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A Brief Computational Study of Decamethyldizincocene Formation via Diethylzinc and Decamethylzincocene

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We have used density functional theory and ab initio methods to study different mechanistic possibilities for the formation of decamethyldizincocene from the reaction between decamethylzincocene and diethylzinc. Our results suggest that decamethyldizincocene could form from the combination of two pentamethylcyclopentadienylzinc radicals. More importantly, our data show that homolytic dissociation of decamethylzincocene into pentamethylcyclopentadienylzinc and pentamethylcyclopentadienyl radicals is 6.7 kcal/mol less costly than the analogous dissociation of zincocene. If such an energy difference is coupled with the fact that the activation barrier to form the half-sandwich product pentamethylcyclopentadienylethylzinc is 11.8 kcal/mol more costly than to form cyclopentadienylethylzinc, we can rationalize why dizincocene does not form experimentally.

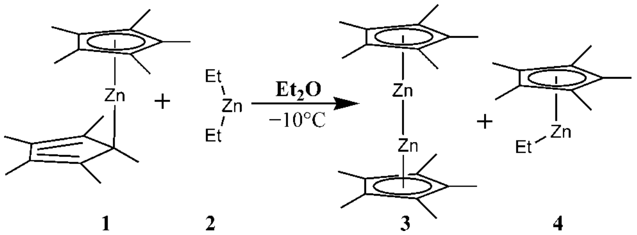
Introduction

Four years ago, the Carmona group published the first synthesis of decamethyldizincocene (**3**),[1] the first compound to contain a direct bond between two Zn atoms (Scheme 1). Research groups had been trying to synthesize these types of compounds (with direct bonds between first-row transition metals) for years without any success. Intriguingly, a graduate student in the Carmona group discovered **3** while attempting to synthesize the half-sandwich Zn complex with the formula $Zn(\eta^5\text{-}C_5(CH_3)_5)(C_2H_5)$ (**4**) by reacting decamethylzincocene (**1**) with $ZnEt_2$ (**2**). The desired molecule (**4**) does form during this reaction, but it is only the minor product. The authors have noted that this process seldom produces yields of **3** higher than 30%. More often, yields are much less, and sometimes **3** does not form in any detectable amount at all (despite careful efforts to reproduce the reaction conditions).[2]

Numerous publications have provided a comprehensive understanding of the properties of **3**. Schaefer and co-workers have completed four papers on various structural properties of **3** and other dimetallocenes.[3–6] Xie and Fang contributed a thorough study on the bonding structure of **3**.[7] Kress gave an in-depth analysis of the molecular orbitals and vibrational structure of **3**.[8] Liu et al. studied the aromaticity of dizinc and zinc half-sandwich complexes.[9] Carmona and co-workers published two follow-up works that include a more efficient synthesis[10] of **3** involving $ZnCl_2$ and $KC_5(CH_3)_5$ as well as an in-depth discussion of more related experimental work.[2] Still, there has been no publication on the most intriguing aspect of this compound: what is the mechanism of its formation via (**1**) and (**2**)?

If the methyl groups of **1** and **3** are replaced with hydrogens, they become zincocene and dizincocene, respectively. Curiously, it has been discussed that reacting ZnR_2 (R = Me, Et, iPr, Ph, and others) and zincocene will not form dizincocene in any yield, and only **2** and $ZnPh_2$ will form **3** when reacted with **1**.[2] Obviously, the methyl groups of **1** allow for the formation of **3**, but their exact role needed a detailed investigation. Because of the complexity of this reaction, we have focused solely on **2** in this work, and we will explore the effects of different ZnR_2 reactants in future publications.

SCHEME 1: Reaction of $Zn(\eta^5\text{-}C_5(CH_3)_5)(\eta^1\text{-}C_5(CH_3)_5)$ with $ZnEt_2$ To Form $Zn_2(\eta^5\text{-}C_5(CH_3)_5)_2$ and $Zn(\eta^5\text{-}C_5(CH_3)_5)(C_2H_5)$



1 **2** **3** **4**

Methods

Calculations on the reactants, products, intermediates, and transition states along the reaction paths of formation of dizincocene and **3** were performed, and the resultant geometries for dizincocene formation were used (with methyl groups added) to find the intermediates and the transition states along the formation path of **3**. This facilitates a thorough comparison of these two processes. The formation reactions of the dizinc products were studied from two hypothetical perspectives: (1) neutral charge electrostatic attraction and rearrangement of the reactants, and (2) radical dissociation and recombination of the reactants. For the sake of brevity, an ionic dissociation pathway will not be presented due to prohibitive energy costs: above 100 kcal/mol for heterolytic dissociation of **1** into $Zn[\eta^5\text{-}C_5R_5]^-$ and $[C_5R_5]^+$ ions.[11]

Gaussian 03[12] was used for all calculations. Geometry optimizations were performed using the popular Kohn−Sham

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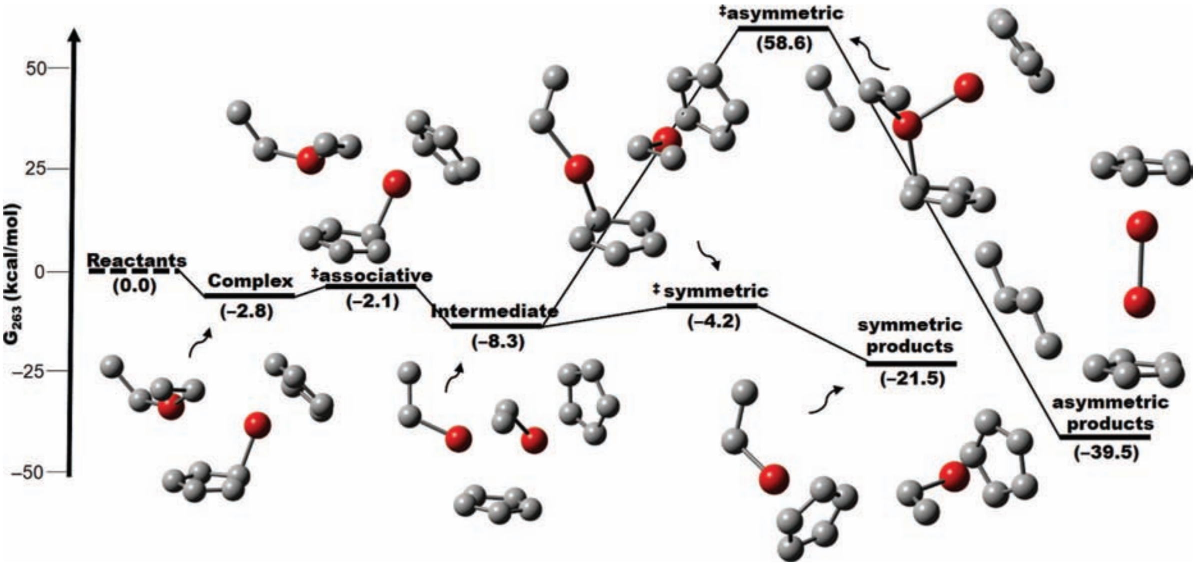


Figure 1. Reaction pathway of $ZnEt_2$ reacting with zincocene (hydrogens removed for clarity). Zinc atoms appear in red.

method B3LYP[13,14] with Dunning's cc-pVDZ basis set[15] whereas the Pople 6-31G* basis set[16] was used exclusively for the Zn atoms. This basis set combination produces a geometry for **3** that agrees very well with the latest experimental neutron diffraction geometry, in which the Zn−Zn bond length is 2.292 (±1) Å.[17] The cc-pVDZ (with 6-31G* for Zn) basis set produces a length of 2.293 Å. However, a more popular selection like cc-pVDZ (with LANL2DZ pseudopotential basis set for Zn) gives an elongated bond length of 2.469 Å. All transition states were analyzed and confirmed by multiplying the imaginary mode Cartesian displacements by a scale factor (which varied depending on the transition state), adding them to the saddle point geometries, and performing geometry optimizations to connect the transition states to their corresponding minima.

All thermodynamic energies reported in this work are free energies at the temperature of the initial experiment,[2] 263 K (G_{263}). Møller−Plesset second-order perturbation theory (MP2)[18] single-point calculations were performed with the B3LYP geometries. Solvent effects were also considered by employing an integral equation formalism polarizable continuum model (PCM) appropriate for diethyl ether with the MP2 single-point energies.[19] The final energies were derived by adding the B3LYP free energy corrections to the PCM-MP2 single-point energies. Our current computational resources do not allow for the computation of MP2 Hessians for molecules of this size, so the B3LYP thermal data and optimized geometries are our best alternative.

To compute the homolytic dissociation energies of $Zn(\eta^5\text{-}C_5R_5)(\eta^1\text{-}C_5R_5)$ into $Zn(\eta^5\text{-}C_5R_5)^\bullet$ and $C_5R_5^\bullet$ radicals (R = H, CH_3), the counterpoise optimization method proposed by Simon et al.[20] was employed. These unrestricted B3LYP energies were improved using spin-projected MP2 (PMP2) in an analogous fashion to the electrostatic mechanism. PMP2 was used because there is a large spin contamination effect for the $C_5R_5^\bullet$ species ($\langle S^2\rangle \approx 0.97$, and $\langle S^2\rangle \approx 0.78$ after annihilation), due to the unpaired electron participating in the π system. Solvent effects were considered for the homolytic dissociation energies by employing the same PCM model as for the neutral charge electrostatic mechanism. The overall dissociation energies were derived by taking the B3LYP geometries and computing PCM-MP2 single-point energies with them. The counterpoise correction was obtained by computing counterpoise-corrected single-point MP2 energies (from the counterpoise optimized geometries of the parent zincocenes). Finally, the B3LYP free energy corrections were added. The exact same procedure was employed to compute the association energy of **3** from two $Zn(\eta^5\text{-}C_5(CH_3)_5)^\bullet$ radical units.

Results and Discussion

Neutral Charge Electrostatic Dizincocene Formation. We have discovered that **2** can attack zincocene in a sideways fashion, cutting open the sandwich structure while forming an intermediate (Figure 1). The activation barrier for this process is just 0.7 kcal/mol (from the complex to ‡ associative). At this point in the reaction, the intermediate can do one of the following two things. It can overcome a 4.1 kcal/mol symmetric barrier (‡ symmetric) to form two equivalents of symmetric products $Zn(\eta^5\text{-}C_5H_5)(C_2H_5)$, which are considerably more stable than the reactants (−21.5 kcal/mol). On the basis of their experimental data, the Carmona group hypothesized a mechanism like this last year.[21] Alternatively, the intermediate can overcome an asymmetric barrier (‡ asymmetric) with a steep 66.9 kcal/mol activation barrier to form the asymmetric products, dizincocene and butane. Obviously, the activation barrier for the asymmetric process is much too high relative to the symmetric process to form dizincocene, even though the asymmetric products are much more thermodynamically stable than the reactants (−39.5 kcal/mol).

Neutral Charge Electrostatic Decamethyldizincocene Formation. Not surprisingly, the reactive species in the analogous formation of **3** are similar in geometry (excluding the methyl groups) compared to the dizincocene pathway (Figure 2). Note that the MP2 single-point energies predict that the reactants will immediately reach the intermediate without an associative barrier. Although the asymmetric barrier is energetically similar to the dizincocene reaction (64.2 vs 66.9 kcal/mol), the symmetric barrier is much higher in this case (15.9 vs 4.1 kcal/mol), probably due mostly to steric repulsions between the ethyl and methyl groups. However, this difference is not enough to suggest that **3** forms via the asymmetric barrier. Based on these results, it is reasonable to conclude that **3** does not form via simple neutral charge electrostatic attraction and rearrangement of **1** and **2**.

Radical Dissociation of Parent Zincocenes. There apparently is a moderate difference in the homolytic dissociation

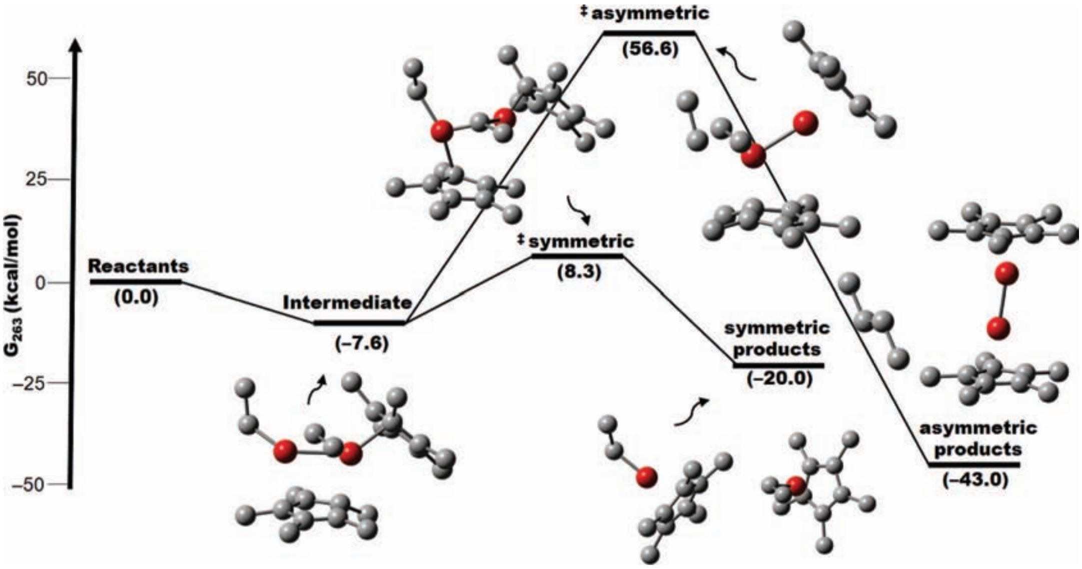
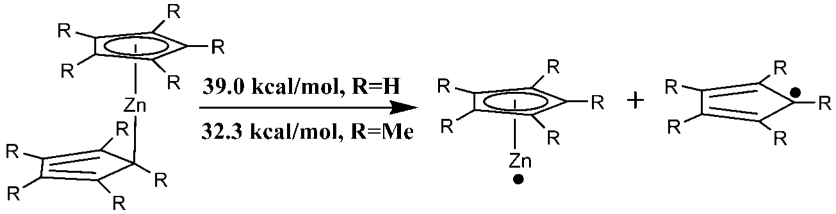


Figure 2. Reaction pathway of $ZnEt_2$ reacting with decamethylzincocene (hydrogens removed for clarity). Zinc atoms appear in red.

SCHEME 2: Dissociation of $Zn(\eta^5\text{-}C_5R_5)(\eta^1\text{-}C_5R_5)$ into $Zn(\eta^5\text{-}C_5R_5)^\bullet$ and $(C_5R_5)^\bullet$ Radicals



energies of zincocene (39.0 kcal/mol) and **1** (32.3 kcal/mol) due to the methyl groups stabilizing the resulting radicals from the cleavage of **1** (Scheme 2). These data alone are not significant enough for us to suggest that dizincocene formation will not occur, as it does not experimentally. On the other hand, if this difference in dissociation energy is coupled with the large difference in the symmetric activation barriers in the formation of **4** and $Zn(\eta^5\text{-}C_5H_5)(C_2H_5)$ (15.9 vs 4.1 kcal/mol), it is possible that during the formation of **3**, the homolytic dissociation of **1** competes with the formation of the symmetric products (32.3 vs 15.9 kcal/mol). Further, dizincocene formation would not be possible due to a prohibitive energy difference between these two processes (39.0 vs 4.1 kcal/mol).

Conclusion

This study has excluded the possibility of decamethyldizincocene forming via a neutral charge electrostatic or ionic dissociation mechanism. Our results therefore show that the most likely scenario is that, experimentally, some **1** reacts with **2** to form **4** through ‡ symmetric, releasing about 20.0 kcal/mol. Once enough energy has been accumulated this way, the remaining **1** in solution could begin to dissociate into $Zn(\eta^5\text{-}C_5(CH_3)_5)^\bullet$ and $C_5(CH_3)_5^\bullet$ radicals. Two $Zn(\eta^5\text{-}C_5(CH_3)_5)^\bullet$ units should readily combine to form (**3**), given their considerable association energy (42.6 kcal/mol). This large energy release could then further fuel the radical dissociation of **1** and consequently form more **3**. Our conclusion therefore supports the experimental hypothesis that **3** forms via the combination of two $Zn(\eta^5\text{-}C_5(CH_3)_5)^\bullet$ radical units.[2]

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Supporting Information Available: Optimized Cartesian geometries for all stationary points are available free of charge via the Internet at http://pubs.acs.org.

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