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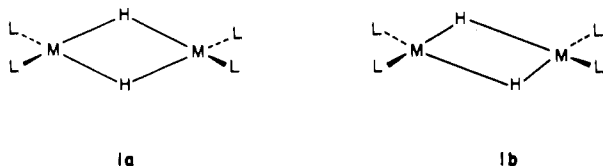
## Hydride Bridges between LnCp<sub>2</sub> Centers

J. V. ORTIZ\*† and ROALD HOFFMANN‡

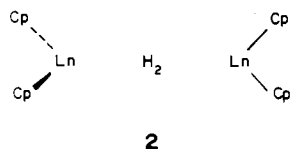
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d orbitals of d<sup>0f<sup>x</sup></sup> LnCp<sub>2</sub> fragments stabilize bridging hydrides in a variety of geometries. SmCp<sub>2</sub> a<sub>1</sub> orbitals are markedly different from MCp<sub>2</sub> a<sub>1</sub> orbitals, where M is an early transition metal of the fourth or fifth period. Symmetric hydride bridges are more stable than asymmetric ones. Various deployments of symmetric bridges use different LnCp<sub>2</sub> orbitals. When the Cp–Ln–Cp planes coincide in (Cp<sub>2</sub>LnH)<sub>2</sub>, the Ln<sub>2</sub>H<sub>2</sub> plane is perpendicular to the Cp<sub>2</sub>Ln planes. When the Cp<sub>2</sub>Ln planes are orthogonal, the Ln<sub>2</sub>H<sub>2</sub> plane bisects them. Possible placements of terminal hydrides are determined by the 2a<sub>1</sub> orbital of the SmCp<sub>2</sub> fragment. Bonding in complexes of the type (LnCp<sub>2</sub>X)<sub>3</sub>X<sup>−</sup> (X = H, Cl) is discussed.

Discrete organolanthanide hydride molecules have recently been synthesized. The hydrides form bridges between two or three metal atoms, but the symmetry of their deployment is uncertain. Precedents from main-group and transition-element electron-deficient structures include symmetric (1a) and asymmetric (1b) bridges, and it is interesting to inquire about the symmetry or asymmetry of the lanthanide hydrides.

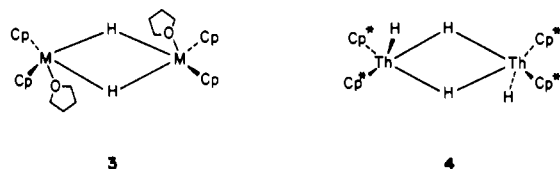


An unusual arrangement of ligands has appeared in which the terminal L–M–L planes are nearly perpendicular<sup>1</sup> (2). The



positions of the hydrogen bridges are unknown. Counting the Cp rings as anions and the bridging ligands as hydrides gives Ln<sup>3+</sup>. For the lanthanides, this implies an atomic configuration of 5d<sup>0</sup>6s<sup>0</sup>6p<sup>0</sup>4f<sup>x</sup>.

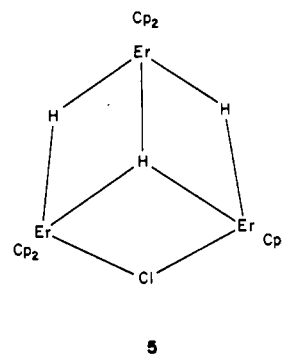
Compounds of the formula (Cp<sub>2</sub>(THF)M(μ-H))<sub>2</sub>, where M = Y, Er, Lu, also have structures with bridging hydrides and oxygen ligands that lie within or close to the M<sub>2</sub>H<sub>2</sub> plane<sup>2</sup> (3). The



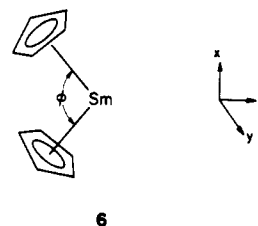
oxidation state remains 3+. Related structures with Zr instead of lanthanides replace the oxygen ligands with more hydrides,<sup>3</sup> moving to a Zr<sup>4+</sup> oxidation state for two more hydrides. Similar compounds are obtained in the actinide series. Thus, Marks and co-workers, working with Th complexes, observe the placement of terminal hydrides above and below the M<sub>2</sub>H<sub>2</sub> plane in (Cp<sup>\*</sup><sub>2</sub>ThH(μ-H))<sub>2</sub><sup>4</sup> (4). A trinuclear system, (Cp<sub>2</sub>ErH)<sub>3</sub>Cl<sup>−</sup> (5), has also emerged from these studies. Two distinct types of bridging, between two or three centers, are observed in this Er(III) complex.<sup>5</sup> The lanthanide hydrides are a fascinating group of compounds. The geometrical preferences of the dinuclear and trinuclear hydrides in this series are the subject of our work.

### The Cp<sub>2</sub>Sm Fragment and Its Relationship to Corresponding Transition-Metal Fragments

The lanthanide hydride complexes that we have mentioned all contain a d<sup>0</sup> Cp<sub>2</sub>Ln<sup>+</sup> fragment, which then forms a natural starting



point for our theoretical discussion. Let us examine the orbitals of the Cp<sub>2</sub>Sm<sup>+</sup> fragment as a function of the angle Cp(centroid)–M–Cp(centroid), φ, defined, along with the coordinate system we will use throughout this work, in 6. Placing the Sm



atom at the origin of the coordinate system, we see that at φ = 180° the line connecting the metal atom to the Cp centroids will overlap with the x axis. As φ is made smaller, the Cp centroids are located in the xz plane at points with neg. z values.

Valence energy levels of the SmCp<sub>2</sub><sup>+</sup> fragment as a function of the Cp(centroid)–M–Cp(centroid) angle are displayed in Figure 1. The f-orbital levels at the bottom are only slightly perturbed by the ligand environment, the largest destabilization with respect to the atomic f orbital H<sub>ii</sub> being approximately 0.1 eV. Hybridizations with the s, p, and d orbitals of Sm are therefore very small. The remaining levels are all unoccupied. Combinations of Cp π\*(e<sub>2</sub>) levels lie between the Sm d and f orbitals. These interact little with further ligands and will not concern us further.

At the D<sub>5h</sub> sandwich geometry (φ = 180°) the orbitals split into a typical pattern, a<sub>1g</sub> < e<sub>2g</sub> < e<sub>1g</sub>. There is a tricky problem with the coordinate systems here. The natural choice for the z axis

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- (1) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401–3.
- (2) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008–14.
- (3) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889–94.
- (4) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science (Washington, D.C.)* **1979**, *203*, 172–4. Fagan, P. J.; Manriquez, J. M.; Maata, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–67. Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939–41.
- (5) Evans, W. J.; Meadows, J. H.; Wayda, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015–7.

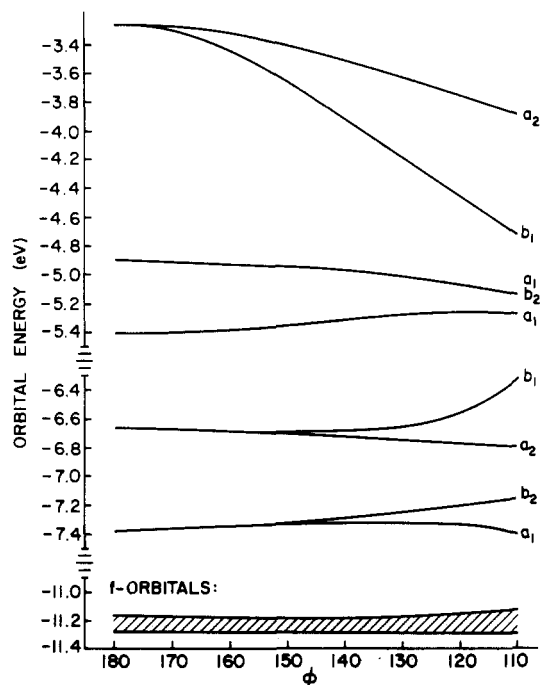


Figure 1.

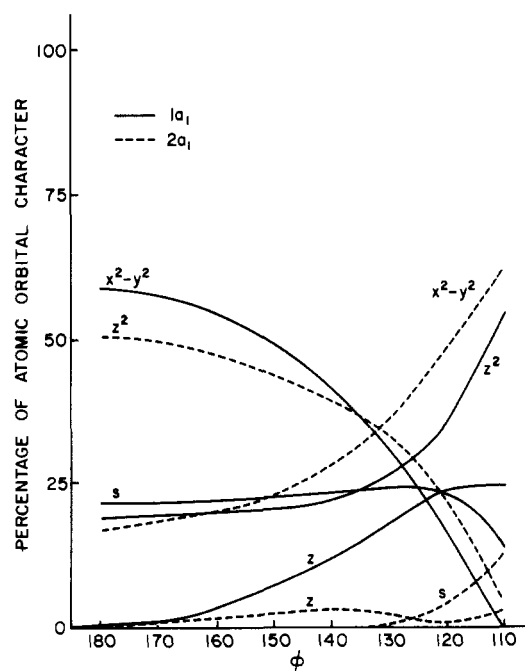
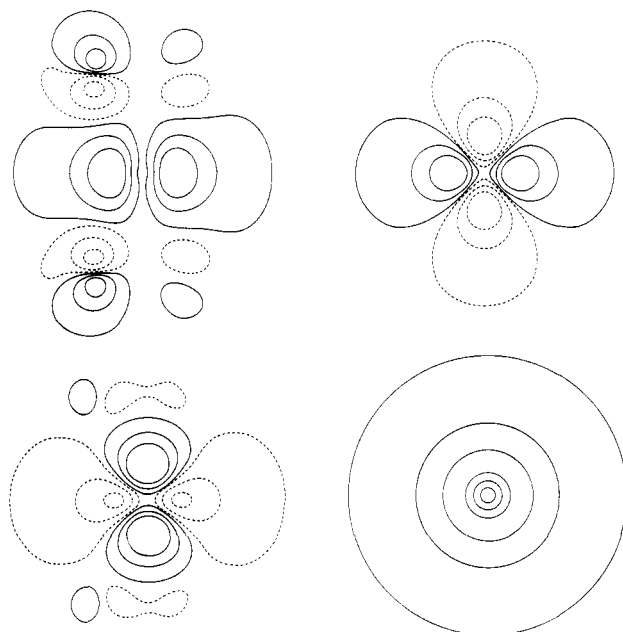


Figure 2.

in the  $D_{5h}$  structure would be the fivefold axis. But the moment  $\phi$  decreases from  $180^\circ$ , and the symmetry is lowered to  $C_{2v}$ , the  $C_2$  axis orthogonal to the original fivefold axis is the canonical choice for the  $z$  axis. We have taken consistently that latter axis system, as 6 shows. Thus the fivefold axis is  $x$  and the orbitals that we would have called  $z^2$  ( $a_{1g}$ ),  $x^2 - y^2$ ,  $xy$  ( $e_{2g}$ ), and  $xz$ ,  $yz$  ( $e_{1g}$ ) had we had  $z$  as the fivefold axis now become  $x^2$  ( $a_{1g}$ ),  $y^2 - z^2$ ,  $yz$  ( $e_{2g}$ ), and  $xy$ ,  $xz$  ( $e_{1g}$ ). As  $\phi$  is varied, the degeneracies are removed. The two highest d levels, labeled  $a_2$  and  $b_1$ , are predominantly  $xy$  and  $xz$  Sm orbitals. Their composition changes very little with  $\phi$ . Below these are the nearly degenerate set of  $a_1$  and  $b_2$  orbitals that correlate with  $yz$  and  $y^2 - z^2$  orbitals in the  $\phi = 180^\circ$  case. Finally, there is the lowest  $a_1$  d orbital, which correlates with  $x^2$  in the  $\phi = 180^\circ$  case. As  $\phi$  decreases, the lowest orbital is gradually transformed, at small  $\phi$ , into a mix of  $s$ ,  $z$ , and  $z^2$  that points away from the two Cp rings. The second  $a_1$  d orbital becomes mostly  $x^2 - y^2$  in character, but only for small

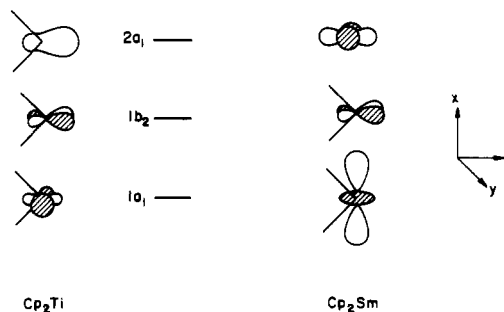
Figure 3.  $SmCp_2$  orbital plots: (bottom row)  $1a_1$ ; (top row)  $2a_1$ ; (left column)  $xz$  plane; (right column)  $yz$  plane.

$\phi$ . Figure 2 shows the changes in atomic orbital character for the  $a_1$  orbitals. The  $b_2$  orbital remains chiefly a  $yz$  orbital throughout.

At  $\phi = 130^\circ$ , some orbital plots were made. Figure 3 gives the  $xz$  and  $yz$  plots of the lowest  $a_1$  d orbital. The  $x^2$  character is clearly dominant. The same cross sections for the next highest  $2a_1$  level are also shown in the figure. A  $z^2 - y^2$  orbital is depicted.

We now see the primary difference between the orbitals of  $Cp_2Ti$ , a typical transition-metal analogue, and the lanthanide. In reference to our earlier work,<sup>6</sup> in  $Cp_2Ti$  the  $1a_1$  level approximates a  $y^2$  orbital and  $2a_1$  is a hybrid of  $s$ ,  $z$ , and  $z^2$ . There is a tendency in that direction in the  $Cp_2Sm$  case, but the character of the  $a_1$  levels is reversed and, more importantly, the hybridization is not so well developed. In a comparison of  $Cp_2Ti$  and  $Cp_2Sm$  at the same  $\phi$ , the  $Cp_2Sm$  levels are much more like those at  $\phi = 180^\circ$  than the transition-metal levels. Later in the paper we will consider the changes in the nature of the orbitals as one moves across the lanthanide series.

The orbital diagrams are informative, but not very portable. If we need small symbols to inform us of the primary orbital character of the frontier orbitals, we would suggest those in 7.



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The energy differences between the d orbitals are much smaller than in the case of  $TiCp_2$ .<sup>6</sup> With the avoided crossing of the two levels of  $a_1$  symmetry, three orbitals are within a few tenths of an electron volt. This will facilitate mixings of the fragment orbitals in the formation of  $\sigma$  bonds in the  $yz$  plane. Another important result is the rapid stabilization of the  $b_1$  level as  $\phi$

(6) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* 1976, 98, 1729-42.

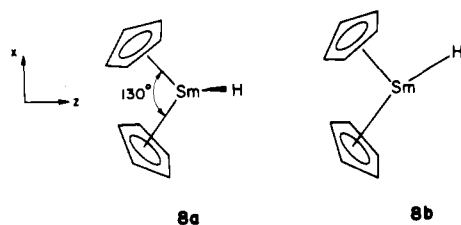
decreases. Donors approaching the *xz* plane might employ this acceptor orbital.

Calculations on the Cp<sub>2</sub>Sm molecule predict an ordinary sandwich arrangement,  $\phi = 180^\circ$ , to be most stable. Distortions of the Cp–Sm–Cp angle are not energetically costly, however. Reducing the angle from 180 to 130° requires only 0.06 eV, as none of the *d* levels are filled and the *f* orbitals are insensitive to environmental changes. Collapse of this angle below 120° is chiefly prevented by repulsions between the  $\pi$  levels of the individual Cp units. Recently (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm has been synthesized and its structure determined.<sup>7</sup> The ring centroid–Sm–ring centroid angle in this remarkable monomeric compound is 140.1°.

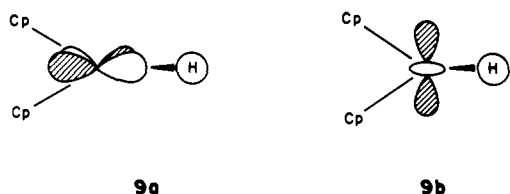
We are now ready to form some of the Cp<sub>2</sub>Ln hydrides.

### Cp<sub>2</sub>SmH and (Cp<sub>2</sub>SmH)<sub>2</sub>

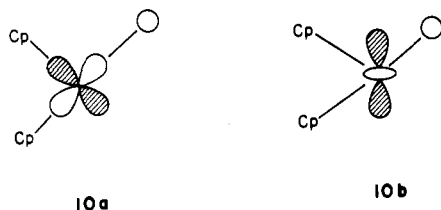
It is useful to begin by analyzing the preferred disposition of a single hydride relative to a single Cp<sub>2</sub>Sm unit. Consider the hypothetical Cp<sub>2</sub>SmH (8a), where H lies in the *yz* plane but not



along the *z* axis. Good H<sup>-</sup> to Cp<sub>2</sub>Sm<sup>+</sup> overlap populations from 1s to 1a<sub>1</sub> and 1s to 1b<sub>2</sub> stabilize the hydride. In the latter case, one of the lobes of *yz* interacts with the 1s orbital as in 9a. In

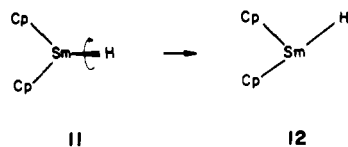


the former case, the 1s orbital sees the central, circular lobe of the *x*<sup>2</sup> orbital (9b). Suppose the hydride is rotated into the *xz* plane, as in 8b. The 1s to 1b<sub>1</sub> interaction then becomes important, as shown in 10a. The interaction with 1b<sub>2</sub> vanishes as the hydride



is in a nodal plane of this orbital. The 1s to 1a<sub>1</sub> interaction (10b) is diminished by this geometrical change since the hydride is starting to approach a nodal plane of 1a<sub>1</sub>.

The geometrical change described is 11 → 12. For this transit



the overlap population of 1s with 1a<sub>1</sub> will decline, with 1b<sub>2</sub> will decrease and vanish, and with 1b<sub>1</sub> will increase from zero. The net effect of 1b<sub>1</sub> and 1b<sub>2</sub> is very small, slightly favoring the final structure. The determining factor that causes the energy to rise for the transit is the fall of 1s to 1a<sub>1</sub> overlap population.

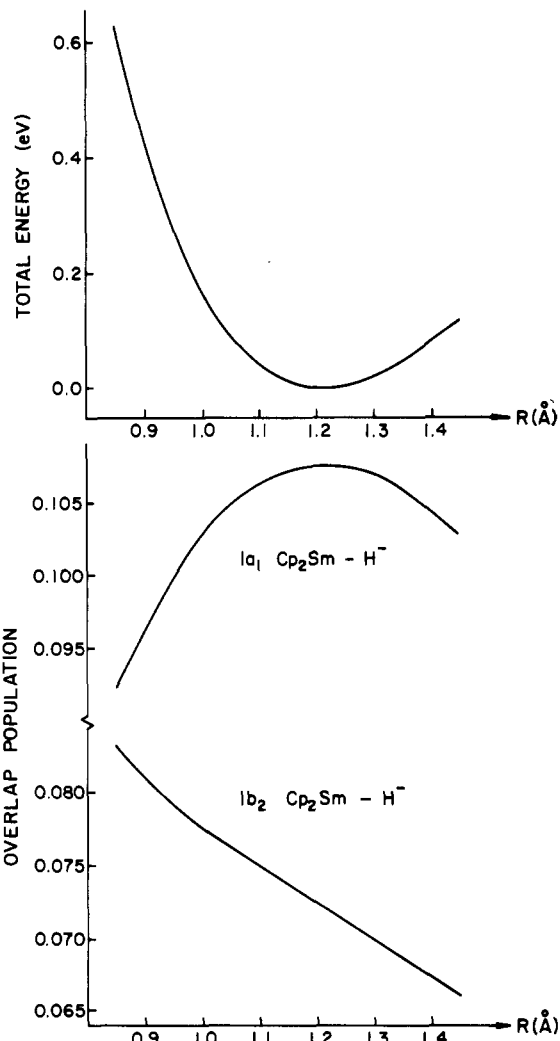
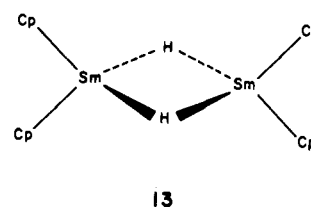
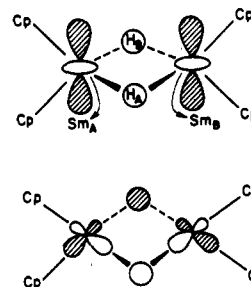


Figure 4.

Let us now consider the formation of a symmetrically bridged (Cp<sub>2</sub>SmH)<sub>2</sub> dimer, in the geometry of 13. One analysis of the



bonding might begin from 2 (Cp<sub>2</sub>Sm)<sup>+</sup> and 2 H<sup>-</sup>. The two hydride levels would form symmetric and antisymmetric combinations, and these in turn would be stabilized by mixing with the empty *d* orbitals of Cp<sub>2</sub>Sm<sup>+</sup>, primarily 1a<sub>1</sub> and 1b<sub>2</sub>. The resultant orbitals are shown schematically in 14.



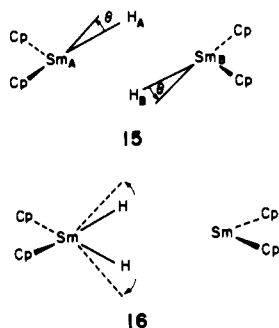
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(7) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* 1984, 106, 4270–2.

Calculations with  $\phi = 130^\circ$  and a Sm–Sm distance of 3.905 Å show the variation of total energy as the distance from the Sm–Sm midpoint for both hydrides,  $R$ , is changed (see Figure 4). The minimum, though shallow, reflects the competition of two dominant fragment overlap population curves, also shown in Figure 4. Largest of the hydride interactions is that with the  $1a_1$  d orbital, and the minimum of the energy curve nearly coincides with the maximum of this fragment overlap population. The  $2a_1$ –hydride interaction is much smaller.  $1b_2$  to hydride overlap populations are second in importance. They tend to shift the optimal Sm–H distance downward from the maximum suggested by the  $1a_1$ –hydride interaction alone.

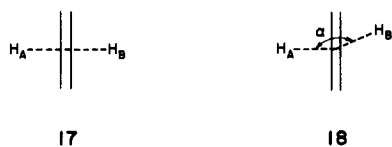
As the extended Hückel method is often unreliable in determining bond lengths, the particular structure obtained here should not be taken too seriously. The observation of geometrical trends is the object of the study. As these trends depend on the variation of overlap and on the relative energies of the fragment orbitals, the location of a particular minimum is not of decisive importance.

With use of the optimized symmetric structure as a reference, distortions of the hydrogens within the  $\text{Sm}_2\text{H}_2$  plane can be studied. For example, with fixed  $\text{Sm}_A\text{--H}_A$  and  $\text{Sm}_B\text{--H}_B$  distances, the angle  $\theta$  describes a motion that destroys one of the reflection planes in the molecule but not the inversion center (15). In other



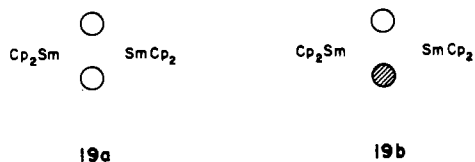
words, the hydrogen bridging is made asymmetrical. The computed energy rises as  $\theta$  is increased from the symmetric bridging position. However, we do not necessarily trust these results because the extended Hückel method is not very good at dealing with the bond length changes that would accompany such a deformation. A deformation that would lead to  $(\text{Cp}_2\text{SmH}_2)^-(\text{Cp}_2\text{Sm})^+$  ion pairs (16) was also tested, and there was resistance to it.

Distortions that destroy the  $\text{Sm}_2\text{H}_2$  plane are studied by variations in dihedral angles. In the reference structure, each  $\text{Sm}_2\text{H}$  plane forms a dihedral angle of  $90^\circ$  with the planes defined by the Sm atom and the centroids of the Cp ligands. This arrangement is symbolized by the diagram 17, where the two solid



lines stand for the Cp(centroid)–Sm–Cp(centroid) planes and the two dotted lines stand for the  $\text{Sm}_2\text{H}$  planes. The variation of the angle  $\alpha$ , defined in 18, from  $180^\circ$  destroys the  $\text{Sm}_2\text{H}_2$  plane but leaves the symmetric Sm–H–Sm bridges intact.  $\text{H}_A$  does not move from its original position; only  $\text{H}_B$  is affected by changing  $\alpha$ .

Resistance to the reduction of  $\alpha$  depends on two orbital energies (see Figure 5). The first crucial orbital has dominant contributions from the two hydride orbitals in symmetric combination (19a). This orbital mixes with  $\text{Cp}_2\text{Sm}^+$  orbitals of the  $a_1$  type.



The higher lying antisymmetric combination (19b) mixes with

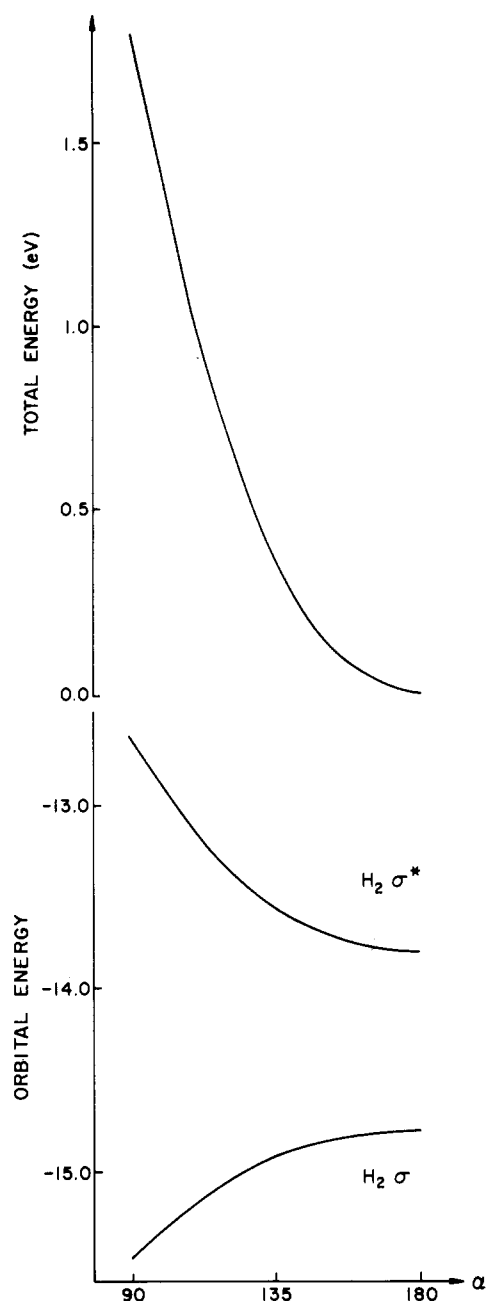
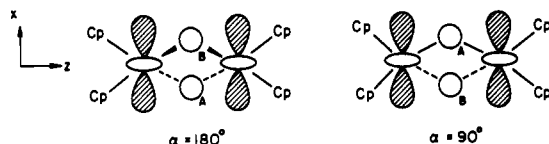


Figure 5.

$\text{Cp}_2\text{Sm}^+$  orbitals of  $b_2$  symmetry. Delocalization into the  $\text{SmCp}_2^+$  orbitals stabilizes both the  $\text{H}_2 \sigma$  and  $\sigma^*$  orbitals. As  $\alpha$  is varied, the two hydrides approach each other; the net effect is repulsive. Stabilization of the  $\text{H}_2 \sigma$  orbital is exceeded by destabilization of the  $\text{H}_2 \sigma^*$  orbital. Computed overlap populations between the hydrogen atoms indeed become more negative as  $\alpha$  decreases.

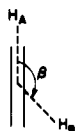
A decrease in  $\alpha$  also deprives the  $\text{H}_B$  orbital of overlap with the  $b_2$  orbitals of the  $\text{Cp}_2\text{Sm}^+$  fragments. Both of these effects could also be observed for an analogous distortion of diborane. The present system is distinct in that the  $\text{Cp}_2\text{Sm}^+$  fragment, unlike  $\text{BH}_2$ , has a low-lying empty  $b_1$  level. The loss of  $\text{H}_B\text{--}1b_2(\text{Cp}_2\text{Sm})$  overlap population is balanced by the increase in  $\text{H}_B\text{--}1b_1$  overlap population. The overall loss of  $\text{H}_B\text{--Cp}_2\text{Sm}$  overlap population may be traced to a decline in  $\text{H}_B\text{--}1a_1$  overlap (see Figure 6). At  $\alpha = 180^\circ$ , the  $\text{H}_B$  orbital overlaps with the central lobe of the  $x^2$  orbital, a principal constituent of the  $\text{Cp}_2\text{Sm}$   $1a_1$  fragment molecular orbital. As  $\alpha$  is reduced, the  $\text{H}_B$  orbital approaches the node of the  $x^2$  orbital (see 20). The  $\text{H}_B$  orbital originally interacts with the circular projection of the  $x^2$  orbital in the  $yz$  plane. At  $\alpha = 90^\circ$ ,  $\text{H}_B$  is in the  $xz$  plane and realizes much less overlap with  $x^2$ . Interactions with the  $2a_1$  orbital, which has large  $z^2 - y^2$



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contributions, run counter to the  $1a_1$  interactions, although the magnitudes of the overlap populations are not as large.  $H_B$  initially lies close to the node of the  $z^2 - y^2$  orbital. At  $\alpha = 90^\circ$ , the  $H_B$  orbital sees only the lobe along the  $z$  axis.

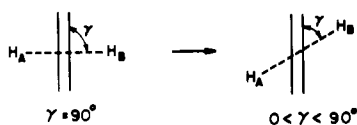
In the previous distortion, the  $H_2 \sigma^*$  destabilization and the overlap effects between  $H_B$  and the  $Cp_2Sm$  fragment orbitals favored the  $\alpha = 180^\circ$  structure. Should the stationary  $H_A$  atom be fixed in the  $Sm_2Cp_4$ (centroid) plane, however, as in 21, with



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$\beta$  the free dihedral angle, these two factors will work against each other.  $H_2 \sigma^*$  destabilization favors  $\beta = 180^\circ$ . Hydride to  $Cp_2Sm$  bonding favors  $\beta = 90^\circ$ . A compromise is computed to be reached at  $\beta = 135^\circ$ . As in the previous case, the  $1b_1$  and  $1b_2$  interactions with  $H_B$  move in opposite directions with the dihedral angle changes and approximately cancel each other's effect on the energy.

Now let us effect a twisting of dihedral angles without changing the distance between the hydrides. One way to do this is to keep the  $Sm_2H_2$  plane of the symmetrical structure but to vary its dihedral angle with the  $Sm_2Cp_4$ (centroid) plane (22). As  $\gamma$



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decreases, the energy rises (Figure 7) for the reasons that might have been surmised on the basis of the last two distortions. Overlap population with  $1a_1$  of the  $SmCp_2$  group declines with  $\gamma$ , but this trend is partially offset by the  $2a_1$  interaction. The rise of  $H-1b_1$  bonding balances the fall for  $H-1b_2$ .

In all the calculations of distortions, the  $Cp$ (centroid)- $Sm$ - $Cp$ (centroid) angle has been frozen at  $130^\circ$ . Variation of this angle will have some minor effects on the  $Cp_2Sm-H$  interactions. As the angle is compressed,  $1a_1$  will acquire more  $z^2$  character and will start to forsake its  $x^2$  origin.  $p_z$  contributions also increase as the angle is reduced. Therefore, the preference of the  $1a_1$  orbital for hydride in the plane perpendicular to  $Cp$ (centroid)- $Sm$ - $Cp$ (centroid) over hydride in the plane parallel will be reduced. To a  $z^2$  orbital mixed with  $p_z$ , such geometrical variations should not matter much. Similarly, as  $2a_1$  goes from being like  $z^2 - y^2$  to geometries where  $x^2 - y^2$  is a better description, the distinction between hydrides in the  $xz$  vs.  $yz$  planes should disappear.

Another geometrical variation that will be of interest later in this discussion is shown in 23-25. At all times the dihedral angle



23

24

25

between the two  $Sm_2H$  planes is  $90^\circ$ . The ordering of the energies is  $23 < 24 < 25$ ; no barriers to interconversion were discovered

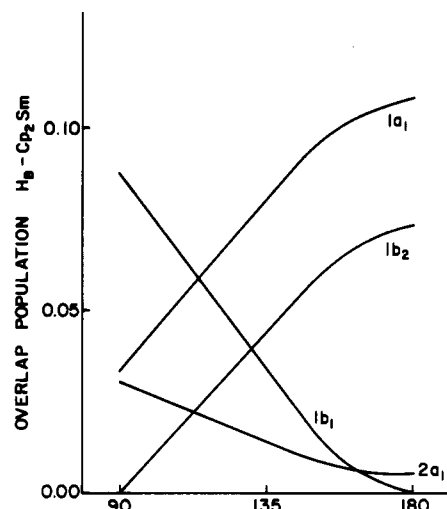


Figure 6.

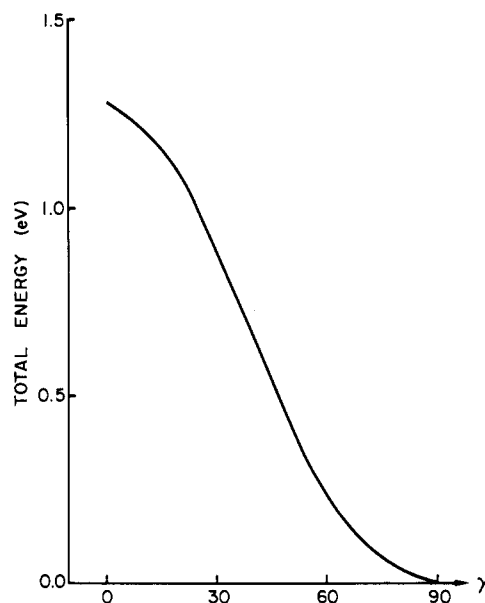


Figure 7.

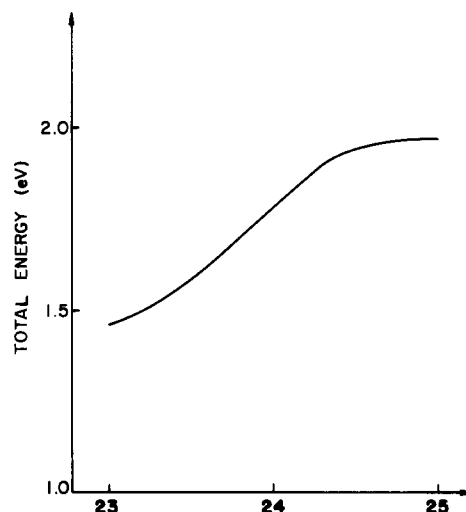
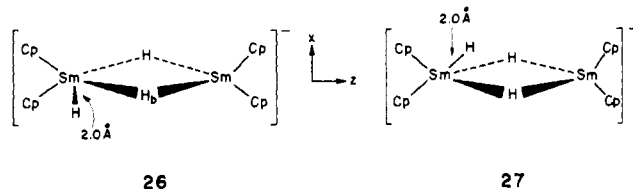


Figure 8.

(Figure 8). As might have been expected, the structure that most resembles the reference structure is favored. The dropoff of the  $H-Cp_2Sm$  bonding overall is sharpest when the  $Sm_2H$  dihedral angle with the  $Cp$ (centroid)- $Sm$ - $Cp$ (centroid) plane approaches  $0^\circ$ .

**Cp<sub>2</sub>Ln Tri- and Tetrahydrides**

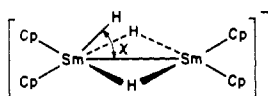
How might an additional hydride attach itself to the reference (Cp<sub>2</sub>SmH)<sub>2</sub> complex? The negligible participation of the 2a<sub>1</sub> and 1b<sub>1</sub> fragment MO's of Cp<sub>2</sub>Sm<sup>+</sup> in the binding of the two bridging hydrides suggests that two types of acceptor sites are available. The 2a<sub>1</sub> Cp<sub>2</sub>Sm orbital, primarily a z<sup>2</sup> - y<sup>2</sup> orbital, has a lobe pointing in the y direction. Calculations on (Cp<sub>2</sub>SmH)<sub>2</sub>H<sup>-</sup> place the extra hydride in the Sm<sub>2</sub>H<sub>2</sub> bridge (yz) plane, as in 26.



Overlap populations with the 1a<sub>1</sub> and 1b<sub>1</sub> orbitals of the nearby Cp<sub>2</sub>Sm<sup>+</sup> fragment are 0.05 and 0.01, respectively, but the chief source of the 0.42-eV binding energy relative to H<sup>-</sup> + (Cp<sub>2</sub>SmH)<sub>2</sub> is the extra hydride's overlap population with the 2a<sub>1</sub> orbital of 0.13. The terminal hydride to Sm bond length of 2.0 Å is taken from a similar Zr complex's structure;<sup>3</sup> the terminal hydride to Sm bond is parallel to the y axis. This extra hydride resists motion that alters the H<sub>t</sub>-Sm-H<sub>b</sub> angle of approximately 60°. Motions out of the yz plane result in rapid loss of overlap population with the 2a<sub>1</sub> Cp<sub>2</sub>Sm orbital. Repulsions with other ligands about the Sm, especially the bridging hydrides, and overlap with the Cp<sub>2</sub>Sm 2a<sub>1</sub> orbital determine the terminal hydride's position.

As was mentioned before, motion of the terminal hydride out of the yz plane produces a rise in energy due to loss of overlap with the 2a<sub>1</sub> Cp<sub>2</sub>Sm orbital. On the basis of the hope that the 1b<sub>1</sub> Cp<sub>2</sub>Sm orbital might come to the rescue, geometries of the type 27 were investigated. Unfortunately, with the Cp(centroid)-Sm-Cp(centroid) angle set to 130°, the terminal hydrogen atom comes uncomfortably close to the atoms of the Cp ring. Terminal hydrides that donate electron density to the 1b<sub>1</sub> Cp<sub>2</sub>Sm orbital are not feasible.

If the Sm-H<sub>t</sub> bond length is increased to 2.29 Å, the Sm-H<sub>b</sub> length obtained from previous calculations, more promising hypothetical structures result. With the hydride restricted to the Sm<sub>2</sub>Cp<sub>4</sub>(xz) plane, a structure (28) with the angle between the



28

Sm-H and Sm-Sm vectors,  $\chi$ , equal to about 45° was obtained. This suggested the placement of the extra hydride in a bridge position, equidistant from the two Sm atoms. The deployment of the hydrides is symbolized by 29. The total energy of this



29

30

structure is 1.9 eV above the (Cp<sub>2</sub>SmH)<sub>2</sub> + H<sup>-</sup> limit, due chiefly to the H<sub>A</sub>-H<sub>C</sub> distance of 1.70 Å. Noteworthy in this calculation is the 1b<sub>1</sub> Cp<sub>2</sub>Sm to H<sub>C</sub> overlap population of 0.11. Overall, the interaction of the H<sub>C</sub> hydride orbital with the symmetric combination of H<sub>A</sub> and H<sub>B</sub> (mixed with 1a<sub>1</sub> orbitals of the Cp<sub>2</sub>Sm fragments) is repulsive.

Suppose that this antagonism is alleviated somewhat by arranging the hydrides as in 30. The energy declines by 1.3 eV. The H<sub>A</sub>-H<sub>B</sub> overlap population climbs from -0.07 to -0.03; the 1a<sub>1</sub> to H<sub>C</sub> overlap population rises from -0.46 to 0.03. Repulsions between hydrides have been reduced. The 1b<sub>1</sub> Cp<sub>2</sub>Sm overlap population with H<sub>C</sub> goes from 0.12 to 0.11, an insignificant decline.

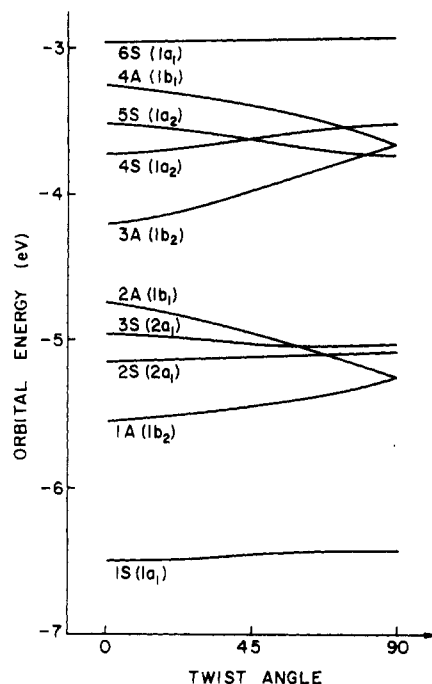
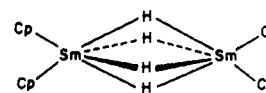


Figure 9.

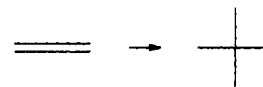
In summary, the placement of additional electron-pair donors on the symmetric (Cp<sub>2</sub>SmH)<sub>2</sub> complex may take advantage of two empty d-like orbitals on the Cp<sub>2</sub>Sm fragments. Terminal ligands in the Sm<sub>2</sub>H<sub>2</sub> plane donate to the 2a<sub>1</sub> orbital of Cp<sub>2</sub>Sm, and bridging ligands in the Sm<sub>2</sub>Cp<sub>4</sub> plane donate to the 1b<sub>1</sub> orbitals of the Cp<sub>2</sub>Sm fragment. In the latter case, a symmetric combination of the 1b<sub>1</sub> orbitals is available, so that one could imagine the addition of two hydrides to give a tetrabridged structure (31).



31

**Twisting the Cp<sub>2</sub>Sm Planes Relative to Each Other**

The previous calculations have maintained the coplanarity of the two Cp(centroid)<sub>2</sub>Sm planes. Let us now consider twisting one of the Cp(centroid)-Sm-Cp(centroid) planes so that the dihedral angle of this plane with its partner on the other Sm center becomes 90°, as indicated symbolically in 32. Suppose further



32

that the bridging hydrides are eliminated from the molecule, but with the remaining internuclear distances of (Cp<sub>2</sub>Sm)<sub>2</sub><sup>2+</sup> remaining intact. The twisting of the dihedral angle reduces repulsions between Cp rings. With a dihedral angle of 90°, the energy is about 0.8 kcal/mol (about 0.03 eV) lower than that of the original eclipsed structure.

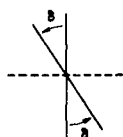
Effects of changing this dihedral angle on the d-orbital levels of (Cp<sub>2</sub>Sm)<sub>2</sub><sup>2+</sup> are summarized in the Walsh diagram of Figure 9. All of these energy levels are unoccupied, so their behavior has no effect on the total energy. The lowest level depicted in the diagram is a bonding combination of the two Cp<sub>2</sub>Sm<sup>+</sup> 1a<sub>1</sub> fragment MO's, the x<sup>2</sup>-like orbitals. Its energy rises slightly as the x axis of the one of the Cp<sub>2</sub>Sm<sup>+</sup> fragments forms a 90° angle with the x axis of the other Cp<sub>2</sub>Sm<sup>+</sup> fragment. The overlap integral steadily declines from 0.51 to 0.49.

The symmetry operation that is preserved throughout the variation of dihedral angle is the C<sub>2</sub> axis defined by the two Sm

atoms. The lowest levels classified as antisymmetric with respect to this operation are formed from the  $b_1$  and  $b_2$  fragment MO's of the Cp<sub>2</sub>Sm<sup>+</sup> fragments. When the dihedral angle reaches 90°, the levels become degenerate bonding combinations. A similar trend obtains for the antibonding combinations, 3A and 4A. Bonding and antibonding combinations of the Cp<sub>2</sub>Sm<sup>+</sup> 2a<sub>1</sub> fragment MO's (2S and 3S) have a small splitting due to an overlap integral that never exceeds 0.06. To the extent that donation to the 1S and 1A levels occurs, the preference for the twisted structure will be offset.

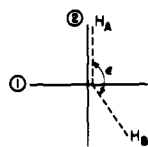
The degeneracy of the 1A and 2A levels at a 90° dihedral angle implies the existence of four equivalent bridging sites between the Sm atoms. The first two hydrides (or other  $\sigma$  electron pair donors) can be expected to occupy positions between the Sm atoms. Since the 2A level ends up below the 2S and 3S levels, extra hydrides may occupy the remaining bridging positions instead of the terminal positions. Splittings of the 1A, 2A, 2S, and 3S levels are smaller when the dihedral angle is 90°; fluxional behavior with respect to the hydride positions may obtain.

Suppose that the twisting of one of the Cp-Sm-Cp planes is repeated in the presence of the bridging hydrides. To represent this process, the dihedral angle  $\delta$  (33) is varied, where the solid



33

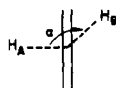
lines stand for Cp-Sm-Cp planes and the dotted line stands for the Sm<sub>2</sub>H<sub>2</sub> plane. Going from  $\delta = 0^\circ$ , the reference structure, to  $\delta = 90^\circ$  costs 0.6 eV. One can account for this rise with the orbitals of the (Cp<sub>2</sub>Sm)<sub>2</sub><sup>2+</sup> fragment, but we will not go through the argument here. With the dihedral angle between the Cp-Sm-Cp planes fixed at 90°, we can return to the question of the hydride positions. Hydrides equidistant from the Sm atoms form Sm-H-Sm planes. The variation of the dihedral angle of one such Sm-H-Sm plane with the Cp-Sm-Cp planes is represented by 34. The position of H<sub>A</sub> is fixed such that the Sm-H<sub>A</sub>-Sm plane



34

has dihedral angles with the first and second Cp-Sm-Cp planes of 90 and 0°, respectively. The Sm-H<sub>B</sub>-Sm plane forms a dihedral angle of  $\epsilon$  with the Sm-H<sub>A</sub>-Sm plane.

$\epsilon = 180^\circ$  gives the lowest energy, which is below that of the  $\epsilon = 90^\circ$  structure by 1.2 eV. This result is similar to what occurs for 35, a case we discussed earlier, where the energy difference



35

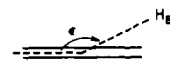
between the two corresponding structures is 1.8 eV. In the latter case, the H<sub>A</sub><sup>-</sup>H<sub>B</sub><sup>-</sup> repulsions are compounded by the preference of the Cp<sub>2</sub>Sm groups in the plane perpendicular to the Cp-Sm-Cp plane. When one of the Cp-Sm-Cp planes is twisted 90°, there are four more or less equivalent bridging positions. Therefore, as  $\alpha$  goes from 180 to 90°, losses in overlap population between H<sub>B</sub> and the first Cp<sub>2</sub>Sm fragment are partially compensated by gains in overlap population with the second Cp<sub>2</sub>Sm fragment. This leaves the repulsions between hydrides as the major obstacle to decreasing  $\alpha$ .

The structures represented by 36 are lower in energy than their



36

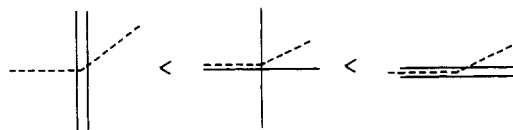
counterparts 37, but higher in energy than 35. A simple for-



37

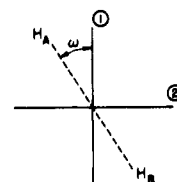
mulation of this ordering is that the hydrides prefer to be in Sm-H-Sm planes that are perpendicular to Cp-Sm-Cp planes. This trend holds for  $90^\circ < \epsilon < 180^\circ$ , but for  $\epsilon = 90^\circ$  the energies are approximately the same.

As usual, the main participants in bonding to the hydride bridges are 1a<sub>1</sub>, 1b<sub>1</sub>, and 1b<sub>2</sub> fragment MO's of the Cp<sub>2</sub>Sm units. When  $\alpha$  is varied from 180 to 90°, the first Cp<sub>2</sub>Sm 1b<sub>2</sub> overlap population with H<sub>B</sub> (see 34) goes from 0 to 0.087 and its partner fragment MO, 1b<sub>1</sub>, goes from 0.077 to 0. Similarly, for the second Cp<sub>2</sub>Sm 1b<sub>2</sub> to H<sub>B</sub> overlap population, the variation is from 0.082 to 0, while the 1b<sub>1</sub> overlap population goes from 0 to 0.081. In other words, the sums of all the Cp<sub>2</sub>Sm 1b<sub>1</sub> and 1b<sub>2</sub> fragment MO interactions with the hydrides remain nearly constant. The big changes occur in the Cp<sub>2</sub>Sm 1a<sub>1</sub> interactions with the hydrides. The second Cp<sub>2</sub>Sm 1a<sub>1</sub> overlap population goes from 0.11 to 0.02 from  $\alpha = 180^\circ$  to  $\alpha = 90^\circ$ , and the first Cp<sub>2</sub>Sm 1a<sub>1</sub> overlap population goes from 0.07 to 0.11. The x<sup>2</sup> character of this orbital suffices to explain the preference for  $\alpha = 180^\circ$  and the energy ordering of the three structures (38).



38

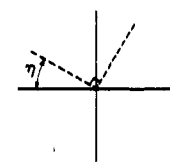
In a geometrical transit that freezes the distance between hydrides, the preferences of the fragment MO's are more ambiguous. Again, with the dihedral angle between the two Cp-Sm-Cp planes fixed at 90°, the Sm<sub>2</sub>H<sub>2</sub> quartet of atoms is locked in a plane. The dihedral angle of this plane with the Cp<sub>4</sub>Sm<sub>2</sub> frame,  $\omega$  (39),



39

is varied. The  $\omega = 45^\circ$  configuration is actually preferred to  $\omega = 0^\circ$  by about 0.09 eV. No overriding trends involving overlap populations or orbital energies emanate from these calculations. It suffices to say that, depending on the detailed balancing of electronic and steric factors, different values of  $\omega$  may be observed.

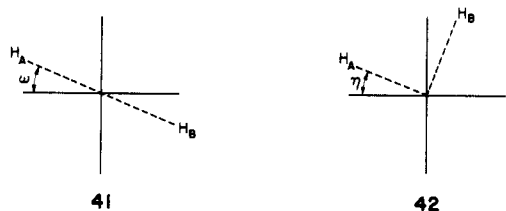
The equanimity of the Sm<sub>2</sub>Cp<sub>4</sub> framework toward Sm<sub>2</sub>H<sub>2</sub> plane rotations is continued when the Sm<sub>2</sub>H<sub>A</sub> planes have a dihedral angle of 90°, as in 40. This geometrical variation favors  $\eta = 45^\circ$



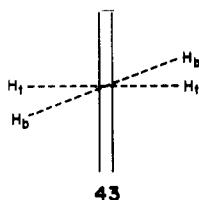
40

over  $\eta = 0^\circ$  by 0.09 eV. As in the previous case, there are no

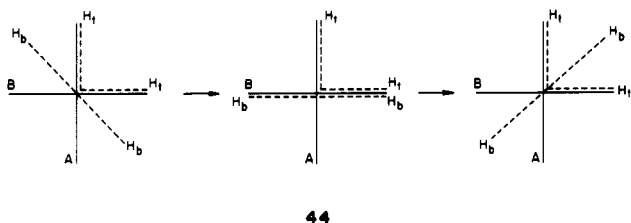
dominant trends that reflect a steadfast principle of bonding. One may expect that the structures with the  $90^\circ$  dihedral angle between the  $\text{Sm}_2\text{H}_A$  and  $\text{Sm}_2\text{H}_B$  planes will be unfavorable relative to those where the hydrides are more remote from each other. The energy difference between **41** and **42** is generally about 0.17 eV.



Similar arrangements of the bridging hydrides are expected when each Sm has a terminal hydride also. The terminal hydride demands the attention of the  $2a_1$  MO of each  $\text{Cp}_2\text{Sm}$  fragment. The action of the  $1a_1$ ,  $1b_1$ , and  $1b_2$  orbitals on bridging hydrides is undisturbed. At the same time, the repulsions between bridging and terminal hydrides will play a role in determining the geometry. For example, if the two  $\text{Cp}_2\text{Sm}$  planes are parallel, one expects the terminal hydrides to reside in a perpendicular plane. On the basis of the previous calculations, the bridging hydrides will lie in the same plane. A series of calculations in which the plane containing the bridging hydrides and the Sm atoms is allowed to rotate (**43**) produces a nonzero angle between the  $\text{Sm}_2(\text{H}_b)_2$  plane



and the  $\text{Sm}_2(\text{H}_t)_2$  plane. Repulsions between the bridging and terminal hydrides do play a part for these structures. In case the two  $\text{Cp}_2\text{Sm}$  planes are orthogonal, there are two structures that give a  $45^\circ$  dihedral angle for the  $\text{Sm}_2(\text{H}_b)_2$  plane. These differ in energy by a miniscule amount. A barrier to rotation of the plane between the two stable forms (**44**) amounts to 0.18 eV, the maximum energy occurring when the  $\text{Sm}_2(\text{H}_b)_2$  plane eclipses one of the  $\text{Cp}_2\text{Sm}$  planes.



### Moving across the Lanthanide Series

Experimentally one can usually produce a variety of organo-lanthanide species, so that it becomes interesting to outline the differences, if any, as one changes the element. There should be some variation in the diagonal matrix elements of the Hamiltonian, the  $H_{ii}$ 's. These energies are taken to be averages of the spin-orbital energies from Desclaux's relativistic atomic calculations.<sup>8</sup> Some of these numbers are given in Table I. The  $6p$  and  $7p$  parameters are chosen to be the same as the  $6s$  and  $7s$  parameters, respectively.  $f$ -orbital levels are ignored here, since in all applications undertaken for lanthanides so far, no chemical importance is attached to these orbitals. In the sixth period, one notices no great differences between La, Ce, and Hf. In going across the inner transition file, however, the  $6s$  and  $5d$  levels cross each other.  $H_{ss}$  is lower than  $H_{dd}$  in period 7 as well, except for Th.

The spatial extent of the atomic orbitals changes little within the lanthanide series, so a comparison between  $\text{SmCp}_2$  and  $\text{LuCp}_2$

Table I.  $H_{ii}$  Parameters (eV) for Inner Transition Elements

	La	Ce	Gd	Lu	Hf		
6s	-4.89	-4.97	-5.44	-6.05	-4.84		
5d	-6.41	-6.43	-6.06	-5.22	-6.56		
	Ac	Th	Pa	U	Np	Lw	104
7s	-5.19	-5.70	-5.41	-5.51	-5.60	-6.74	-6.75
6d	-4.79	-5.90	-5.08	-5.12	-5.11	-4.11	-4.11

Table II. Metal Atomic Orbital Contributions for  $\text{MCp}_2$  MO's

symmetry	energy, eV	electrons in AO's
		Lutetium
$1a_2$	-2.51	$1.80\ xz$
$1b_1$	-3.37	$1.67\ xy, 0.19\ x$
$2a_1$	-4.34	$0.62\ z^2, 0.95\ x^2 - y^2, 0.06\ z, 0.05\ s$
$1b_2$	-4.67	$1.07\ yz, 0.62\ y$
$1a_1$	-5.59	$0.69\ z, 0.68\ s, 0.33\ z^2, 0.29\ x^2 - y^2$
		Samarium
$1a_2$	-3.63	$1.90\ xz$
$1b_1$	-4.19	$1.9\ xy$
$2a_1$	-5.02	$0.70\ x^2 - y^2, 0.67\ z^2, 0.05\ z, 0.01\ s$
$1b_2$	-5.02	$1.9\ yz$
$1a_1$	-5.29	$0.62\ x^2 - y^2, 0.51\ z^2, 0.48\ s, 0.36\ z$

will tell us something about the chemical effects of the  $H_{ii}$  choices. With the  $\text{Cp-M-Cp}$  angle fixed at  $130^\circ$ , orbitals summarized in Table II result.  $H_{dd}$  being higher than  $H_{ss}$  and  $H_{pp}$  causes two main changes.  $1a_1$  is no longer  $x^2$ -like: its  $s$  and  $p_z$  character contribute to a lobe that points away from the Cp rings.  $2a_1$  of  $\text{LuCp}_2^+$  is more like a  $x^2 - y^2$  orbital and less like a  $y^2 - z^2$  orbital. Both fragments have  $b_2$  orbitals available for bonding.

In previous sections, we saw how the fragment MO's of  $\text{SmCp}_2^+$  bond with bridging hydrides as the hydride is twisted out of the  $yz$  plane and into the  $xz$  plane. The preferences of the  $b_1$  and  $b_2$  orbitals generally canceled each other out. Nodal properties of the  $x^2$ -like orbital,  $1a_1$ , proved decisive in explaining the reluctance of the hydrides to undergo such distortions. With the increased contributions of  $s$  and  $p_z$  in the  $1a_1$  orbital of  $\text{LuCp}_2^+$ , this trend may not be as important in determining the positions of bridging hydrides. Thus, the effect of changing the  $\text{Cp-M-Cp}$  angle may be reinforced or moderated by changes in the metal's atomic orbital energy levels.

### Model for the $\text{Cp}_6\text{Er}_3\text{H}_3\text{Cl}^-$ Trimer Hydride

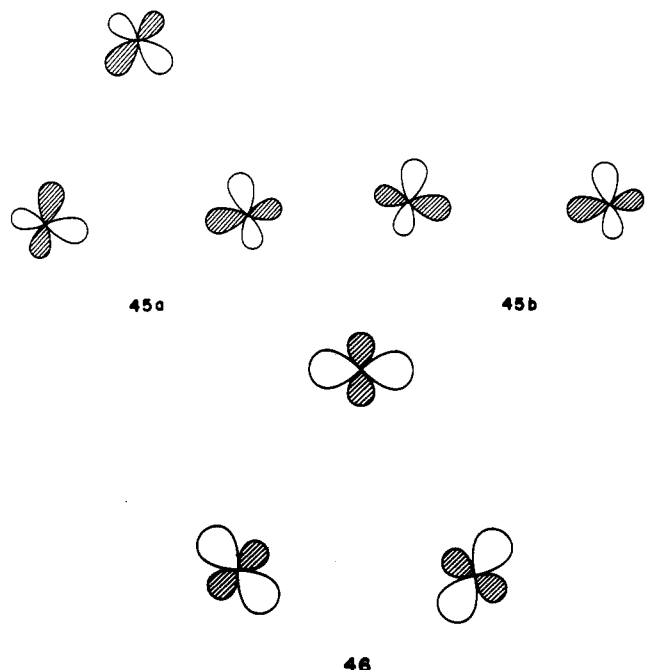
The molecule in question, an interesting lanthanide cluster hydride, is just a little too big for our computer programs. So we replaced  $\text{Cp}^-$  by three hydride anions, i.e. studied  $\text{LaH}_6^{3-}$  in place of  $\text{LaCp}_2^+$ . We also used the lutetium parameters as a better approximation to erbium than samarium, so that the calculation was on  $\text{LuH}_6^{3-}$ . Two equilateral triangles of hydrides (residing where the localized  $\pi$  orbitals of the Cp ring would be) are employed. Once again, the angle described by the centroid of one triangle, the metal atom, and the other centroid is  $130^\circ$ . Orbital energies are slightly lower than for  $\text{LuCp}_2^+$  (by between 0.2 and 1.0 eV), but the percentages of metal atomic orbital character are nearly the same.

Plots of the  $\text{LuH}_6^{3-}$  orbitals are shown in Figure 10. The  $yz$  plane, normal to the  $\text{H}_3(\text{centroid})\text{-Sm-H}_3(\text{centroid})$  plane, is depicted. The  $1a_1$  orbital is similar to the  $2a_1$  orbital of the  $\text{TiCp}_2^{2+}$  fragment.<sup>6</sup> This orbital has one lobe pointing away from the ligands with a slight dimple on the side near the ligands. The  $1b_2$  orbital is a combination of  $yz$  and  $p_y$  directed away from the ligands. Finally, the  $2a_1$  ligand's largest lobes lie along the  $y$  axis, with  $z^2$  combinations giving the central lobe the opposite sign.

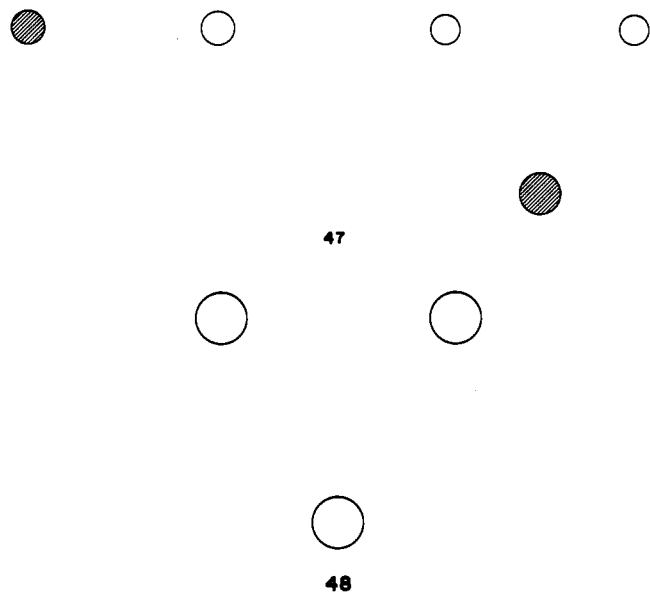
When the  $\text{LuH}_6^{3-}$  units are arranged in an equilateral triangle of sides 3.7 Å (between the Lu atoms),<sup>5</sup> the unoccupied  $d$  levels mix according to the scheme of Figure 11. The  $1a_1'$  level is a symmetric combination of the  $\text{LuH}_6^{3-}$   $1a_1$  levels and should be ideally suited for stabilizing an  $s$  orbital in the center of the triangle. Degenerate combinations of the  $1b_2$  orbitals of  $\text{LuH}_6^{3-}$  are next, shown in **45**. Next is the symmetric combination of  $\text{LuH}_6^{3-}$   $2a_1$  levels, the  $2a_1'$  orbital of the trimer (**46**). These are

(8) Desclaux, J. P. *At. Data Nucl. Data Tables* 1973, 12, 317-59.





the main actors in the interaction with the bridging hydride and chloride. Three such bridging groups, e.g. hydrides, would also give e and a<sub>1</sub> combinations 47 and 48. These are a nice match



for 45 and 46, respectively.

Calculations on (LuH<sub>6</sub>)<sub>3</sub>H<sub>4</sub><sup>13-</sup> corroborate this reasoning. The bridging hydrides are 2.4 Å from both the nearest Lu atoms. Dividing this molecule into three fragments, (LuH<sub>6</sub>)<sub>3</sub><sup>9-</sup>, H<sub>3</sub><sup>3-</sup>, and H<sup>-</sup>, allows overlap populations between the fragment MO's to be calculated. The central hydride orbital has an overlap population of 0.52 with 1a<sub>1</sub>' of (LuH<sub>6</sub>)<sub>3</sub><sup>9-</sup>, but only 0.11 with 2a<sub>1</sub>'. On the other hand, the 1a<sub>1</sub>' orbital of H<sub>3</sub><sup>3-</sup> has an overlap population of 0.32 with 2a<sub>1</sub>' of (LuH<sub>6</sub>)<sub>3</sub><sup>9-</sup> and only 0.12 with 1a<sub>1</sub>'. The mixing of the H<sub>3</sub><sup>3-</sup> and (LuH<sub>6</sub>)<sub>3</sub><sup>9-</sup> e sets gives overlap populations of 0.50 for each interaction. All other bonding interactions are negligible by comparison.

Now let us go from hydride bridges to chloride bridges. The Lu-Lu distance is increased to 3.9 Å and the Lu to bridging Cl<sup>-</sup> distance is 2.7 Å. In D<sub>3h</sub> symmetry, the central chloride's s and p<sub>z</sub> orbitals will transform according to the a<sub>1</sub>' and a<sub>2</sub>'' irreducible representations, respectively, while the p<sub>x</sub> and p<sub>y</sub> orbitals form a set of e' orbitals. The three bridging chlorides have s orbitals that form a<sub>1</sub>' and e' combinations. p<sub>z</sub> orbitals of these atoms become a<sub>2</sub>'' and e'' after symmetry projection. One can rotate the p<sub>x</sub> and p<sub>y</sub> orbitals on each chloride so that one p orbital points toward

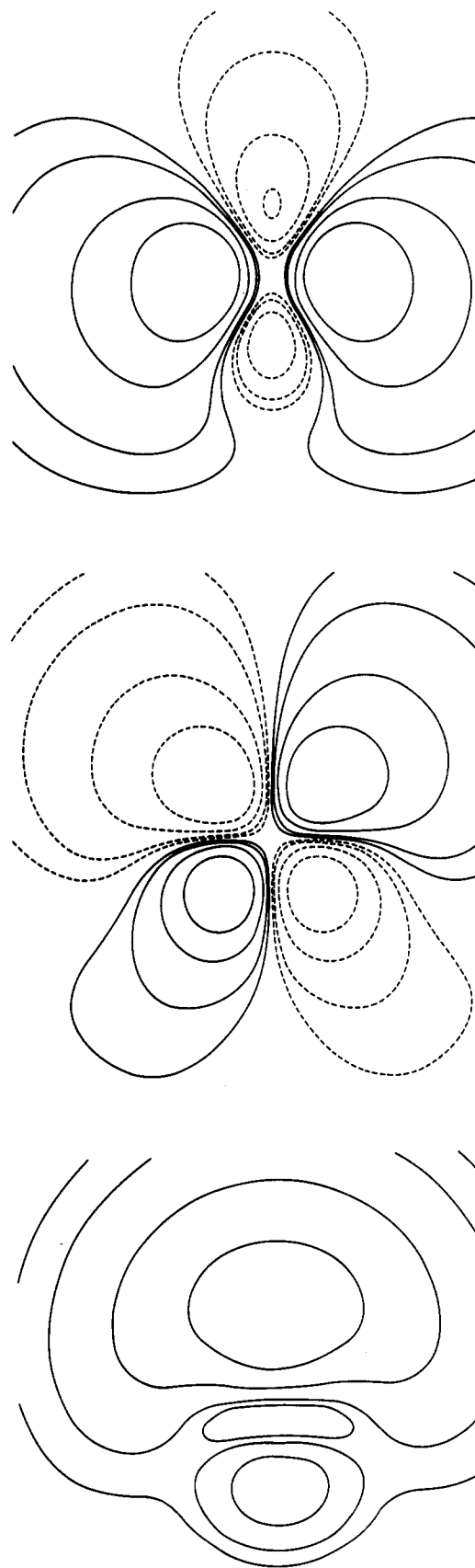
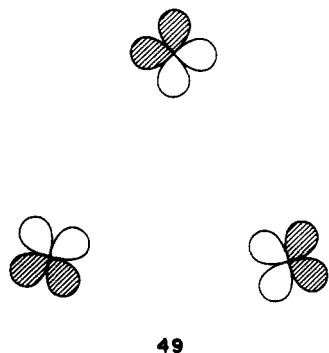
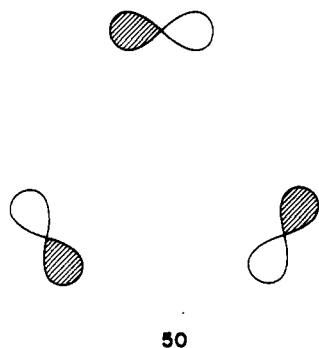


Figure 10. LuH<sub>6</sub><sup>3-</sup> orbital plots: (bottom) 1a<sub>1</sub>; (center) 1b<sub>2</sub>; (top) 2a<sub>1</sub>. All plots are in the yz plane.

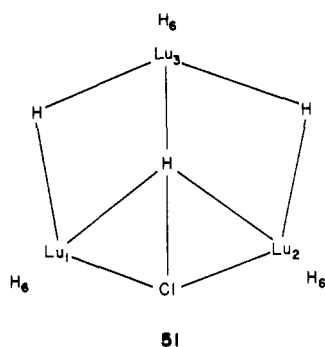
the centroid of the Cl<sub>3</sub><sup>3-</sup> triangle and the other p orbital is perpendicular to the line connecting the chloride to the centroid (49). Calling the former group the p<sub>c</sub> orbitals and the latter the p<sub>p</sub> orbitals, one easily sees the p<sub>c</sub> orbitals forming a<sub>1</sub>' and e' orbitals and the p<sub>p</sub> orbitals forming a<sub>2</sub>'' and e'' combinations.



An examination of the final overlap populations between the  $\text{Cl}^-$ ,  $\text{Cl}_3^{3-}$ , and  $(\text{LuH}_6)_3^{9-}$  fragments shows which interactions are most important. By far the biggest interaction is between the s orbital of the central chloride and the  $1a_1'$  orbital of  $(\text{LuH}_6)_3^{9-}$ . This overlap population of 0.41 is benefited partly by its closer Lu-Cl distance of 2.25 Å. Next in importance is the 0.29 overlap population obtained for the  $e'$  combination of the  $\text{Cl}_3^{3-}$  s orbitals interacting with the  $1e'$  orbital of  $(\text{LuH}_6)_3^{9-}$ .  $2a_1'$  and  $1a_2''$  of  $(\text{LuH}_6)_3^{9-}$  stabilize the  $a_1'$  combination of the bridging chlorides' s orbitals and the  $p_z$  orbital of the central chloride, respectively. These overlap populations are about 0.24. A surprisingly large overlap population of 0.25 occurs between the  $a_2'$  combination of the  $p_p$  orbitals and the very high lying  $a_2'$  combination of the  $\text{LuH}_6^{3-}$   $1b_1$  orbitals (50).



A crystal structure report on the anion  $(\text{ErCp}_2)_3\text{H}_3\text{Cl}^-$  shows little symmetry.<sup>5</sup> For the purpose of calculations, the  $C_{2v}$  model 51 is used. The chloride, central hydride, and top Lu atom define



the  $C_2$  axis. In the experimental structure, only the Lu-Lu distance seem to retain this symmetry. All of the other distances, especially those involving hydrides, are different from each other. Many calculations were done in an effort to expose the source of these apparent asymmetries. Unfortunately, none were discovered; the calculations support the  $C_{2v}$  hypothesis. The energy was lowered when the central hydride was slightly closer to the  $\text{Lu}_3$  atom than to the  $\text{Lu}_1$  and  $\text{Lu}_2$  atoms. The external hydrides could be moved closer to  $\text{Lu}_3$  without an energetic penalty. In fact, this probably is another instance of the calculations producing unreliable bond lengths. A similar effect obtained when these same hydrides were moved close to  $\text{Lu}_1$  and  $\text{Lu}_2$ . What is interesting, however, is the energy maximum that emerged when the bridging hydrides were placed on normals from the midpoints of the  $\text{Lu}_1\text{-Lu}_3$  and  $\text{Lu}_2\text{-Lu}_3$

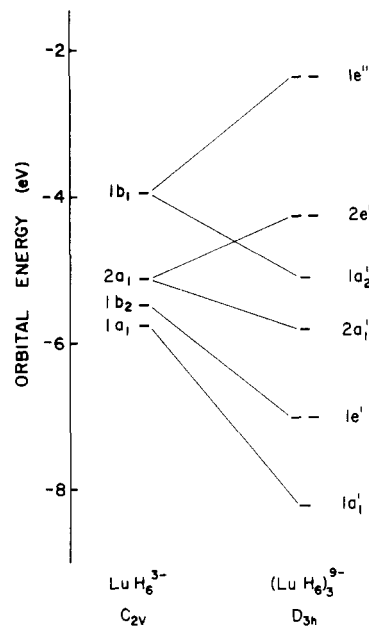


Figure 11.

Table III. Parameters Used in Extended Hückel Calculations<sup>a</sup>

orbital		$H_{ii}$ , eV	$\zeta_1$	$\zeta_2$	coeff 1	coeff 2
Sm	6s	-4.86	1.400			
	6p	-4.86	1.400			
	5d	-6.06	2.747	1.267	0.7184	0.4447
	4f	-11.28	6.907	2.639	0.7354	0.4597
Lu	6s	-6.05	1.666			
	6p	-6.05	1.666			
	5d	-5.12	2.813	1.210	0.7044	0.4880
	4f	-22.40	9.136	3.666	0.7330	0.4459
C	2s	-21.40	1.625			
	2p	-11.40	2.275			
H	1s	-13.60	1.300			

<sup>a</sup>The d and f orbitals are formed by a linear combination of two simple Slater functions.

bonds. These hydrides will sit on one side or the other, but not in the middle.

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#### Appendix

All calculations were performed by using the extended Hückel method<sup>9</sup> with weighted  $H_{ij}$ 's.<sup>10</sup> The extended Hückel parameters used in our calculations are listed in Table III. Parameters for Lu and Sm were obtained from the spin-orbital energies and expectation values of ref 8. An average over the spin components for each orbital energy was used to estimate the  $H_{ii}$  parameters. A similar average was taken for the value of  $r$  at which the orbital amplitude is a maximum, the expectation value of  $r$ , and the expectation value of  $r^2$ . All three of these values were used to choose the exponents and coefficients of the d and f orbitals; only the  $r$  expectation values figured in the  $\zeta$  values for s and p orbitals. Parameters for the 5d orbital of Sm were obtained by interpolation between the d orbitals of Ce and Gd.

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