

## Bis(arene) Actinide Sandwich Complexes, ( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>R<sub>3</sub>)<sub>2</sub>An: Linear or Bent?

Jun Li and Bruce E. Bursten\*

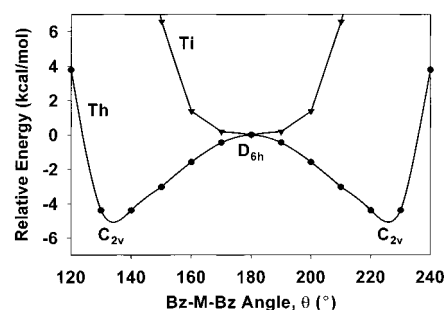
Department of Chemistry, The Ohio State University  
Columbus, Ohio 43210

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The syntheses of the sandwich complexes ferrocene, ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>-Fe, in 1951<sup>1</sup> and uranocene, ( $\eta^8$ -C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>U, in 1968<sup>2</sup> ushered in the modern era of organotransition metal and organoactinide chemistry, respectively. Ferrocene and uranocene are examples of *linear* sandwich complexes, that is, those in which the (ring centroid)–M–(ring centroid) angle (denoted  $\theta$ ) is 180°. In the case of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>M chemistry, a number of *bent* ( $\theta < 180^\circ$ ) complexes are known when M is a main-group or rare-earth element.<sup>3</sup> The explanation for the bent structures of these complexes has been the subject of some debate concerning the relative importance of covalent, electrostatic, and steric interactions.<sup>4</sup>

Arenes are generally poorer ligands than cyclopentadienyl and substituted cyclopentadienyl ligands. Bis(benzene) chromium, Bz<sub>2</sub>-Cr (Bz =  $\eta^6$ -C<sub>6</sub>H<sub>6</sub>), characterized shortly after ferrocene, was the first of a number of linear transition-metal bis(benzene) sandwich complexes that have been synthesized and investigated.<sup>5,6</sup> However, until recently bis(arene) complexes of the f-elements have been unknown. Cloke et al. used metal-atom synthesis to make a series of bis(arene) lanthanide complexes and obtained a crystal structure for (TBB)<sub>2</sub>Gd (TBB =  $\eta^6$ -1,3,5-C<sub>6</sub>H<sub>3</sub><sup>t</sup>Bu<sub>3</sub>), which has a linear geometry.<sup>7</sup> With respect to actinide complexes, which is the focus of this contribution, Pires de Matos, Marshall, and co-workers recently used mass spectrometry to identify [Bz<sub>2</sub>An]<sup>+</sup> and [(TBB)<sub>2</sub>An]<sup>+</sup> (An = Th, U).<sup>8</sup> These discoveries suggest that it might be possible to synthesize and isolate neutral bis(arene) actinide complexes.

Theoretical treatments of linear sandwich complexes have developed in parallel with their syntheses. We and others have recently addressed the structure and bonding in linear ( $\eta^n$ -C<sub>n</sub>H<sub>n</sub>)<sub>2</sub>M ( $n = 6, 7, 8$ ) sandwich complexes by using advanced theoretical electronic structure methods.<sup>9</sup> Bis(arene) sandwich complexes of the lanthanide (Ln) and actinide (An) elements have been studied recently by using molecular mechanics,<sup>10</sup> density functional,<sup>11</sup> and ab initio methodologies.<sup>12</sup> All of these calculations on bis(arene) Ln and An sandwich complexes assumed a linear sandwich



**Figure 1.** Relative LDA energies for ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ti and ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Th as a function of the (centroid)–M–(centroid) angle  $\theta$ . For each complex, the energy for  $\theta = 180^\circ$  is chosen to be zero.

structure based on the experimental structures of (TBB)<sub>2</sub>Gd and uranocene. However, in view of the bent structures of several Cp<sub>2</sub>Ln complexes,<sup>3</sup> it struck us that the linear structure of (TBB)<sub>2</sub>Gd may be largely due to steric interactions rather than an intrinsic electronic preference and that the assumption of a linear structure for ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>An complexes might therefore be incorrect. In this contribution, we report optimized geometries of Bz<sub>2</sub>An (An = Th–Am) and ( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>R<sub>3</sub>)<sub>2</sub>An (An = Th, U, Pu; R = Me, <sup>t</sup>Bu) obtained by using local density approximation (LDA)<sup>13</sup> and Perdew-Wang (PW91)<sup>14</sup> gradient-corrected relativistic density functional theory (DFT) methods.<sup>15,16</sup> These DFT methods are found to be able to reproduce the experimental geometries and vibrational frequencies of organoactinide complexes with satisfactory accuracy.<sup>17</sup> The (TTB)<sub>2</sub>An calculations that we report here are, to date, the largest full geometry optimizations to be carried out on an actinide system.

As a first step, we have calculated the LDA energy curves for Bz<sub>2</sub>Ti and Bz<sub>2</sub>Th to compare the structures of transition metal and actinide complexes that both have metal atoms with four valence electrons. As shown in Figure 1, Bz<sub>2</sub>Ti has a minimum energy with a linear structure ( $\theta = 180^\circ$ ) and a steep potential for bending, consistent with its experimentally determined linear geometry.<sup>18</sup> In contrast, Bz<sub>2</sub>Th is predicted to have a significantly bent structure (LDA:  $\theta = 135^\circ$ ; PW91:  $\theta = 139^\circ$ ).<sup>19</sup> Linear Bz<sub>2</sub>Th is a transition state, as confirmed by the imaginary frequency (328i cm<sup>-1</sup>) for the bending of linear Bz<sub>2</sub>Th at the optimized linear (*D*<sub>6h</sub>) structure of the complex. These results confirm our suspicion that Bz<sub>2</sub>An complexes do not necessarily prefer to be linear.

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(19) The molecules were bent along a coordinate that constrains four of the C–H bonds to lie in a mirror plane of the bent molecule. An alternative bending coordinate, in which the mirror plane bisects four of the C–C bonds, leads to energies that are similar or slightly higher than those that we report here.

**Table 1.** DFT (PW91) Geometries and Relative Energies for Linear and Bent Bz<sub>2</sub>An (An = Th–Am) Sandwich Complexes

compd	linear		bent		$\Delta E_{B-L}$ <sup>b</sup> (kcal/mol) <sup>a</sup>
	An–Bz (Å) <sup>a</sup>	$\theta$ (deg)	An–Bz (Å) <sup>a</sup>	$\theta$ (deg)	
Bz <sub>2</sub> Th	2.309	180	2.271	138.5	–4.6
Bz <sub>2</sub> Pa	2.200	180	2.171	141.9	–10.1
Bz <sub>2</sub> U	2.156	180	2.129	137.0	–10.2
Bz <sub>2</sub> Np	2.146	180	2.111	136.2	–10.2
Bz <sub>2</sub> Pu	2.156	180	2.117	135.3	–6.5
Bz <sub>2</sub> Am	2.160	180	2.122	135.6	–0.3

<sup>a</sup> Actinide–(benzene centroid) distance. <sup>b</sup>  $\Delta E_{B-L} = E_{\text{bent}} - E_{\text{linear}}$  where  $E_{\text{bent}}$  and  $E_{\text{linear}}$  are the total energies at the optimized geometries in the bent and linear geometries, respectively.

We obtain a similar result for Bz<sub>2</sub>U. Linear ( $D_{6h}$ ) Bz<sub>2</sub>U is a high-order saddle point with several imaginary frequencies. We therefore examined several possible distortions of Bz<sub>2</sub>U, all of which produce structures lower in energy than the linear one. The lowest-energy structure for Bz<sub>2</sub>U is a bent ( $C_{2v}$ ) sandwich with planar rings and  $\theta = 137^\circ$ . This bent structure is 10.2 kcal/mol lower than the linear structure.

Table 1 lists the optimized (PW91) geometries and relative energies for the linear ( $D_{6h}$ ) and bent ( $C_{2v}$ ) forms of the early actinide Bz<sub>2</sub>An (An = Th–Am) complexes. For each of these complexes the bent form has a lower energy and a shorter An–Bz distance, suggesting that (i) the bent structure is favored over the linear structure for all of the early-actinide complexes, and (ii) the An–Bz bonding interactions are stronger in the bent sandwich structure than in the linear one. Preliminary calculations of the An–Bz binding energies in the linear and bent forms provide support for these conclusions.<sup>20</sup> An orbital analysis of the reasons for the preference for bent Bz<sub>2</sub>An indicates that the combined Bz → An 6d and Bz → An 5f donation is greater (and hence leads to more covalency) in the bent geometry than in the linear geometry. The decrease in the energy separation of the bent and linear forms of Bz<sub>2</sub>An as one proceeds from the early to the later actinide elements (Table 1) is primarily due to contraction of the An 5f orbitals, which leads to lesser differential donation in the linear and bent geometries. A full analysis of these factors will be presented in a future publication.

Most efforts to synthesize isolable bis(arene) f-element complexes have employed bulky arenes, such as TBB.<sup>7,21</sup> Because of the steric demands of these substituted arenes, it is not obvious that the results obtained for the Bz<sub>2</sub>An complexes can be readily extendable to “bulked-up” sandwich complexes, such as (TBB)<sub>2</sub>An. To assess the effects of bulky ligands, we have calculated fully optimized structures for the linear and bent forms of the sandwich complexes ( $\eta^6$ -1,3,5-C<sub>6</sub>H<sub>3</sub>R<sub>3</sub>)<sub>2</sub>An (An = Th, U, Pu; R = H, Me, <sup>t</sup>Bu). Table 2 presents the energies and values of  $\theta$  obtained in these calculations. Surprisingly, bis(mesitylene) complexes ( $\eta^6$ -1,3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)<sub>2</sub>An are predicted to be bent, nearly as much as are unsubstituted Bz<sub>2</sub>An complexes; apparently, the addition of three methyl substituents per ring does not provide enough steric interaction to overcome the electronic preference for a bent structure. However, when <sup>t</sup>Bu substituents are used, forming (TBB)<sub>2</sub>An complexes, a linear structure analogous to the experimental structure of (TBB)<sub>2</sub>Gd is preferred over a bent one.<sup>22</sup> The bending potential for the (TBB)<sub>2</sub>An complexes is quite stiff because of severe interligand contacts in the bent form. Figure 2 compares the optimized structures of ( $\eta^6$ -1,3,5-C<sub>6</sub>H<sub>3</sub>R<sub>3</sub>)<sub>2</sub>U (R = Me, <sup>t</sup>Bu).

(20) Preliminary unrestricted Kohn–Sham (UKS) calculations on linear and bent Bz<sub>2</sub>An complexes yield Bz–An binding energies of 60 and 62 kcal/mol for linear (<sup>1</sup>A<sub>1g</sub>; e<sub>2g</sub><sup>4</sup>5f<sup>0</sup>) and bent (<sup>1</sup>A<sub>1</sub>; 8b<sub>2</sub><sup>2</sup>7a<sub>2</sub><sup>0</sup>11b<sub>1</sub><sup>0</sup>) Bz<sub>2</sub>Th, and 55 and 58 kcal/mol for linear (<sup>3</sup>E<sub>2g</sub>; 3e<sub>2g</sub><sup>3</sup>3e<sub>2g</sub><sup>2</sup>5f<sup>1</sup>) and bent (<sup>3</sup>B<sub>2</sub>; 8b<sub>2</sub><sup>2</sup>7a<sub>2</sub><sup>1</sup>11b<sub>1</sub><sup>1</sup>) Bz<sub>2</sub>U, referenced to the process Bz<sub>2</sub>An → 2Bz + An. These calculations indicate that An–Bz bonding is apparently thermodynamically favorable.

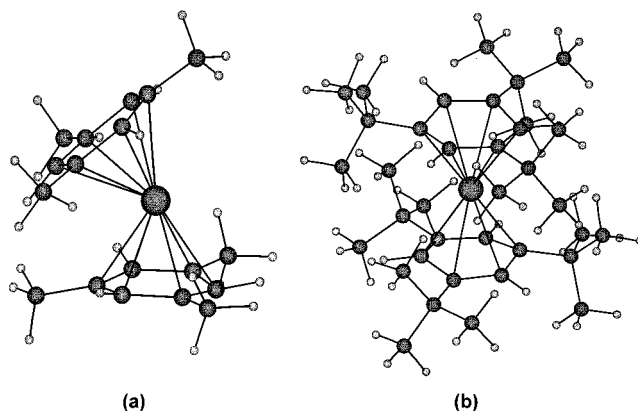
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(22) The geometry optimization for (TBB)<sub>2</sub>U was started with a bent initial structure ( $\theta = 150^\circ$ ) and no symmetry constraints ( $C_1$  symmetry). Optimization led to a structure with ( $\theta = 180^\circ$ ) and nearly perfect  $D_{3d}$  symmetry.

**Table 2.** DFT (PW91) Energies and Centroid–An–Centroid Angle  $\theta$  for ( $\eta^6$ -1,3,5-C<sub>6</sub>H<sub>3</sub>R<sub>3</sub>)<sub>2</sub>An (An = Th, U, Pu; R = H, Me, <sup>t</sup>Bu) Complexes

compd	linear		bent		$\Delta E_{B-L}$ <sup>a</sup> (kcal/mol) <sup>a</sup>
	$E$ (eV)	$\theta$ (deg)	$E$ (eV)	$\theta$ (deg)	
(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> Th	–156.8969	180	–157.0940	138.5	–4.6
(C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub> ) <sub>2</sub> Th	–256.4178	180	–256.4473	142.4	–5.3
(C <sub>6</sub> H <sub>3</sub> <sup>t</sup> Bu <sub>3</sub> ) <sub>2</sub> Th	–553.4077	180	–553.2026	170.0 <sup>b</sup>	4.7
			–552.1159	160.0 <sup>b</sup>	29.8
(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> U	–157.5073	180	–157.9475	137.0	–10.2
(C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub> ) <sub>2</sub> U	–257.1507	180	–257.4980	139.8	–8.0
(C <sub>6</sub> H <sub>3</sub> <sup>t</sup> Bu <sub>3</sub> ) <sub>2</sub> U	–553.8190	180	–553.5337	170.0 <sup>b</sup>	6.6
			–552.1551	160.0 <sup>b</sup>	38.4
(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> Pu	–156.3889	180	–156.6706	135.3	–6.5
(C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub> ) <sub>2</sub> Pu	–256.0194	180	–256.2167	137.5	–4.5
(C <sub>6</sub> H <sub>3</sub> <sup>t</sup> Bu <sub>3</sub> ) <sub>2</sub> Pu	–552.6833	180	–552.3058	170.0 <sup>b</sup>	8.7
			–550.6870	160.0 <sup>b</sup>	46.0

<sup>a</sup>  $\Delta E_{B-L} = E_{\text{bent}} - E_{\text{linear}}$  where  $E_{\text{bent}}$  and  $E_{\text{linear}}$  are the total energies at the optimized geometries in the bent and linear geometries, respectively. <sup>b</sup> Because the linear structures are the minima for the (C<sub>6</sub>H<sub>3</sub><sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>An complexes, the energies for their “bent” structures are calculated at fixed values of  $\theta = 160^\circ$  and  $\theta = 170^\circ$ .

**Figure 2.** Fully optimized PW91 structures for (a) ( $\eta^6$ -1,3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)<sub>2</sub>U and (b) ( $\eta^6$ -1,3,5-C<sub>6</sub>H<sub>3</sub>Bu<sub>3</sub>)<sub>2</sub>U. The structures were optimized without imposing specific symmetry constraints on the final geometries.<sup>22</sup>

Some recent results in the chemistry of sandwich complexes of substituted-Cp ligands, such as ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>Ba (R = Me, CHMe<sub>2</sub>),<sup>23</sup> ( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>R)<sub>2</sub>Pb (R = H, Me, SiMe<sub>2</sub><sup>t</sup>Bu),<sup>24</sup> and ( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>R)<sub>2</sub>Ti (R = SiMe<sub>3</sub>, SiMe<sub>2</sub><sup>t</sup>Bu),<sup>25</sup> demonstrate analogous dependence of linear or bent structure on the steric bulk of the ligands.

In summary, our DFT calculations have shown that, unlike linear Bz<sub>2</sub>M complexes of the transition metal sandwich complexes, the Bz<sub>2</sub>An actinide sandwich complexes intrinsically prefer a bent structure. The full geometry optimizations show that when the C<sub>6</sub>H<sub>6</sub> ligand is substituted with a very bulky arene such as TBB, the steric repulsion overcomes the electronic preference for a bent geometry. Thus, we predict that (TBB)<sub>2</sub>An complexes will exhibit a linear geometry but that this linear geometry is an exception to the preferred bent geometry of Bz<sub>2</sub>An complexes.

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