

2008

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Erick Cerpa

Francisco J. Tenorio

Maryel Contreras

Manuel Villanueva

Hiram I. Beltran

*See next page for additional authors*

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## Recommended Citation

Cerpa, Erick, Francisco J. Tenorio, Maryel Contreras, Manuel Villanueva, Hiram I. Beltran, Thomas Heine, Kelling J. Donald, and Gabriel Merino. "Pentadienyl Complexes of Alkali Metals: Structure and Bonding." *Organometallics* 27, no. 5 (2008): 827-833. doi:10.1021/om070244t.

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**Authors**

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# Pentadienyl Complexes of Alkali Metals: Structure and Bonding<sup>†</sup>

Erick Cerpa,<sup>‡</sup> Francisco J. Tenorio,<sup>‡</sup> Maryel Contreras,<sup>‡</sup> Manuel Villanueva,<sup>‡</sup>  
Hiram I. Beltrán,<sup>§</sup> Thomas Heine,<sup>⊥</sup> Kelling J. Donald,<sup>¶</sup> and Gabriel Merino<sup>\*,‡</sup>

Facultad de Química, Universidad de Guanajuato, Noria Alta s/n CP 36050, Guanajuato, Gto. México,  
Departamento de Ciencias Naturales, DCNI, UAM-Cuajimalpa, Av. Pedro A. de los Santos 84, San Miguel  
Chapultepec, 11850, México, D. F., Physikalische Chemie, TU Dresden, D-01062 Dresden, Germany, and  
Department of Chemistry, Gottwald Center for the Sciences, University of Richmond,  
Richmond, Virginia 23173

Received March 16, 2007

A systematic density functional study of the structure and bonding in the alkali-metal pentadienyl complexes  $C_5H_7E$  ( $E = Li-Cs$ ) and their analogues derived from the 2,4-dimethylpentadienyl ligand is performed. The bonding in these structures has been analyzed in some detail with reference to molecular orbital analysis, and energy partition analysis, obtained by density functional calculations. An energy decomposition analysis indicates that the electrostatic interaction is the main factor to be considered in the stabilization of the gas-phase complexes we have studied. The stability of the U-shaped minimum energy structure decreases (the potential energy surface becomes more shallow) as the metal atom gets larger. We trace this behavior to a weakening of the metal–ligand binding due to the increasing diffuseness of the metal p orbitals on going down group 1. A significant pyramidalization at the terminal carbons in the coordinate U-shaped structure correlates with the strength of the metal–ligand binding. Initial results for the structural preferences of the complexes in solution for the lithium pentadienyl complex are examined in view of contrary experimental data. There still remains plenty of work to be done in modeling metal complexes in solution, and we suggest a way forward.

## Introduction

The chemistry of pentadienyl complexes has been actively investigated over the past two decades. Numerous papers on the synthesis and characterization of pentadienyl complexes of transition metals are available in the literature,<sup>1–5</sup> and the structure and bonding in analogous allylic systems that contain heteroatoms have been studied by various workers, as well.<sup>6–8</sup> Less attention has been directed toward the main-group pentadienyl complexes, even though they are quite common reagents in organic and organometallic chemistry.<sup>9–18</sup>

Pratt and Streitwieser published in 2000 a detailed ab initio computational study of the pentadienyllithium ( $C_5H_7Li$ ) and pentadienylsodium ( $C_5H_7Na$ ) complexes.<sup>19</sup> They determined that the U-shaped pentadienyl structure is the most stable conformation for both complexes. The preference in these metal pentadienyl compounds,  $C_5H_7E$ , for one conformer over another was explained by the extents of electron delocalization in the organic ligand and the electrostatic attraction between the alkali metal and the pentadienyl fragment.

To date, however, no systematic study of geometries and stability for heavier alkali-metal pentadienyl complexes has been performed. To build up an improved understanding of the key interactions determining the electronic structure and reactivity of alkali-metal pentadienyl complexes, we carried out a computational (density functional theory (DFT)) investigation of the structure and stability of a series of pentadienyl compounds. To provide information on the nature of the metal–ligand interaction, we analyzed the molecular orbitals and employed an energy decomposition analysis (EDA). We report, as well, a comparison of the geometrical and bonding properties of the pentadienyl complexes with those of the 2,4-dimethylpentadienyl ( $C_7H_{11}^-$ ) analogues. The driving force for chemical

\* To whom correspondence should be addressed. E-mail: gmerino@quijote.ugto.mx.

<sup>†</sup> Dedicated to Rosalinda Contreras on the occasion of her 60th birthday.

<sup>‡</sup> Universidad de Guanajuato.

<sup>§</sup> UAM-Cuajimalpa.

<sup>⊥</sup> TU Dresden.

<sup>¶</sup> University of Richmond.

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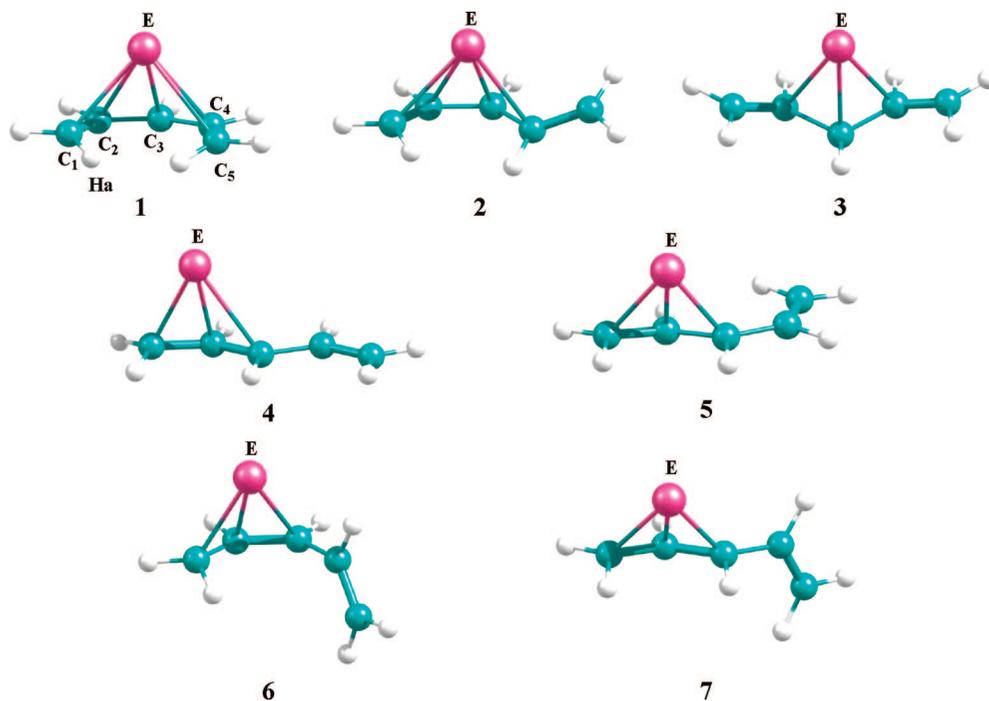
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**Figure 1.** Geometries of the local minima and the transition states of  $C_5H_7E$  complexes ( $E =$  alkali metal).

bond formation in the title compounds is analyzed in terms of their computed dissociation energies.

Much of the chemistry of the pentadienyl compounds takes place in solution. We have performed a series of computational studies of the lithium pentadienyl compounds in solvents spanning a wide range of dielectric constants.

## Results and Discussion

### Conformational Analysis of the Pentadienyl Complexes.

We start with an exploration of the potential energy surface of a set of alkali-metal pentadienyl complexes:  $C_5H_7E$  ( $E =$  Li–Cs). A key feature of pentadienyl ligands is their ability to adopt a variety of bonding modes and to shuttle easily between them. At least three different local minima and two transition state structures were obtained at the BP86/TZ2P level (see Figure 1). The number of imaginary frequencies for each stationary point is given in the Supporting Information (Table 1-SI). In each local minimum, the alkali metal is coordinated to three or more carbon atoms of the dienyl system.

Of the seven conformers shown in Figure 1, the U-shaped structure (**1**) is the most stable minimum-energy structure obtained for each of the alkali-metal pentadienyl complexes studied in this article. As one goes from  $E =$  Li to  $E =$  Cs, the structural changes on the organic fragment in **1** are surprisingly negligible, except for a pyramidalization at the terminal carbon  $C_1$  (Figure 1), which shows up as a nonzero  $C_3-C_2-C_1-H_a$  dihedral angle (Figure 1) in the metal pentadienyl complexes. Geometric parameters of structure **1** for the different alkali metals are collected in Table 1.

The sickle-shaped (S) structure **2** in Figure 1, in which the pentadienyl group acts as an  $\eta^4$  ligand, is less stable than the U-shaped structure. The energy difference between **1** and **2** decreases from 7.7 kcal mol<sup>-1</sup> for  $E =$  Li to 1.9 kcal mol<sup>-1</sup> for  $E =$  Cs. The structures in Figure 1 with lower hapticities, **3–5** (it is difficult to define absolutely the hapticity in these conformers), are less stable than **1** and **2**. The symmetric W-shaped structure **3** is a minimum for all  $E$  except lithium, for which it is only a transition-state structure. An asymmetric

**Table 1.** Selected Geometrical Parameters for the U-Shaped Minimum Energy Structures of  $C_5H_7E$  and  $C_7H_{11}E^a$

	E–C <sub>1</sub>	E–C <sub>2</sub>	E–C <sub>3</sub>	C <sub>1</sub> –C <sub>2</sub>	C <sub>2</sub> –C <sub>3</sub>	C <sub>1</sub> –C <sub>5</sub>	$\theta$
$C_5H_7Li$	2.248	2.140	2.123	1.387	1.425	3.224	–21.9
$C_5H_7Na$	2.543	2.595	2.658	1.390	1.419	3.305	–19.0
$C_5H_7K$	2.895	2.868	2.859	1.384	1.422	3.358	–14.2
$C_5H_7Rb$	3.068	3.032	3.014	1.384	1.421	3.346	–13.4
$C_5H_7Cs$	3.249	3.174	3.121	1.381	1.422	3.344	–12.3
$C_5H_7^-$				1.382	1.420	3.401	0.0
$C_7H_{11}Li$	2.220	2.155	2.122	1.391	1.430	3.181	–22.9
$C_7H_{11}Na$	2.523	2.613	2.657	1.394	1.424	3.251	–20.0
$C_7H_{11}K$	2.878	2.878	2.850	1.387	1.427	3.295	–14.9
$C_7H_{11}Rb$	3.049	3.045	3.005	1.386	1.426	3.288	–14.1
$C_7H_{11}Cs$	3.225	3.181	3.108	1.383	1.427	3.287	–13.0
$C_7H_{11}^-$				1.382	1.424	3.333	0.0

<sup>a</sup> Bond lengths are given in angstroms and angles in degrees.  $\theta$  is the  $C_3-C_2-C_1-H_a$  dihedral angle.

**Table 2.** Relative Energies of the  $C_5H_7E$  and  $C_7H_{11}E$  Conformers in kcal mol<sup>-1</sup>, including the ZPE Correction<sup>a</sup>

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
$C_5H_7Li$	0.0	7.7	14.8	9.4	11.7	20.0	19.9 (12.2)
$C_5H_7Na$	0.0	6.5	10.0	8.8		20.2	21.6 (15.1)
$C_5H_7K$	0.0	3.3	4.7			19.1	20.4 (17.1)
$C_5H_7Rb$	0.0	2.7	3.5			18.7	20.0 (17.5)
$C_5H_7Cs$	0.0	1.9	2.1			17.7	18.7 (16.8)
$C_5H_7^-$	0.0	–0.6	–3.4			17.0	17.4 (18.0)
$C_7H_{11}Li$	0.0	10.4	18.3	14.1	13.3	18.7	18.5 (8.1)
$C_7H_{11}Na$	0.0	8.7	14.0	13.9	12.8	20.0	20.2 (11.5)
$C_7H_{11}K$	0.0	5.7	9.0			19.4	19.2 (13.5)
$C_7H_{11}Rb$	0.0	4.9	7.9			19.2	18.9 (14.0)
$C_7H_{11}Cs$	0.0	4.2	6.6			18.4	17.8 (13.6)
$C_7H_{11}^-$	0.0	1.4	3.0			15.3	17.3 (15.9)

<sup>a</sup> See Figure 1 to identify the conformers. The values given in parentheses correspond to the relative energies between **7** and **2**.

variant of the W-shaped structure **4** collapses to conformer **3** for  $E =$  K, Rb, Cs. This structure is a local minimum for  $C_5H_7Li$  and  $C_5H_7Na$  but is higher in energy than **1** by  $\sim 9$  kcal mol<sup>-1</sup> (see Table 2). Structure **5** is a local minimum for  $E =$  Li only, being 11.7 kcal mol<sup>-1</sup> higher in energy than structure **1**.

An energetic ordering similar to that obtained for the  $C_5H_7E$  structures (Table 2) is observed for the  $C_7H_{11}E$  ( $E =$  Li–Cs)

**Table 3. Calculated Energies (in kcal mol<sup>-1</sup>) for the Hypothetical Reactions (1) ( $\Delta E_1$ ) and (2) ( $\Delta E_2$ )<sup>a</sup>**

	$\Delta E_1$	$\Delta E_2$
C <sub>5</sub> H <sub>7</sub> Li	-155.7	-66.4
C <sub>5</sub> H <sub>7</sub> Na	-130.7	-45.7
C <sub>5</sub> H <sub>7</sub> K	-114.5	-47.9
C <sub>5</sub> H <sub>7</sub> Rb	-110.0	-46.8
C <sub>5</sub> H <sub>7</sub> Cs	-106.3	-49.6
C <sub>7</sub> H <sub>11</sub> Li	-159.0	-70.3
C <sub>7</sub> H <sub>11</sub> Na	-133.6	-49.3
C <sub>7</sub> H <sub>11</sub> K	-117.1	-51.1
C <sub>7</sub> H <sub>11</sub> Rb	-112.6	-50.0
C <sub>7</sub> H <sub>11</sub> Cs	-109.2	-53.1

<sup>a</sup> The values include the ZPE correction.

isomers, in which we have substituted for the bulkier methyl (-CH<sub>3</sub>) substituent at carbons C<sub>2</sub> and C<sub>4</sub>. Schlosser and Rauschschwalbe reported that 2,4-dimethylpentadienylpotassium adopts a U shape,<sup>18</sup> which fits well with our results. We have been interested in investigating the effect of these substitutions on the steric strain in the W and S conformations and a possible stabilization of the U-shaped structure.

Structures **6** and **7** correspond to the transition states for a simple rotation around the two middle C-C bonds. Both of these structures have the vinyl group almost perpendicular to the plane of the allylic system. It is clear, from the relative energies of **6** compared to those of **1** in Table 3, that the rotational barriers involving structure **6**, a transition state in going from **1** to **2**, is lowered slightly as E gets larger. We find that this observation is completely in line with the trends we obtain for the metal-ligand interaction energy. The relative energy between **7** and **2** is useful, since **7** is not connected directly to **1**. Note that the latter energy differences increase gradually from Li to Rb. In the case of the Cs complex, this barrier is slightly lower than that in the Rb compound. Both torsional barriers clearly illustrate the role of electronic delocalization in preserving the planarity of the carbon backbone.

**Structural Preferences in Solution.** Structural preferences in the gas phase may be easily altered in solution. Experimental evidence of a clear predominance of the W-shaped conformer of the pentadienyl has been reported for pentadienyllithium in tetrahydrofuran<sup>5</sup> and for pentadienylpotassium in liquid ammonia.<sup>14</sup> Some NMR data are available, as well, for comparison in THF solution: pentadienylpotassium shows a U-shaped conformation, and the lithium analogue takes the W conformation. In contrast to the preference for the W-shaped structure for the lithium complex, our theoretical results suggest a preference for the U-shaped geometry in a number of different solvents. We discuss the solvent effect on pentadienyllithium in the last section.

Some general trends are identified from the above results: (i) a reduction in the hapticity decreases the stability of the conformers, (ii) the relative energy of the conformers is smaller for the heavier alkali-metal complexes, (iii) the rotational barriers are slightly dependent on the metal size, and (iv) the substitution of hydrogen atoms by methyl groups at the positions 2 and 4 in alkali-metal pentadienyl complexes favors the U-shaped structure.

**Conformational Analysis of the Free Pentadienyl Anion.** For the free pentadienyl anion, the most stable conformer in the gas phase is the W-shaped structure. The U-shaped conformer is higher in energy than the W-shaped conformer by 3.4 kcal mol<sup>-1</sup>, being destabilized by a (hard-sphere repulsive) steric interaction, which cannot be compensated by electron delocalization. The U-shaped conformer satisfies all prerequisites for  $\eta^5$  coordination to the metal in the gas phase,

including the maximization of electrostatic attraction between the cation and the organic ligand. Without the stabilizing interaction with the metal, however, the U-shaped structure becomes untenable. The free 2,4-dimethylpentadienyl anion shows a different behavior, preferring a U-shaped conformation. As we will see below, there are other reasons (mainly the simple symmetry argument) for this conformational preference of the 2,4-dimethylpentadienyl anion.

**Stability of Pentadienyl Complexes of Alkali Metals.** We calculated the reaction energies for the theoretical reaction (1), which represents the pentadienyl complex formation from the organic anion at the local minimum structure and the corresponding alkali metal cation. Let us mention that the geometry of the global minimum energy structure of C<sub>5</sub>H<sub>7</sub><sup>-</sup> and C<sub>7</sub>H<sub>11</sub><sup>-</sup> are different. The results are given in Table 2.



The theoretically predicted energies for reaction 1 ( $\Delta E_1$ ) are, of course, negative (by more than 100 kcal mol<sup>-1</sup>), indicating a large electrostatic attraction between both fragments (see Table 3). The ionic formation energy of the pentadienyl complexes from C<sub>5</sub>H<sub>7</sub><sup>-</sup> and E<sup>+</sup> decreases significantly going from Li (-156 kcal mol<sup>-1</sup>) to Cs (-106 kcal mol<sup>-1</sup>). Substitution at positions 2 and 4 for methyl groups increases the  $\Delta E_1$  values by 2-3 kcal mol<sup>-1</sup>. The ionic binding energy derived for eq 1 is instructive; however, the molecule in the gas phase can dissociate to give neutral fragments. Rayon and Frenking have pointed out that, for alkali-metal cyclopentadienyl complexes,<sup>20</sup> the interaction between the organic anion and the metal cation must be not confused with the original driving force for bond formation—the attraction between the neutral metal E and C<sub>5</sub>H<sub>7</sub>.

In contrast to the results for the ionic interaction (1), the energy related to the complex formation from the neutral fragments ( $\Delta E_2$ ; see Table 3) remains nearly constant (-46 kcal mol<sup>-1</sup>), except for the lithium complex (-66.4 kcal mol<sup>-1</sup>).<sup>21,22</sup> This trend in the bond energies is similar to the pattern obtained by Rayon and Frenking for the alkali-metal cyclopentadienyl complexes and is explained by the significantly stronger metal-ligand interaction for E = Li, compared to the metal-ligand interactions for the heavier metals.<sup>20</sup>



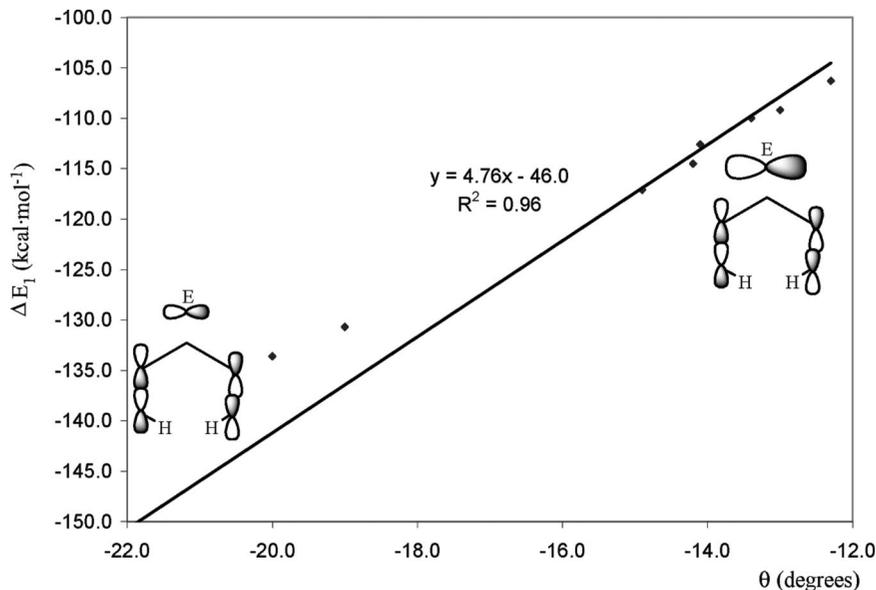
**Out-of-Plane Hydrogen Atoms.** Coordination of the alkali metal to the pentadienyl anion is accompanied by a rotation of the hydrogen atoms linked to C<sub>1</sub> out of the C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> plane (see Table 1). A linear relationship is found between the C<sub>3</sub>-C<sub>2</sub>-C<sub>1</sub>-H<sub>a</sub> dihedral angle  $\theta$  and the energy values for the hypothetical reaction 1 (see Figure 2). The rotation of the hydrogen atoms out of the plane of the C backbone (a pyramidalization of the C<sub>1</sub>-C<sub>2</sub> bond and the two C-H bonds at C<sub>1</sub>) is indicative of a significant rehybridization at C<sub>1</sub> in preparation for bonding with the metal.

There is an earlier discussion in the literature about the out-of-plane bending of ring C-H bonds in cyclopentadienyl complexes. The "electrostatic interpretation" was first proposed by Alexandratos et al.<sup>23</sup> A "covalent interpretation" was

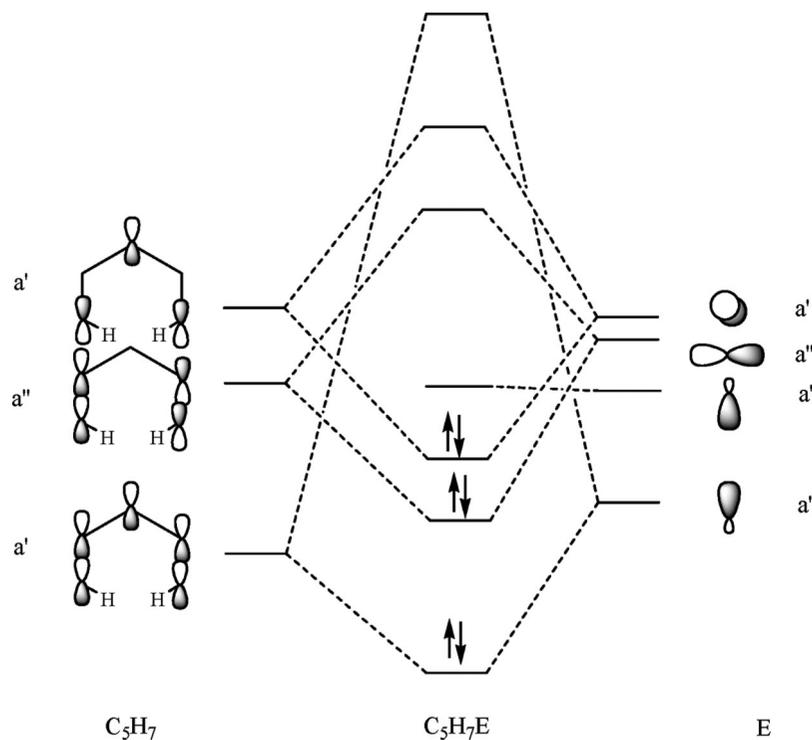
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**Figure 2.** Correlation of the dihedral angle  $\theta$  in the  $C_5H_7E$  and  $C_7H_{11}E$  ( $E = Li-Cs$ ) complexes (defined as the angle  $C_3-C_2-C_1-H_a$ ) with the  $\Delta E_1$  values given in  $\text{kcal mol}^{-1}$ , including ZPE correction.



**Figure 3.** Orbital diagram for pentadienyl complexes of alkali metals.

proposed by Jemmis and Schleyer.<sup>24</sup> In a molecular orbital picture, the nonplanarity in the title complexes is explained by the interaction of the p orbitals of the approaching E atom that are parallel to the plane of the organic moiety with the  $\pi$  system of pentadienyl, in particular with the  $a''$  orbital. This interaction gets weaker going from  $E = Li$  to  $E = Cs$  as the p orbitals become more diffuse, such that the rotation of the hydrogen atoms out of the  $C_1-C_2-C_3$  plane is strongest in the lithium complex. The dihedral angle  $\theta$  is, therefore, a sensitive probe for the strength of the pentadienyl–metal interaction.

**Bonding Analysis.** In this section, we will combine a molecular orbital analysis with the energy partitioning analysis results in order to understand the metal–ligand interaction and to rationalize correlations between the energy contributions and conformational and isomer stability.

The orbitals of the pentadienyl fragment are familiar.<sup>25</sup> Figure 3 is a construction of the  $\pi$  molecular orbitals (MOs) of the  $C_5H_7E$  complex from the interaction of  $C_5H_7$  with the metal. The HOMO of each of the alkali-metal pentadienyl complexes corresponds to the combination of the “nonbonding”  $\pi$  molecular orbital of the pentadienyl fragment and the p orbital of the metal atom parallel to the organic moiety.

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Table 4. Energy Decomposition Analysis of C<sub>5</sub>H<sub>7</sub>E and C<sub>7</sub>H<sub>11</sub>E Complexes at the BP86/TZ2P Level<sup>a</sup>

	$\Delta E_{\text{int}}$	$\Delta E_{\text{Pauli}}$	$\Delta E_{\text{elstat}}$	$\Delta E_{\text{orb}}$	$a'$	$a''$	HOMO	$q(\text{E})$
C <sub>5</sub> H <sub>7</sub> Li	-165.4	23.5	-145.5 (77.2)	-43.4 (22.8)	-26.8 (61.8)	-16.6 (38.2)	-4.31	0.38
C <sub>5</sub> H <sub>7</sub> Na	-138.4	23.4	-138 (85.3)	-23.8 (14.7)	-16 (67.2)	-7.8 (32.8)	-3.75	0.49
C <sub>5</sub> H <sub>7</sub> K	-120.9	29.8	-127.7 (84.7)	-23 (15.3)	-14.9 (64.8)	-8.1 (35.2)	-3.39	0.58
C <sub>5</sub> H <sub>7</sub> Rb	-116.2	28.9	-122.7 (84.6)	-22.4 (15.4)	-14.8 (66.1)	-7.6 (33.9)	-3.23	0.59
C <sub>5</sub> H <sub>7</sub> Cs	-112.3	32.1	-119.4 (82.4)	-25.0 (17.6)	-16.8 (67.2)	-8.2 (32.8)	-3.21	0.59
C <sub>7</sub> H <sub>11</sub> Li	-165.8	24.3	-143.1 (77.3)	-47.0 (22.7)	-28.6 (60.8)	-18.4 (39.2)	-4.18	0.37
C <sub>7</sub> H <sub>11</sub> Na	-138.4	24.0	-136 (83.7)	-26.4 (16.3)	-17.2 (65.1)	-9.2 (34.9)	-3.64	0.48
C <sub>7</sub> H <sub>11</sub> K	-120.5	30.5	-125.7 (83.2)	-25.3 (16.8)	-16.0 (63.2)	-9.3 (36.8)	-3.31	0.57
C <sub>7</sub> H <sub>11</sub> Rb	-115.7	29.5	-120.8 (83.2)	-24.4 (16.8)	-15.8 (64.7)	-8.6 (35.3)	-3.16	0.58
C <sub>7</sub> H <sub>11</sub> Cs	-112.1	33.1	-117.9 (81.2)	-27.3 (18.8)	-18.0 (65.9)	-9.3 (34.1)	-3.16	0.58

<sup>a</sup> All energy values are given in kcal mol<sup>-1</sup>. HOMO energies are given in eV. The Hirshfeld atomic charge for atom E is given in au. Percentages are given in parentheses.

The stabilization of the U conformation is achieved because centers 1 and 5 are close enough (3.224 Å for C<sub>5</sub>H<sub>7</sub>Li; see Table 1) for their 2p<sub>z</sub> orbitals to overlap significantly. Interestingly, the distances between C1 and C5 in the 2,4-dimethylpentadienyl complexes are smaller than those calculated for the unsubstituted pentadienyl analogues, indicating an extra stabilization induced by the 1,5-bonding. Thus, the U-shaped conformation is stabilized by electron delocalization, the maximization of metal–anion electrostatic attraction, and the 1,5-bonding. These stabilizing interactions are also responsible for the preference of the U-shaped structure in the 2,4-dimethylpentadienyl complexes. In the latter complexes extra stabilization of the U structure comes from the steric interaction between the methyl substituents on the outside of the U. The general preference we observe for a U geometry (with or without the extra steric support) helps us to better understand the results of Kirss, who obtained cyclopentadienyl derivatives from pentadienyl complexes.<sup>26</sup>

The lowest-lying  $\pi$  orbital completely covers the carbon skeleton and, together with the second occupied  $\pi$ -MO, contributes to the double-bond character of the C<sub>1</sub>–C<sub>2</sub> bond. Considering that the LUMO of the C<sub>5</sub>H<sub>7</sub>E complex is located predominantly at the metal, these complexes may find use as Lewis acids in the building up of donor–acceptor complexes. Recently, two of the authors reported a series of heteroleptic donor–acceptor sandwiches guided by this interpretation of the bonding in metal complexes.<sup>27</sup>

The frontier MO energies are given in Table 4. Note that the negative charge of the C<sub>5</sub>H<sub>7</sub><sup>-</sup> and C<sub>7</sub>H<sub>11</sub><sup>-</sup> anions may result in electron loss of the structure. The positive values for the energies of the HOMO (1.51 and 1.41 eV for C<sub>5</sub>H<sub>7</sub><sup>-</sup> and C<sub>7</sub>H<sub>11</sub><sup>-</sup>, respectively) indicate that these electrons are not bound. Complexation alleviates the HOMO energy and stabilizes the complex (see Table 4).

Typically the bonding model employed for describing the metal–ligand interaction in half-sandwich complexes correlates the metal atomic orbitals with the  $\pi$  orbitals of the organic fragment. Similarly to metallocenes, covalent bonding is commonly discussed in terms of donor–acceptor interactions between the organic anion and the metal cation, in which the electronic charge is donated from the occupied orbitals in pentadienyl to vacant metal orbitals. This model is quite convenient because it involves bonding between two closed-shell fragments.

In order to gain a better quantitative understanding of the bonding between the metal and the pentadienyl moiety, we performed an energy decomposition analysis (EDA, Table

4).<sup>28,29</sup> Our results show that the bonding between the metal cation, E<sup>+</sup>, and the dienyl fragment has an electrostatic character between 77% and 83%. The values of  $\Delta E_{\text{elstat}}$  for the alkali-metal pentadienyl complexes are slightly lower than those reported by Rayon and Frenking for the cyclopentadienyl analogues.<sup>20</sup> In both cases (open and cyclic complexes), the EDA supports an ionic interaction between the metal and the carbon backbone, in line with the atomic partial charge at atom E (see Table 4). The values of the atomic charges justify the partition of the complexes into C<sub>5</sub>H<sub>7</sub><sup>-</sup> + E<sup>+</sup>.<sup>30</sup>

The most important contribution to  $\Delta E_{\text{orb}}$  in each of the complexes is from the interaction of the occupied  $a'$  metal p and sp hybrid orbitals with the corresponding  $a'$  orbitals on the organic fragment. In fact, the contribution of the  $a'$  MOs of the complex to  $\Delta E_{\text{orb}}$  remains between 61 and 67% (going from E = Li to E = Cs) compared to the range between 39 and 33% for  $a''$  MOs. The insensitivity of the ratio of the  $a'$  and  $a''$  orbital contributions to the size of E shows that the relative sizes of the  $a'$  and  $a''$  overlaps vary little with the spatial extent of the p orbitals on going from Li to Cs. Notice, however, that the actual magnitude of the contributions of the  $a'$  and  $a''$  MO interaction terms to  $\Delta E_{\text{orb}}$  decreases as E gets larger. As the metal becomes less electronegative, and the metal orbitals move higher up in energy, the overlap with the organic fragment is reduced, and the contributions to  $\Delta E_{\text{orb}}$  decrease. This general destabilization as E gets larger is especially dramatic on going from Li to Na.

Note that the strongest covalent interactions (23%) are obtained for the lithium complexes. This is another indication that the lithium complexes in the U-shaped conformation have the strongest metal–ligand binding, the strongest covalent attraction, and the strongest 1,5-bonding interactions.

**Solvent Effects.** How to explain the experimentally observed predominance of the W form for pentadienyllithium? To estimate the solvent effects on pentadienyllithium, structures 1–7 were reoptimized by simulating the electric field of a surrounding environment using the conductor-like screening model COSMO.<sup>31</sup> In this approach, the solute is considered as being situated in a cavity inside a structureless medium/continuum, with cavity shapes and medium parameters empirically fitted to reproduce solvation thermochemistry data for a reference set of pure solvents. COSMO calculations were

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**Table 5. Gibbs Free Energy Differences at 298 K for C<sub>5</sub>H<sub>7</sub>Li Calculated at the BP86/TZ2P Level Simulating the Electric Field using the Conductor-Like Screening Model COSMO<sup>a</sup>**

	1	2	3	4	5	6	7
diethyl ether	0.0	3.4	7.0	2.7	4.4	15.7	15.1
tetrahydrofuran	0.0	3.4	6.4	2.0	4.4	15.7	14.4
ammonia	0.0	2.8	5.7	1.4		15.0	14.4
water	0.0	2.7	5.1	0.8	3.1	15.1	14.4

<sup>a</sup> All values are given in kcal mol<sup>-1</sup>.

performed with four dielectric constants, 4.34, 7.58, 16.9, and 78.39, representing diethyl ether, tetrahydrofuran, ammonia, and water as solvent, respectively.

In the case of lithium complexes, calculations predict that in the gas phase this system adopts a U-shaped conformation. Inclusion of solvent effects does not change this trend. The COSMO results, summarized in Table 5, show that on going from low to high dielectric media the Gibbs free energy difference (determined at 298 K) between structure **1** and the distinct conformations decreases significantly, but **1** is still the most stable complex. Interestingly, the asymmetric variant of the W-shaped structure **4** is only 0.8 kcal·mol<sup>-1</sup> less stable than **1**, indicating that structure **4** can also exist at room temperature in solution, in agreement with the experimental results. Note that the transition barriers are also smaller than in the gas phase (see Table 5).

### Summary and Conclusions

The bonding of the alkali metals with the pentadienyl ligand shows a definite preference for the η<sup>5</sup> U-shaped structure in the gas phase. In this regard the bonding is similar to the structural preferences in the analogous transition-metal complexes, indicating the predominance of the metal p orbitals in the bonding (over the d orbitals which are also involved in the bonding to transition metals). We do not observe a preference in the gas phase for geometries other than the U-shaped structure; in fact, a reduction in the hapticity decreases the stability of the conformers. A stronger binding between the pentadienyl and the metals higher up in group **1** is evident, as well, in the stability of the η<sup>3</sup> complexes **4** for E = Li, Na only and **5** for E = Li only.

As observed in previous studies, the free 2,4-dimethylpentadienyl fragment shows a preference for the U-shaped conformation. It is not surprising, therefore, that the metal 2,4-dimethylpentadienyl complexes show an even stronger preference for the U-shaped structure, compared to the metal pentadienyl complex. As we observed for the bonding in the unsubstituted pentadienyl complex, the stability of the U-shaped isomer decreases rapidly on going down the group, which follows the pattern we observe in the metal–ligand (ionic and covalent) binding energies.

Earlier experimental studies suggest that the W-shaped structure is the most stable conformer of the C<sub>5</sub>H<sub>7</sub>Li complex in solution. This is contrary to our gas-phase results, which suggest a preference for the U-shaped structures in the Li complex. However, the asymmetric variant of the W-shaped structure is only 0.8 kcal mol<sup>-1</sup> less stable than the U-shaped structure, indicating that the W-shaped structure can also exist at room temperature in solution, in agreement with the experimental results. A detailed analysis including the solvent effect and a plausible polymerization model, conformed by dimerization and trimerization reaction schemes in solution, is in progress.

### Computational Details

The geometry optimizations were performed using the ADF 2006.01 program package.<sup>32</sup> Geometries were optimized using Becke's exchange functional<sup>33</sup> in conjunction with Perdew's correlation functional<sup>34</sup> (BP86). Uncontracted Slater-type orbitals (STOs) were employed as basis functions in SCF calculations.<sup>35</sup> Triple-ζ-quality basis sets were used, which were augmented by two sets of polarization functions: that is, p and d functions for the hydrogen atom and d and f functions for the other atoms. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle. This level is denoted as BP86/TZ2P. A convergence threshold for the maximum gradient of 1 × 10<sup>-4</sup> hartree bohr<sup>-1</sup> was used. Scalar relativistic effects were taken into account via the zero-order regular approximation (ZORA).<sup>36,37</sup> Stationary points were characterized by harmonic frequency computations at the same theoretical levels. The atomic partial charges have been calculated with the Hirshfeld partitioning scheme.<sup>38</sup>

The metal–ligand interactions were analyzed by means of the energy decomposition analysis (EDA) in ADF, which was developed by Ziegler and Rauk<sup>39,40</sup> following a similar procedure suggested by Morokuma.<sup>41</sup> In the EDA, bond formation between the interacting fragments is divided into three contributions. A detailed description of the physical significance of each contribution has been given by Bickelhaupt and Baerends.<sup>28</sup> The first contribution is calculated from the superposition of the unperturbed fragment densities at the molecular geometry and corresponds to the classical electrostatic effects associated with the Coulombic attraction and repulsion, ΔE<sub>elstat</sub>. The second contribution, ΔE<sub>Pauli</sub>, gives the repulsive interaction energy between the fragments which is caused by the fact that two electrons with the same spin cannot occupy the same region in space. The term comprises the four-electron destabilizing interactions between occupied orbitals. ΔE<sub>Pauli</sub> is calculated by enforcing the Kohn–Sham determinant of AB, which is the result of superimposing fragments A and B, to obey the Pauli principle through antisymmetrization and renormalization. In the third contribution the molecular orbitals relax to their final form to yield the stabilizing orbital interaction ΔE<sub>orb</sub>. This value is calculated in the final step when the Kohn–Sham orbitals relax to their optimal form. Note that the relaxation energy of the Kohn–Sham orbitals includes the effect of electron correlation. The latter term can be divided into contributions of orbitals having different symmetry. The sum of the three terms ΔE<sub>elstat</sub> + ΔE<sub>Pauli</sub> + ΔE<sub>orb</sub> gives the total “instantaneous” interaction energy, ΔE<sub>int</sub>, between the two fragments in the molecule.

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$

EDA has proven to give important information about the nature of the bonding in main-group compounds and transition-metal complexes.<sup>20,29,42</sup>

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Energy differences with inclusion of solvent effects were calculated by the conductor-like screening model, COSMO, of Klamt and Schuurmann,<sup>31</sup> as implemented in the ADF package. COSMO calculations were performed with four dielectric constants; 4.34, 7.58, 16.9, and 78.39, representing diethyl ether, tetrahydrofuran, ammonia, and water as solvent, respectively. The van der Waals surface was used to build the cavity containing the molecule, using the next radii in Å: 2.00 for C, 1.29 for H, and 1.80 for Li.

**Acknowledgment.** We are grateful for financial support from the Direccion de Investigacion y Posgrado of Univer-

sidad de Guanajuato. We thank Angeles Paz, Juvencio Robles, and Esther Sanchez for cheerful discussions. Invaluable technical help was provided by Ariana Teissier. E.C. acknowledges Conacyt for a fellowship.

**Supporting Information Available:** Tables giving the number of imaginary frequencies of the stationary points of the C<sub>5</sub>H<sub>7</sub>E complexes and total energies and atomic coordinates of all optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM070244T