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$\mathrm{Cp_2ZrCH(SiMe_3)CCCH(SiMe_3)}$: A Five-Membered 1-Zirconacyclopent-3-yne?

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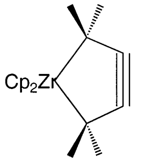
Density functional theory calculations at the B3LYP level were performed to study the electronic structure of a recently synthesized zirconocene complex, $\mathrm{Cp_2ZrCHRCCCHR}$ ($\mathrm{R = SiMe_3}$). Through detailed bonding analyses and stability studies, we conclude that the originally proposed metallacyclopentyne form cannot adequately describe the complex. Instead, a resonance hybrid between a cumulene complex form and a metallacyclopentyne Lewis structure is required to account for the structure and stability of the complex.

Introduction

Recently, Suzuki and co-workers reported the synthesis and characterization of a five-membered metallacyclic complex,[1] $\mathrm{Cp_2ZrCHRCCCHR}$ ($\mathrm{R = SiMe_3}$). On the basis of the X-ray structural data, NMR spectroscopic investigation, and reactivity studies, the complex has been considered as 1-zirconacyclopent-3-yne (**A**), a



A

five-membered cyclic alkyne. The isolability of such a complex is remarkable, because cyclic alkynes are highly strained and tend to be unstable.[2] Theoretically, the strain energies of cyclopentyne and cyclohexyne have been estimated to be 74.8 and 41.2 kcal/mol, respectively.[2]

Questions can immediately be raised. Where does the stability of the complex originate in view of such a highly strained structure? How important are other Lewis structures in addition to the metallacyclopent-3-yne (**A**) to the stability? What would the strain energy be if the complex were classified as a cyclic pentyne? In this paper, we attempt to answer these questions with the aid of density functional theory calculations. For comparison, we will also report our results on a related complex, $\mathrm{Cp^*_2ZrCRCCCR}$ ($\mathrm{R = SiMe_3}$), reported as zirconacyclocumulene, by Rosenthal and co-workers.[3,4]

Computational Methods

In the calculations, $\mathrm{SiMe_3}$ and Cp* have been modeled by $\mathrm{SiH_3}$ and Cp, respectively. Full geometry optimizations and frequency calculations of the model complexes have been performed at the Becke3LYP (B3LYP) level of density functional theory.[5] The effective core potentials (ECPs) and basis sets (sddall)[6] of Stuttgart/Dresden were used to describe Ti, Zr, Hf, and Si. The 6-31G basis set was used to describe the atoms in the Cp ligands, while the 6-31G** basis set was used for all other atoms.[7] All the calculations are performed with the Gaussian 98 software package.[8] Molecular orbitals obtained from the B3LYP calculations were plotted using the Molden v3.5 program written by Schaftenaar.[9] The electron density analysis was carried out with MOPLOT 2.4.[10]

Results and Discussion

Structural Aspects. To answer the questions raised in the Introduction, we performed B3LYP density functional theory calculations on the model complex $\mathrm{Cp_2ZrCH(SiH_3)CCCH(SiH_3)}$. The important structural

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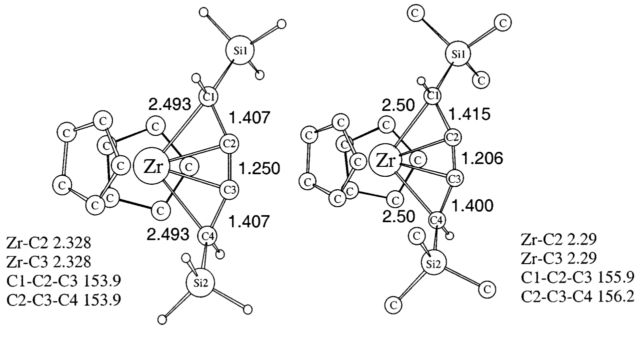
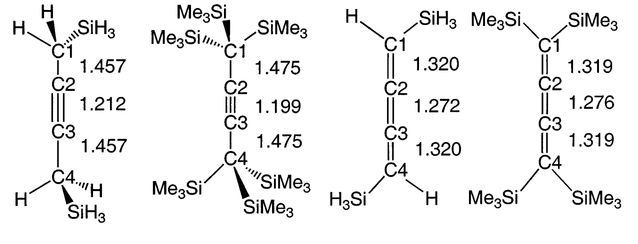


1a (Calculated) **1b** (Experimental)

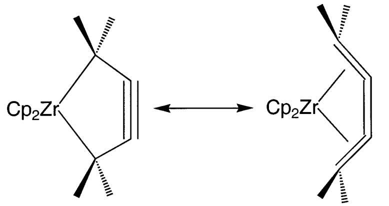
Figure 1. Selected structural parameters of Cp$_2$ZrCHR-CCCHR (R = SiH$_3$ (calculated, **1a**), SiMe$_3$ (experimental, **1b**)). For the purpose of clarity, hydrogen atoms on the Cp rings and methyl groups are omitted. Bond lengths are in angstroms, and bond angles are in degrees.



2a (Calculated) **2b** (experimental) **3a** (Calculated) **3b** (experimental)

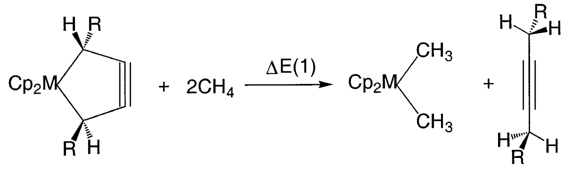
Figure 2. Selected structural parameters of (SiH$_3$)CH$_2$C≡CCH$_2$(SiH$_3$) (calculated, **2a**), (SiMe$_3$)$_3$CC≡CC(SiMe$_3$)$_3$ (experimental, **2b**), (SiH$_3$)CH=C=C=CH(SiH$_3$) (calculated, **3a**) and (SiMe$_3$)$_2$C=C=C=C(SiMe$_3$)$_2$ (experimental, **3b**). Bond lengths are in angstroms, and bond angles are in degrees.

parameters of the B3LYP-optimized geometry of the model complex are summarized in Figure 1, structure **1a**. For comparison, the corresponding structural parameters of the X-ray structure of Cp$_2$ZrCH(SiMe$_3$)-CCCH(SiMe$_3$) are shown by structure **1b**.[1] The calculated bond lengths and bond angles are in good agreement with the experimental values. Both the X-ray and calculated structures show some interesting structural features. The Zr−C1 and Zr−C4 bond distances are much longer, by 0.2 Å, than the Zr−C2 and Zr−C3 distances, suggesting that the Lewis structure (**A**) representing the metallacyclopent-3-yne cannot adequately describe the structure. Figure 2 gives the X-ray structures of (SiMe$_3$)$_3$CC≡CC(SiMe$_3$)$_3$[11] and (SiMe$_3$)$_2$-C=C=C=C(SiMe$_3$)$_2$[12] together with structures of the corresponding calculated model molecules. Comparing the structures in Figures 1 and 2, we can see that the carbon−carbon bond distances in the metallacyclic ring of the zirconocene complex have values between the alkyne and cumulene structures shown in Figure 2. Therefore, a resonance hybrid (**B**) between a cyclopentyne form and a cumulene complex is likely the best description of the X-ray and calculated structures of the title compound.



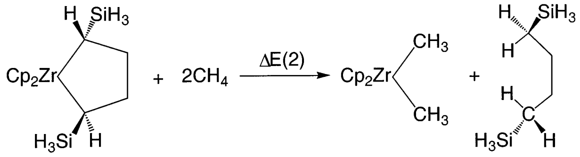
B

Ring Strain for a Metallacyclopent-3-yne. If the title compound were considered as 1-zirconacyclopent-3-yne (**A**), what would the ring strain energy be for such a highly strained species? To answer this question, we designed an isodesmic reaction[13] (eq 1) to calculate the reaction energy (ΔE). In view of eq 1, one would expect that $\Delta E(1)$ could give the information regarding the ring strain energy and should be negative, because the species on the right-hand side of the equation are free of ring strain. Surprisingly, our calculations give unexpected results. $\Delta E(1)$ for Cp$_2$ZrCH(SiH$_3$)CCCH(SiH$_3$) was calculated to be positive and has a value of 18.3 kcal/mol. To validate the isodesmic reaction designed above, we also calculated ΔE(2) for the isodesmic reaction given by eq 2. The $\Delta E(2)$ reaction energy was calculated to be −5.9 kcal/mol, which is negative and small. This result is understandable, because the ring strain energy of the zirconocene complex on the left-hand side of eq 2 is expected to be small.



(1)

R	M	ΔE(1)(kcal/mol)	R	M	ΔE(1)(kcal/mol)
SiH$_3$	Ti	11.9	CH$_3$	Ti	9.6
	Zr	18.3		Zr	13.4
	Hf	12.8		Hf	7.8



(2)

The large positive $\Delta E(1)$ calculated for eq 1 would imply that the metallacyclopent-3-yne in the equation has no ring strain if one views it as a metallacyclopent-3-yne. The results of calculations suggest that the title compound is highly stable. Once again, we cannot explain the stability if we do not invoke the concept of a resonance hybrid (see **B**). The calculations suggest that the resonance energy derived from the resonance hybrid makes significant contribution to the stability of the title compound. Invoking the concept of a resonance hybrid to describe bonding in organometallic compounds is quite common, in particular for those involving metal−π interactions: e.g., Cp$_2$Zr(diene) and Fe(CO)$_3$(diene).[14,15] Following the notation used by

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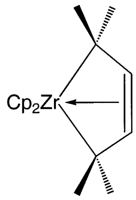
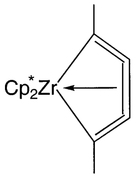
Rosenthal and co-workers,[3,4] we can also have an alternative Lewis structure (**C**), which emphasizes the interaction between the metal center and the alkyne bond of the metallacyclopentyne ring, to describe the bonding in $Cp_2\overline{ZrCH(SiMe_3)CCC}H(SiMe_3)$. However, if we employ such a Lewis structure (**C**), we would expect an incredibly large Zr−alkyne interaction energy in order to give the very large positive Δ*E*(1), because there is a substantially large ring strain energy that could be derived from a five-membered ring containing a C≡C bond.



C

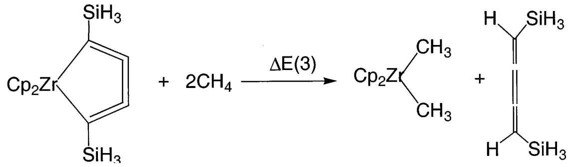
We also expanded our calculations by examining the influence of the metal center and the substituent on Δ*E*(1). The results are presented in eq 1 for comparison. Complexes having silyl substituents apparently have greater Δ*E*(1) values in comparison to those having alkyl substituents, suggesting that silyl substituents have a stabilizing effect on the ring complexes. Interestingly, the Zr complexes have significantly larger reaction energies Δ*E*(1) in comparison to the Ti and Hf complexes. This seems unexpected, in view of the known periodic trend that metal−ligand interactions usually increase down a group of transition metals.[16] A tentative explanation is given below, though other explanations are also possible. The magnitude of the reaction energy Δ*E*(1) reflects a balance between the metal−ligand (the four ring carbons) interaction energy and the ring strain energy of a given ring complex. For the Ti complexes, the metal−ligand interaction energy is expected to be smaller, on the basis of the periodic trend mentioned above. For the Hf complexes, the metal−ligand interaction is expected to be the strongest. However, the ring strain energy increases at the same time as the increase in the metal−ligand interaction. This is because the stronger the metal−ligand interaction, the more distorted the structural unit of the organic ligand. The results shown in eq 1 indicate that the Zr metal center provides the optimal balance between the two types of energies.

$Cp^*_2\overline{ZrC(R)CCC}(R)$. In 1994, Rosenthal and co-workers reported the synthesis and structure of a related five-membered zirconacyclocumulene, $Cp^*_2\overline{ZrC(R)CCC}(R)$ (R = $SiMe_3$).[3,4] Instead of using a resonance hybrid, Rosenthal et al. used a different Lewis structure (see **D**), emphasizing the interaction between the metal center and the π-bond between the two β-carbons.[4,17,18]



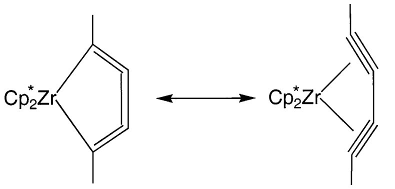
D

This type of interaction has been confirmed by a recent molecular orbital study of Jemmis and co-workers.[19−21] We designed an isodesmic reaction, based on the model complex $Cp_2\overline{ZrC(SiH_3)CCC}(SiH_3)$ (eq 3), to evaluate the ring strain energy if the zirconocene complex is considered as a metallacyclocumulene.



(3)

Δ*E*(3) was calculated to be 23.1 kcal/mol. Again, the large positive value of Δ*E*(3) indicates that the zirconocene complex does not have a ring strain if it is described as a metallacyclocumulene. Even taking into account the additional interaction between the metal center and the π-bond between the two β carbons, i.e., the Lewis structure **D**, one still cannot understand the large positive value of Δ*E*(3). One does not expect that the additional interaction is large enough to offset the ring strain energy and at the same time give that amount of extra stabilization energy. In 1984, Johnson and co-workers analyzed the strain energy of a bent butatriene. The strain energy is about 28 kcal/mol when the angles C1−C2−C3 and C2−C3−C4 are about 150°.[22] Therefore, the stability of $Cp^*_2\overline{ZrC(R)CCC}(R)$ can only be described by the hybrid resonance **E**. The importance of the diyne complex form, i.e., the Lewis structure on the right-hand side of **E**, cannot be overlooked. As pointed out by Jemmis and co-workers, the power of Cp_2M (M = Ti, Zr) in stabilizing strained π bonds is remarkable.[19]



E

Electron Density Analyses. To further understand the nature of bonding between the bent-zirconocene fragment (Cp_2Zr) and the cumulene or diyne ligand for the two interesting organometallic compounds discussed above, analyses of the Laplacian, $\nabla^2\rho$, of the B3LYP electron density were performed on the basis of Bader's atoms-in-molecules theory.[23] Parts a and b of Figure 3

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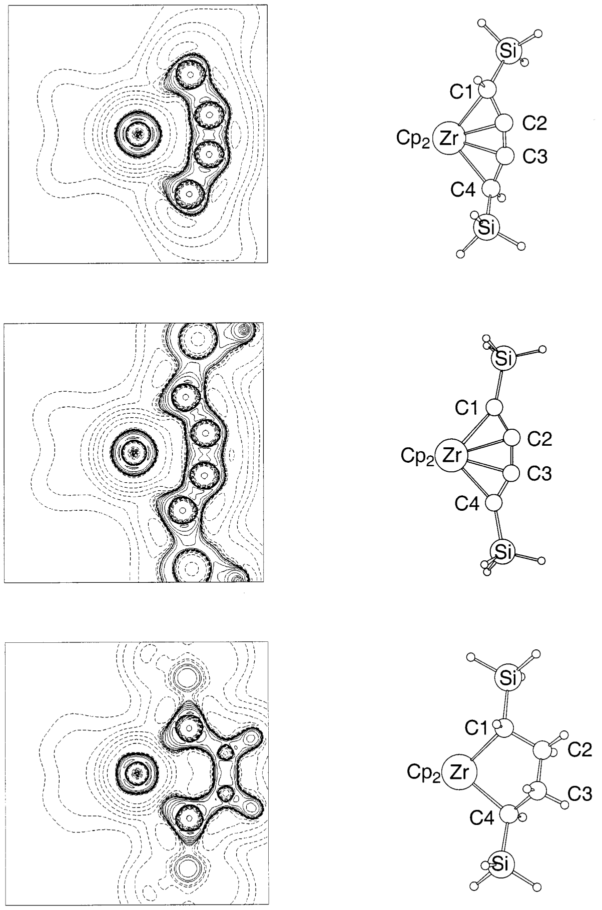

Figure 3. Laplacian plots of electron density for (a, top) $Cp_2ZrCHRCCCHR$ (R = SiH_3), (b, middle) $Cp_2ZrCRCCCR$ (R = SiH_3) on the plane defined by Zr−C2−C3, and (c, bottom) $Cp_2ZrCHRCH_2CH_2CHR$ (R = SiH_3) on the plane defined by Zr−C1−C4.

show the Laplacian plots for $Cp_2ZrCH(SiH_3)CCCH(SiH_3)$ and $Cp_2ZrC(SiH_3)CCC(SiH_3)$, respectively. In the contour plots, solid lines represent local electron density concentration ($\nabla^2\rho < 0$) and dashed lines represent local electron density depletion ($\nabla^2\rho > 0$). Parts a and b of Figure 3 show similar features of the electron density around the metal centers. Four concentrations appear around the Zr center for each of the two complexes. This feature of electron density is very common for a bent group 4 metallocene complex having a formal d^2 electron configuration at the metal center: e.g., $Cp_2Ti(\eta^2\text{-HBcat}')_2$,[24,27] $Cp_2Ti(PMe_3)(\eta^2\text{-HBcat}')$,[25−27] and $Cp_2Ti(\eta^2\text{-}trans\text{-}RC{\equiv}CSiHR_2)$.[28,29] The four concentrations can be associated with an occupied a_1 ($d_{x^2-y^2}$) orbital of a bent Cp_2Zr fragment.[29,30] Clearly, the Laplacian electron density plots given here provide additional support to the claim that Lewis structures having a cumulene complex or a diyne complex formulation make significant contributions to the structural stabilities of the two complexes studied in this paper. The similarity in the bonding situations in the two metallacyclic complexes was also emphasized by Jemmis and co-workers.[19] For comparison, we also calculated the Laplacian of electron density for $Cp_2ZrCH(SiH_3)CH_2CH_2CH(SiH_3)$, a metallacyclopentane which does not have an alternative Lewis structure in its bonding description, except for the metallacyclopentane formulation. Part c of Figure 3 illustrates the Laplacian plot. Interestingly, there are also four concentrations around the metal center. However, these four concentrations are associated with the b_2 (d_{xy}) orbital of a bent Cp_2Zr fragment instead of the a_1 ($d_{x^2-y^2}$) orbital discussed above for the other two complexes, in which resonance hybrids of two Lewis structures have to be invoked. Two of the four concentrations around the metal center appear along the Zr−C σ-bonding directions, indicating covalent bonding interactions between Zr and the two α-carbon atoms. The difference in the feature of electron density around the metal centers reflects a fundamentally different bonding nature between $Cp_2ZrCH(SiH_3)CH_2CH_2CH(SiH_3)$ and the two complexes discussed above. We have to invoke the concept of resonance to describe the bonding in the two complexes discussed above. For $Cp_2ZrCH(SiH_3)CH_2CH_2CH(SiH_3)$, the metallacyclopentane Lewis structure is enough to describe the bonding situation.

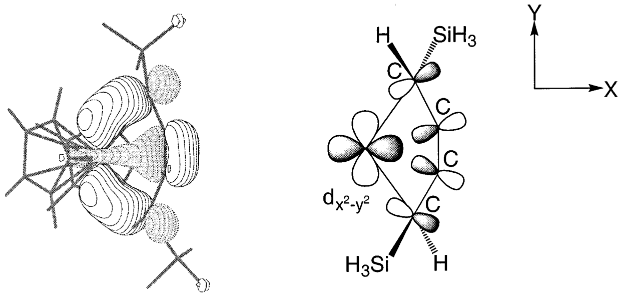

Figure 4. Spatial plots of the highest occupied molecular orbital (HOMO) for the $Cp_2ZrCHRCCCHR$ (R = SiH_3). The molecular orbital was obtained from the B3LYP calculations.

Comments on the Structural and Reactivity Aspects. The X-ray and calculated structures show that the C1−C2 and C3−C4 bonds (Figure 1) are shorter than the single C−C bonds of $(SiMe_3)_3CC{\equiv}CC(SiMe_3)_3$ (Figure 2),[11,12] further suggesting that a metallacyclopent-3-yne description is not enough, because one would expect a ring strain in the metallacyclic structure to cause a bond lengthening. The C2−C3 bond (Figure 1) is only slightly longer than the C≡C bond of $(SiMe_3)_3CC{\equiv}CC(SiMe_3)_3$ (Figure 2). Nevertheless, the bond is not much longer than the central C=C bond of a silyl-substituted butatriene, $(SiMe_3)_2C{=}C{=}C{=}C(SiMe_3)_2$. On the basis of the cumulene complex description (**B**), it is expected that the metal (d)→π^* back-bonding interaction between the d^2 Cp_2Zr fragment[29,30] and the

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cumulene ligand should increase the π-bonding interaction in the central C═C bond of the cumulene ligand. Figure 4 shows the plot of the HOMO, illustrating the metal (d)→π^* back-bonding interaction.[19]

Experimentally, it has been shown that hydrolysis of $Cp_2\overline{ZrCHRCCC}HR$ by acid gave a but-3-yne, $H_2RCC\equiv CCH_2R$.[1] As mentioned above, a resonance hybrid between a cumulene complex form and a metallacyclopentyne Lewis structure is the most reasonable description of the structure. Therefore, it is not surprising that the reactivity displayed in the hydrolysis is related to the metallacyclopentyne form.

Conclusion

Detailed electronic structure studies of $Cp_2\overline{ZrCHRCCC}HR$ (R = $SiMe_3$) suggest that the zirconocene complex can be well described by a resonance hybrid between a metallacyclopentyne form and a cumulene complex Lewis structure. An approach based on isodesmic reactions suggests that the cumulene complex form contributes significantly to the stability of the zirconocene complex. The originally proposed metallacyclopentyne form cannot describe well the structural behavior and the stability of the complex. In a parallel study on the related complex $Cp^*_2\overline{ZrC(R)CCC}(R)$ (R = $SiMe_3$), one finds that a resonance hybrid between a metallacyclocumulene and a diyne complex is also required to adequately describe its structure and stability.

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