donor ability increased markedly. This causes a strong interaction with an occupied metal-based orbital to produce a significant destabilization of the HOMO (HOMO − SHOMO separation = 3.80 eV). This unfavorable destabilization can be somewhat alleviated by increasing the W–W separation to nonbonding distances; however, the HOMO remains at higher energy than in the hydride-bridged isomer **10**.

When two terminal hydride ligands are replaced by phosphine ligands (right side of Figure 5), the overall MO picture is only slightly perturbed from that of **6**. The PH_3 ligands are primarily σ-only donors, similar to the hydrides,

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(19) (a) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086–1090. (b) Adams, R. D.; Collins, D. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

(20) Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576–2585.

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(22) Bursten, B. E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320–3321.

such that they interact in an analogous fashion with the W framework. However, the PH_3 ligands are neutral, two-electron donors making **11′** a formal d^5–d^5 dimer rather than a d^4–d^4 dimer as was found for **6** and **10**. This formal reduction of the dimer causes the $8a_g$ orbital (W–W π^*) to be the HOMO, an electron configuration of $(\sigma/\delta)^2\pi^2\delta^{*2}\pi^{*2}\pi^{*2}$, and a net antibonding interaction between the W atoms. Therefore **11** provides an unequivocal example of a transition-metal dimer with a net *direct* metal–metal antibonding interaction, which is held together solely by its hydride bridges.

Appendix

Molecular orbital calculations were performed on an IBM 3081-D computer system using the Fenske–Hall approximate MO method.[21] Local D_{5h} symmetry was invoked upon the cyclopentadienyl rings, and a C–H distance of 1.08 Å was used for each compound. For the compound $Cp^*_2Re_2H_6$, the Cp* ligands ($Cp^* = \eta^5\text{-}C_5Me_5$) were modeled with Cp ligands ($Cp = \eta^5\text{-}C_5H_5$). Calculations on the geometric isomers **1**, **2**, and **3** were performed by using the Re–Re and Re–H distances from the neutron diffraction study of the isoelectronic dimer $[Re(PEt_2Ph)_2H_2]_2(\mu\text{-}H)_4$:[12] Re–Re = 2.538 Å, $Re\text{–}H_t$ = 1.669 Å, $Re\text{–}H_\mu$ = 1.878 Å. The Re–C(Cp) distance used for **1**, **2**, and **3** was 2.342 Å, with C–C distances of 1.41 Å. The interatomic angles used in **1** were taken from $[CpW(CO)_3]_2$,[17a] whereas **2** was modeled after the geometry of the crystallographically characterized $[CpW(NO)H]_2(\mu\text{-}H)_2$ (**6**),[7a] both idealized to C_{2h} symmetry. The $[ReH]_2(\mu\text{-}H)_4$ core of **3** was modeled after the structure of $[Re(PEt_2Ph)_2H_2]_2(\mu\text{-}H)_4$, using a Re–Re–Cp(centroid) angle of 150° and idealized to C_{2h} symmetry. The geometries of the tungsten dimers **4**, **5**, **6**, **9**, **10**, and **11′** were modeled after the X-ray structure of **6** after idealizing the structure to C_i symmetry. The geometries of the model compounds **7** and **8** were taken from those of **3** and **1**, respectively. For each of the tungsten dimers, the W–W, W–C(Cp), and C–C distances were set at those found in the crystal structure of **6**. All W–(t-H) distances (t = terminal) were set at 1.80 Å, and W–(μ-H) distances were set at 1.90 Å. The W–N and N–O distances used in the calculation of **6**, **7**, and **8** were those found in the crystal structure of **6**. For the model complex $[CpWH_2]_2(\mu\text{-}NO)_2$ (**5**), the following distances were assumed: W–N = 2.033 Å and N–O = 1.231 Å. For the complex $[CpW(CO)_2]_2(\mu\text{-}H)_2$ (**9**), the W–C distance was set at 1.753 Å and the C–O distance of 1.218 Å was used. For the complex $[CpW(NO)I]_2(\mu\text{-}H)_2$ (**10**), the W–N and N–O distances were the same as those in **6**, with a W–I distance of 2.85 Å. For the model complex $[CpW(NO)H]_2(\mu\text{-}I)_2$, a W–I distance of 2.80 Å was used, and calculations were performed at W–W distances of 2.90 and 4.40 Å. For the model compound $[CpW(NO)(PH_3)]_2(\mu\text{-}H)_2$ (**11′**), the same parameters as those for **6** were used with a W–P distance of 2.50 Å and P–H distance of 1.421 Å. The geometry about the P atoms was assumed to be tetrahedral.

All atomic wave functions were generated by using the method of Bursten, Jensen, and Fenske.[22] Contracted double-ζ representations were used for the W and Re 5d AO's, I 5p AO's, P 3p AO's, and C, N, and O 2p AO's. An exponent of 1.16 was used for the hydrogen 1s AO.[23] The basis functions for W and Re were derived for the +2 oxidation state with the 6s exponents fixed at 1.8 and 2.0, respectively, and the 6p exponents fixed at 1.6 and 1.8, respectively. The CO and NO 3σ orbitals, as well as the first three occupied C_5H_5 orbitals, were filled with 2.0 electrons and deleted from the basis transformation set in all calculations.[24] The CO and NO 6σ orbitals, as well as all virtual orbitals of C_5H_5 above the e_2'' level (D_{5h}), were filled with 0.0 electron and deleted from the basis transformation set in all calculations.[24]

The calculations were performed by using a fragment approach. Multiatomic ligands were converged as independent fragments, the resulting *molecular orbitals* of which were than allowed to interact with the dimeric Cp–M–M–Cp frameworks. The CO and PH_3 ligands were converged as neutral molecules. The terminal NO ligands were converged as NO^-, and the bridging NO ligands were converged as NO^+. The cyclopentadienyl ligands were all converged as Cp^-. All calculations were converged with a self-consistent field iterative technique by using a convergence criteria of 0.0010 as the largest deviation between atomic orbitals populations for successive cycles.

Acknowledgment. We gratefully acknowledge Dr. L. F. Rhodes for helpful discussions and The Ohio State University Graduate School for a Presidential Fellowship for R.H.C.

Registry No. **1**, 114221-43-1; **2**, 114221-44-2; **3**, 114221-45-3; **4**, 114221-46-4; **5**, 114221-47-5; **6**, 104870-92-0; **7**, 114221-48-6; **8**, 114221-49-7; **9**, 86307-87-1; **10**, 104780-35-0; **11′**, 114221-50-0; $[Re(PH_3)_2Hz]_2(\mu\text{-}H)_4$, 114221-51-1.

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