Hydride Bridges between LnCp₂ Centers

J. V. ORTIZ*+1 and ROALD HOFFMANN1

Received September 12, 1984

Discrete organolanthanide hydride molecules have recently been synthesized. The hydrides form bridges between two or three metal atoms, but the geometry 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 perpendicular1 (2). The positions of the hydrogen bridges are unknown. Counting the Cp rings as anions and the bridging ligands as hydrides gives Ln³⁺.

For the lanthanides, this implies an atomic configuration of 5d⁶6s²⁶p⁴f. Compounds of the formula (Cp₂(THF)M(μ-H))₂, where M = Y, Er, Lu, also have structures with bridging hydrides and oxygen ligands that lie within or close to the M₂H₂ plane6 (3). The oxidation state remains 3+. Related structures with Zr instead of lanthanides replace the oxygen ligands with more hydrides, moving to a Zr⁵⁺ 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 M₂H₂ plane in (Cp₅ThH(μ-H))₄ (4). A trinuclear system, (Cp₂ErH)₂Cl⁻ (5), has also emerged from these studies. Two distinct types of bridging, between two or three centers, are observed in this Er(III) complex.5 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 Cp₅Sm Fragment and Its Relationship to Corresponding Transition-Metal Fragments

The lanthanide hydride complexes that we have mentioned all contain a d⁶ Cp₅Ln⁺ fragment, which then forms a natural starting point for our theoretical discussion. Let us examine the orbitals of the Cp₅Sm⁺ 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 SmCp₅⁺ 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 H₁₁ being approximately 0.1 eV. Hybridizations with the p, s, and d orbitals of Sm are therefore very small. The remaining levels are all unoccupied. Combinations of Cp π*(ε₂) levels lie between the Sm d and f orbitals. These interact little with further ligands and will not concern us further.

At the D₆h sandwich geometry (φ = 180°) the orbitals split into a typical pattern, a₁g < e₂g < e₁u. There is a tricky problem with the coordinate systems here. The natural choice for the x axis

---

1 University of New Mexico.
1 Cornell University.

---

in the $D_{5h}$ structure would be the fivefold axis. But the moment $\phi$ decreases from 180°, 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 Figure 2 shows. Thus the fivefold axis is $x$ and the orbitals that we would have called $z\sigma$ ($a_{1g}$), $x\pi$-$y\pi$, $xy$ ($e_{1u}$), and $xz$, $yz$ ($e_{2g}$) had we had $z$ as the fivefold axis now become $x^2$ ($a_{1g}$), $y^2$ - $z^2$, $y\pi$ ($e_{1u}$), and $xy$, $xz$ ($e_{2g}$). As $\phi$ is varied, the degeneracies are removed. The two highest d levels, labeled $a_{2g}$ 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 $\phi = 180°$ case. Finally, there is the lowest $a_1$ d orbital, which correlates with $x^2$ in the $\phi = 180°$ case. As $\phi$ decreases, the lowest orbital is gradually transformed, at small $\phi$, into a mix of $s$, $x$, 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 $\phi$. 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 $\phi = 130°$, 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$_2$Ti, a typical transition-metal analogue, and the lanthanide. In reference to our earlier work, in Cp$_2$Ti 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$_2$Sm 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$_2$Ti and Cp$_2$Sm at the same $\phi$, the Cp$_2$Sm levels are much more like those at $\phi = 180°$ 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.

The energy differences between the d orbitals are much smaller than in the case of TiCp$_2$. 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 $\phi$ decreases from 180°.

Figure 1.

Figure 2.

Figure 3. SmCp$_2$ orbital plots: (bottom row) 1a$_1$; (top row) 2a$_1$; (left column) $xz$ plane; (right column) $yz$ plane.

---

7

The energy differences between the d orbitals are much smaller than in the case of TiCp$_2$. 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 $\phi$ decreases from 180°.

---

Hydride Bridges between LnCp₂ Centers decreases. Donors approaching the xz plane might employ this acceptor orbital.

Calculations on the Cp₂Sm molecule predict an ordinary sandwich arrangement, φ = 180°, 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 x orbitals of the individual Cp units. Recently (C₅Me₅)₂Sm has been synthesized and its structure determined. The ring centroid–Sm–ring centroid angle in this remarkable monomeric compound is 140.1°.

We are now ready to form some of the Cp₂Ln hydrides.

Cp₂SmH and (Cp₂SmH)₂

It is useful to begin by analyzing the preferred disposition of a single hydride relative to a single Cp₂Sm unit. Consider the hypothetical Cp₂SmH (8a), where H lies in the yz plane but not along the z axis. Good H⁻ to Cp₂Sm⁺ overlap populations from 1s to 1a₁ and 1s to 1b₂ 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 x² orbital (9b). Suppose the hydride is rotated into the xz plane, as in 8b. The 1s to 1b₁ interaction then becomes important, as shown in 10a. The interaction with 1b₂ vanishes as the hydride is in a nodal plane of this orbital. The 1s to 1a₁ interaction (10b) is diminished by this geometrical change since the hydride is starting to approach a nodal plane of 1a₁.

The geometrical change described is 11 → 12. For this transit the overlap population of 1s with 1a₁ will decline, with 1b₁ will decrease and vanish, and with 1b₂ will increase from zero. The net effect of 1b₁ and 1b₂ 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 1a₁ overlap population.

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 $1a_1$ 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 hydrides within the Sm$_2$H$_2$ plane can be studied. For example, with fixed Sm$_A$–H$_A$ and Sm$_B$–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 (Cp$_2$SmH$_2$)$^+$ (Cp$_2$Sm)$^+$ ion pairs (16) was also tested, and there was resistance to it.

Distortions that destroy the Sm$_2$H$_2$ plane are studied by variations in dihedral angles. In the reference structure, each Sm–H plane forms a dihedral angle of 90° 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 Sm$_2$H planes. The variation of the angle $\alpha$, defined in 18, from 180° destroys the Sm$_2$H$_2$ plane but leaves the symmetric Sm–H–Sm bridges intact. H$_B$ does not move from its original position; only H$_A$ 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 Cp$_2$Sm$^+$ orbitals of the $a_1$ type.

The higher lying antisymmetric combination (19b) mixes with Cp$_3$Sm$^+$ orbitals of $b_1$ symmetry. Delocalization into the SmCp$_3$$^+$ orbitals stabilizes both the H$_2$ $\sigma$ and $\sigma^*$ orbitals. As $\alpha$ is varied, the two hydrides approach each other; the net effect is repulsive. Stabilization of the H$_2$ $\sigma$ orbital is exceeded by destabilization of the 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 H$_B$ orbital of overlap with the $b_1$ orbitals of the Cp$_2$Sm$^+$ fragments. Both of these effects could also be observed for an analogous distortion of diborane. The present system is distinct in that the Cp$_3$Sm$^+$ fragment, unlike BH$_2$, has a low-lying empty $b_1$ level. The loss of H$_B$–$b_1$(Cp$_2$Sm) overlap population is balanced by the increase in H$_A$–$b_1$ overlap population. The overall loss of H$_B$–Cp$_2$Sm overlap population may be traced to a decline in H$_B$–$1a_1$(SmCp$_3$) overlap (see Figure 6). At $\alpha = 180^\circ$, the H$_B$ orbital overlaps with the central lobe of the $x^2$ orbital, a principal constituent of the Cp$_2$Sm $1a_1$ fragment molecular orbital. As $\alpha$ is reduced, the H$_B$ orbital approaches the node of the $x^2$ orbital (see 20). The H$_B$ orbital originally interacts with the circular projection of the $x^2$ orbital in the $yz$ plane. At $\alpha = 90^\circ$, H$_B$ is in the $xz$ plane and realizes much less overlap with $x^2$. Interactions with the $2a_1$ orbital, which has large $z^2 - y^2$...
Hydride Bridges between LnCp₂ Centers

contributions, run counter to the 1a₁ interactions, although the magnitudes of the overlap populations are not as large. H₆ initially lies close to the node of the z² - y² orbital. At α = 90°, the H₆ orbital sees only the lobe along the z axis.

In the previous distortion, the H₂ σ⁺ destabilization and the overlap effects between H₆ and the Cp₂Sm fragment orbitals favored the α = 180° structure. Should the stationary H₆ atom be fixed in the Sm₂Cp₄(centroid) plane, however, as in 21, with β the free dihedral angle, these two factors will work against each other. H₂ σ⁺ destabilization favors β = 180°. Hydride to Cp₂Sm bonding favors β = 90°. A compromise is computed to be reached at β = 135°. As in the previous case, the 1b₁ and 1b₂ interactions with H₆ 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 Sm₂H₂ plane of the symmetrical structure but to vary its dihedral angle with the Sm₂Cp₄(centroid) plane (22). As γ 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 1a₁ of the SmCp₂ group declines with γ, but this trend is partially offset by the 2a₁ interaction. The rise of H-1b₁ bonding balances the fall for H-1b₂.

In all the calculations of distortions, the Cp(centroid)–Sm–Cp(centroid) angle has been frozen at 130°. Variation of this angle will have some minor effects on the Cp₂Sm–H interactions. As the angle is compressed, 1a₁ will acquire more z² character and will start to forsake its x² origin. pₓ contributions also increase as the angle is reduced. Therefore, the preference of the 1a₁ orbital for hydride in the plane perpendicular to Cp(centroid)–Sm–Cp(centroid) over hydride in the plane parallel will be reduced. To a z² orbital mixed with pₓ such geometrical variations should not matter much. Similarly, as 2a₁ goes from being like z² - y² to geometries where x² - y² is a better description, the distinction between hydrides in the xy 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 between the two Sm₂H planes is 90°. The ordering of the energies is 23 < 24 < 25; no barriers to interconversion were discovered.

(Figure 8). As might have been expected, the structure that most resembles the reference structure is favored. The dropoff of the H–Cp₂Sm bonding overall is sharpest when the Sm₂H dihedral angle with the Cp(centroid)–Sm–Cp(centroid) plane approaches 0°.
Cp₂Ln Tri- and Tetrarhydrates

How might an additional hydride attach itself to the reference (Cp₂SmH)₂ complex? The negligible participation of the 2a₁ and 1b₁ fragment MO's of Cp₂Sm⁺ in the binding of the two bridging hydrides suggests that two types of acceptor sites are available. The 2a₁, Cp₂Sm orbital, primarily a z² - y² orbital, has a lobe pointing in the y direction. Calculations on (Cp₂SmH)₂⁺ place the extra hydride in the Sm₂H₂ bridge (y₂) plane, as in 26.

Overlap populations with the 1a₁ and 1b₁ orbitals of the nearby Cp₂Sm⁺ fragment are 0.05 and 0.01, respectively, but the chief source of the 0.42-eV binding energy relative to H⁺ + (Cp₂SmH)₂ is the extra hydride's overlap population with the 2a₁ orbital of 0.13. The terminal hydride to Sm bond length of 2.0 Å is taken from a similar Zr complex's structure; the terminal hydride to Sm bond is parallel to the y axis. This extra hydride resists motion that alters the H₆-Sm-H₆ angle of approximately 60°. Motions out of the yz plane result in rapid loss of overlap population with the 2a₁ Cp₂Sm orbital. Repulsions with other ligands about the Sm, especially the bridging hydrides, and overlap with the Cp₂Sm 2a₁ 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 2a₁ Cp₂Sm orbital. On the basis of the hope that the 1b₁ Cp₂Sm 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 1b₁, Cp₂Sm orbital are not feasible.

If the Sm-H₆ bond length is increased to 2.29 Å, the Sm-H₆ length obtained from previous calculations, more promising hypothetical structures result. With the hydride restricted to the Sm₂Cp₄ (xz) plane, a structure (28) with the angle between the Sm-H and Sm-Sm vectors, χ₁, 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 structure is 1.9 eV above the (Cp₂SmH)₂⁺ limit, due chiefly to the H₆-H₆ distance of 1.70 Å. Noteworthy in this calculation is the 1b₁ Cp₂Sm to H₆ overlap population of 0.11. Overall, the interaction of the H₆ hydride orbital with the symmetric combination of H₆ and H₆ (mixed with 1a₁ orbitals of the Cp₂Sm 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 H₆-H₆ overlap population climbs from -0.07 to 0.03; the 1a₁ to H₆ overlap population rises from -0.46 to 0.03. Repulsions between hydrides have been reduced. The 1b₁ Cp₂Sm overlap population with H₆ goes from 0.12 to 0.11, an insignificant decline. That the bridging hydrides are eliminated from the molecule, but with the remaining internuclear distances of (Cp₂Sm)₂⁺ 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 (Cp₂Sm)₂⁺ 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 Cp₂Sm⁺ 1a₁ fragment MO's, the x²-like orbitals. Its energy rises slightly as the x axis of the one of the Cp₂Sm⁺ fragments forms a 90° angle with the x axis of the other Cp₂Sm⁺ 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 C₂ axis defined by the two Sm
Hydride Bridges between LnCp, Centers

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 Sm2H2 quartet of atoms is locked in a plane. The dihedral angle of this plane with the Cp2Sm frame, ω (39), is varied. The ω = 45° configuration is actually preferred to ω = 0° 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 ω may be observed.

The equanimity of the Sm3Cp3 framework toward Sm2H2 plane rotations is continued when the Sm2Hα planes have a dihedral angle of 90°, as in 40. This geometrical variation favors η = 45° over η = 0° by 0.09 eV. As in the previous case, there are no

The structures represented by 36 are lower in energy than their counterparts 37, but higher in energy than 35. A simple for...

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° < ϵ < 180°, but for ϵ = 90° the energies are approximately the same.

As usual, the main participants in bonding to the hydride bridges are 1a1, 1b1, and 1b2 fragment MO's of the Cp2Sm units. When α is varied from 180 to 90°, the first Cp2Sm 1b2 overlap population with Hα (see 34) goes from 0 to 0.087 and its partner fragment MO, 1b1, goes from 0.077 to 0. Similarly, for the second Cp2Sm 1b2 to Hα overlap population, the variation is from 0.082 to 0, while the 1b1 overlap population goes from 0 to 0.81. In other words, the sums of all the Cp2Sm 1b2 and 1b1 fragment MO interactions with the hydrides remain nearly constant. The big changes occur in the Cp2Sm 1a1 interactions with the hydrides. The second Cp2Sm 1a1 overlap population goes from 0.11 to 0.02 from α = 180° to α = 90°, and the first Cp2Sm 1a1 overlap population goes from 0.07 to 0.11. The χ2 character of this orbital suffices to explain the preference for α = 180° and the energy ordering of the three structures (38).

In a geometrical transit that freezes the distance between hydrides, the reference structure, to δ = 90° costs 0.6 eV. One can account for this rise with 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 Hα is fixed such that the Sm–Hα–Sm plane has dihedral angles with the first and second Cp–Sm–Cp planes of 90 and 0°, respectively. The Sm–Hβ–Sm plane forms a dihedral angle of ϵ with the Sm–Hα–Sm plane.

ϵ = 180° gives the lowest energy, which is below that of the ϵ = 90° structure by 1.2 eV. This result is similar to what occurs for 35, a case we discussed earlier, where the energy difference between the two corresponding structures is 1.8 eV. In the latter case, the Hα·Hα repulsions are compounded by the preference of the Cp–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 α goes from 180 to 90°, losses in overlap population between Hα and the first Cp–Sm fragment are partially compensated by gains in overlap population with the second Cp–Sm fragment. This leaves the repulsions between hydrides as the major obstacle to decreasing α.

The lowest levels classified as antisymmetric with respect to this operation are formed from the b1, and b2 fragment MO's of the Cp2Sm+ 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 Cp2Sm+ 2a1, 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 σ 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 δ (33) is varied, where the solid lines stand for Cp–Sm–Cp planes and the dotted line stands for the Sm2H2 plane. Going from δ = 0°, the reference structure, to δ = 90° costs 0.6 eV. One can account for this rise with 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 Hα is fixed such that the Sm–Hα–Sm plane has dihedral angles with the first and second Cp–Sm–Cp planes of 90 and 0°, respectively. The Sm–Hβ–Sm plane forms a dihedral angle of ϵ with the Sm–Hα–Sm plane.

ϵ = 180° gives the lowest energy, which is below that of the ϵ = 90° structure by 1.2 eV. This result is similar to what occurs for 35, a case we discussed earlier, where the energy difference between the two corresponding structures is 1.8 eV. In the latter case, the Hα·Hα repulsions are compounded by the preference of the Cp–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 α goes from 180 to 90°, losses in overlap population between Hα and the first Cp–Sm fragment are partially compensated by gains in overlap population with the second Cp–Sm fragment. This leaves the repulsions between hydrides as the major obstacle to decreasing α.
dominant trends that reflect a steadfast principle of bonding. One may expect that the structures with the 90° dihedral angle between the Sm₃H₆ and Sm₃H₆ 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 2a₁ MO of each Cp₂Sm fragment. The action of the 1a₁, 1b₁, and 1b₂ 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 Cp₂Sm 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 Sm₃(H₆)₂ plane and the Sm₃(H₆)₂ plane. Repulsions between the bridging and terminal hydrides do play a part for these structures. In case the two Cp₂Sm planes are orthogonal, there are two structures that give a 45° dihedral angle for the Sm₃(H₆)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 Sm₃(H₆)₂ plane eclipses one of the Cp₂Sm planes.

Moving across the Lanthanide Series

Experimentally one can usually produce a variety of organolanthanide 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. 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. $H_{6s}$ is lower than $H_{5d}$ 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 SmCp₂ and LuCp₂

<table>
<thead>
<tr>
<th>Period</th>
<th>La</th>
<th>Ce</th>
<th>Gd</th>
<th>Lu</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>5s</td>
<td>4.09</td>
<td>4.97</td>
<td>5.44</td>
<td>6.05</td>
<td>4.84</td>
</tr>
<tr>
<td>5d</td>
<td>6.41</td>
<td>6.43</td>
<td>6.06</td>
<td>5.22</td>
<td>6.56</td>
</tr>
</tbody>
</table>

Table I. H₉ Parameters (eV) for Inner Transition Elements

Table II. Metal Atomic Orbital Contributions for MCCp₂ MO's

```markdown
<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Energy, eV</th>
<th>Electrons in AO's</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a₁</td>
<td>-2.51</td>
<td>1.80 xz</td>
</tr>
<tr>
<td>1b₁</td>
<td>-3.37</td>
<td>1.67 xy, 0.19 x</td>
</tr>
<tr>
<td>2a₁</td>
<td>-4.34</td>
<td>0.62 z², 0.95 x² - y², 0.06 x, 0.05 s</td>
</tr>
<tr>
<td>1b₂</td>
<td>-4.07</td>
<td>0.67 yz, 0.62 y</td>
</tr>
<tr>
<td>1a₁</td>
<td>-5.39</td>
<td>0.69 z, 0.68 s, 0.33 z², 0.29 x² - y²</td>
</tr>
<tr>
<td>2a₁</td>
<td>-5.02</td>
<td>0.70 x² - y², 0.67 x², 0.05 x, 0.01 s</td>
</tr>
<tr>
<td>1b₂</td>
<td>-5.02</td>
<td>1.9 yz, 0.19 y</td>
</tr>
<tr>
<td>1a₁</td>
<td>-5.29</td>
<td>0.62 x² - y², 0.51 z², 0.48 s, 0.36 z</td>
</tr>
</tbody>
</table>
```

will tell us something about the chemical effects of the H₉ choices. With the Cₚ-M-Cₚ angle fixed at 130°, orbitals summarized in Table II result. H₉b being higher than H₉a and H₉d causes two main changes. 1a₁ is no longer x²-like: its s and p character contribute to a lobe that points away from the Cp rings. 2a₁ of LuCp⁺ is more like a x² - y² orbital and less like a x² - z² orbital. Both fragments have b₁ orbital available for bonding. In previous sections, we saw how the fragment MO's of SmCp₂⁺ bond with bridging hydrides as the hydride is twisted out of the xy plane and into the xz plane. The preferences of the b₁ and b₂ orbitals generally cancel each other out. Nodal properties of the x²-like orbital, 1a₁, proved decisive in explaining the reluctance of the hydrides to undergo such distortions. With the increased contributions of s and p in the 1a₁ orbital of LuCp⁺, this trend may not be so important in determining the positions of bridging hydrides. Thus, the effect of changing the Cₚ-M-Cₚ angle may be reinforced or moderated by changes in the metal's atomic orbital energy levels.

Model for the Cₚ₅Er₃H₆Cl Trimer Hydride

The molecule in question, an interesting lanthanide cluster hydride, is just a little too big for our computer programs. So we replaced Cₚ by three hydride anions, i.e. studied LaH₆⁻ in place of LaCp₂⁺. We also used the lutetium parameters as a better approximation to erbium than samarium, so that the calculation was on LuH₆⁻. Two equilateral triangles of hydrides (residing where the localized x 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°. Orbital energies are slightly lower than for LuCp⁺ (by between 0.2 and 1.0 eV), but the percentages of metal atomic orbital character are nearly the same.

Plots of the LuH₆⁻ orbitals are shown in Figure 10. The yz plane, normal to the H₃(cen)₃-Sm-H₃(cen)₃ plane, is depicted. The 1a₁ orbital is similar to the 2a₁ orbital of the TcCp₂⁺ fragment. This orbital has one lobe pointing away from the ligands with a slight dimple on the side near the ligands. The 1b₂ orbital is a combination of yz and p₁ directed away from the ligands. Finally, the 2a₁ ligand's largest lobes lie along the x axis, with x² combinations giving the central lobe the opposite sign. When the LuH₆⁻ units are arranged in an equilateral triangle of sides 3.7 Å (between the Lu atoms), the unoccupied d levels mix according to the scheme of Figure 11. The 1a₁' level is a symmetric combination of the LuH₆⁻ 1a₁ levels and should be ideally suited for stabilizing an s orbital in the center of the triangle. Degenerate combinations of the 1b₂ orbitals of LuH₆⁻ are next, shown in 45. Next is the symmetric combination of LuH₆⁻ 2a₁ levels, the 2a₁' orbital of the trimer (46). These are

Hydride Bridges between LnCp$_2$ Centers

the main actors in the interaction with the bridging hydride and chloride. Three such bridging groups, e.g., hydrides, would also give $e$ and $a_1$ combinations 47 and 48. These are a nice match for 45 and 46, respectively.

Calculations on (LuH$_2$)$_3$H$_2^-$ corroborate this reasoning. The bridging hydrides are 2.4 Å from both the nearest Lu atoms. Dividing this molecule into three fragments, (LuH$_2$)$_3^{2-}$, H$_3^-$, and H$,^-$, allows overlap populations between the fragment MO's to be calculated. The central hydride orbital has an overlap population of 0.52 with 1a$_1'$ of (LuH$_2$)$_3^{2-}$, but only 0.11 with 2a$_1'$. On the other hand, the 1a$_1'$ orbital of H$_3^-$ has an overlap population of 0.32 with 2a$_1'$ of (LuH$_2$)$_3^{2-}$ and only 0.12 with 1a$_1'$. The mixing of the H$_3^-$ and (LuH$_2$)$_3^{2-}$ 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$^-$ distance is 2.7 Å. In $D_{3h}$ symmetry, the central chloride's s and p$_z$ orbitals will transform according to the $a_1'$ and $a_2''$ irreducible representations, respectively, while the p$_x$ and p$_y$ orbitals form a set of $e'$ orbitals. The three bridging chlorides have s orbitals that form $a_1'$ and $e'$ combinations. p$_z$ orbitals of these atoms become $a_2''$ and $e''$ after symmetry projection. One can rotate the p$_z$ and p$_y$ orbitals on each chloride so that one p orbital points toward the centroid of the Cl$_3^{2-}$ triangle and the other p orbital is perpendicular to the line connecting the chloride to the centroid (49). Calling the former group the p$_z$ orbitals and the latter the p$_y$ orbitals, one easily sees the p$_z$ orbitals forming $a_1'$ and $e'$ orbitals and the p$_y$ orbitals forming $a_2'$ and $e'$ combinations.

Figure 10. LuH$_2^{3-}$ orbital plots: (bottom) 1a$_1'$; (center) 1b$_1'$; (top) 2a$_1'$. All plots are in the yz plane.
An examination of the final overlap populations between the Cl1-, Cl2-, and (LuH3)3+ fragments shows which interactions are most important. By far the biggest interaction is between the s orbital of the central chloride and the 1a1' orbital of (LuH3)3+. 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 Cl1's s orbitals interacting with the 1e' orbital of (LuH3)3+ 2a1' and 1a2' of (LuH3)3+ stabilize the a1' combination of the bridging chlorides' s orbitals and the p_y orbital of the central chloride, respectively. These overlap populations are about 0.24. A surprisingly large overlap population of 0.25 occurs between the a1' combination of the p_y orbitals and the very high lying a2' combination of the LuH31- 1b1 orbitals (50).

A crystal structure report on the anion (ErCp3)3H3Cl- shows little symmetry. For the purpose of calculations, the C2v model 51 is used. The chloride, central hydride, and top Lu atom define the C2 axis. In the experimental structure, only the Lu–Lu distance seems 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 hypothesis. The energy was lowered when the central hydride was slightly closer to the Lu3 atom than to the Lu1 and Lu2 atoms. The external hydrides could be moved closer to Lu3 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 Lu1 and Lu2. What is interesting, however, is the energy maximum that emerged when the bridging hydrides were placed on normals from the midpoints of the Lu1–Lu3 and Lu2–Lu3 bonds. These hydrides will sit on one side or the other, but not in the middle.

Acknowledgment. We are grateful to the National Science Foundation for its support of this work through Research Grant CHE 7828048 to Cornell University. Acknowledgment is made (by J.V.O.) to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Sandia University Research Program for partial support of this research. Discussions with W. J. Evans were important to us in stimulating this work.

Appendix

All calculations were performed by using the extended Hückel method9 with weighted $H_{ij}^{el}$. 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 $H_{ij}$ 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 $f$ 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.

Table III. Parameters Used in Extended Hückel Calculations*  

<table>
<thead>
<tr>
<th>orbital</th>
<th>$H_{ij}^{el}$ (eV)</th>
<th>$\ell_1$</th>
<th>$\ell_2$</th>
<th>coeff 1</th>
<th>coeff 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm</td>
<td>6s</td>
<td>-4.86</td>
<td>1.400</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6p</td>
<td>-4.86</td>
<td>1.400</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5d</td>
<td>-6.06</td>
<td>2.747</td>
<td>1.267</td>
<td>0.7184</td>
</tr>
<tr>
<td></td>
<td>4f</td>
<td>-11.28</td>
<td>6.907</td>
<td>2.639</td>
<td>0.7354</td>
</tr>
<tr>
<td>Lu</td>
<td>6s</td>
<td>-6.05</td>
<td>1.666</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6p</td>
<td>-6.05</td>
<td>1.666</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5d</td>
<td>-5.12</td>
<td>2.813</td>
<td>1.210</td>
<td>0.7044</td>
</tr>
<tr>
<td></td>
<td>4f</td>
<td>-22.40</td>
<td>9.123</td>
<td>3.666</td>
<td>0.7330</td>
</tr>
<tr>
<td>C</td>
<td>2s</td>
<td>-21.40</td>
<td>1.625</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>-11.40</td>
<td>2.275</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>1s</td>
<td>-13.60</td>
<td>1.300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The d and f orbitals are formed by a linear combination of two simple Slater functions.