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Dependence of the Structure and Stability of Cyclocumulenes and Cyclopropenes on the Replacement of the CH_2 Group by Titanocene and Zirconocene: A Density Functional Theory Study

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Density functional theory (DFT) studies of the energetics of the isomers of C_5H_4—cyclocumulene (**1**), ethynylcyclopropene (**2**), diethynylmethane (**3**), and their organometallic analogues obtained by replacing the CH_2 groups by Cp_2Ti and Cp_2Zr (**4**−**6**)—show that the relative energies of the hydrocarbons are dramatically altered in the transition-metal analogues. The metallacyclocumulenes are comparable in energy to **5** and **6**. The relative energies also explain the experimental observation that the metallacyclopropene (**5**) is more favorable for the Ti complex. Substituents on the carbon skeleton help to fine-tune the energetics. The bonding situations in **4** and the recently characterized five-membered zirconacyclopentyne complex **9** are very similar and are in tune with their structures.

Introduction

A major part of organometallic chemistry can be viewed profitably as resulting from the replacement of small groups in organic structures by transition-metal fragments.[1] The transformation of the organic moiety as a result of the attachment of a metal fragment is so delicate and specific that seemingly similar fragments make large changes in the system.[2] Here we consider the relative thermodynamic stabilities of cyclocumulene (**1**; Chart 1), alkynylcyclopropene (**2**), dialkynylmethane (**3**), and the isomers obtained by the replacement of the CH_2 group by Cp_2Ti and Cp_2Zr. The resulting metallacyclocumulenes (**4**), metallacyclopropenes (**5**), and metal bis(acetylides) (**6**) are important intermediates in the transformations of conjugated and nonconjugated alkadiynes by Cp_2Ti and Cp_2Zr.[3,4] The reactivities of the Ti and the Zr complexes differ dramatically. Using similar reaction conditions where **4** is generated, Ti forms the C−C-coupled structure **7**, whereas Zr favors the structure **8**, where coupling between the two internal carbon atoms is absent. The three-membered metallacyclopropene **5** with M = Ti and $R^1 = R^2 = SiMe_3$ has been reported recently.[5] Attempts to synthesize similar complexes for Zr have been unsuccessful so far. On the other hand, the five-membered metallacyclocumulene complex **4**, as well as the bis(acetylide) complex **6**, are known for both Ti and Zr.[6−9] The experimentally reported structures of **4**−**6** are given in Chart 2. A recent report also describes a similar structure of a five-membered zirconacyclopentyne complex (**9**).[10] The structural similarity between **4** and **9** prompted us to compare the nature of bonding in them.

Metallacyclocumulenes are the key intermediates in the C−C single bond cleavage reaction of butadiynes and in different coupling reactions catalyzed by titanocene and zirconocene.[11] The metallacyclocumulenes **4** exist in a dynamic equilibrium with their respective three-membered (η^2) isomers **5** (Scheme 1). The three-membered metallacyclopropenes may also convert to the degenerate alternative through a sliding of the metallocene unit along the butadiyne chain.[12] The bis(σ-alkynyl) complexes of Ti and Zr (**6**) are known to undergo photochemical rearrangement to the cyclocumulenic complex **4**.[9,11] These bis(acetylide) complexes were used for the preparation of homo- and heterobinuclear complexes containing bridging σ−π alkynyl groups between the metal centers.[13] Experimental and

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Chart 1

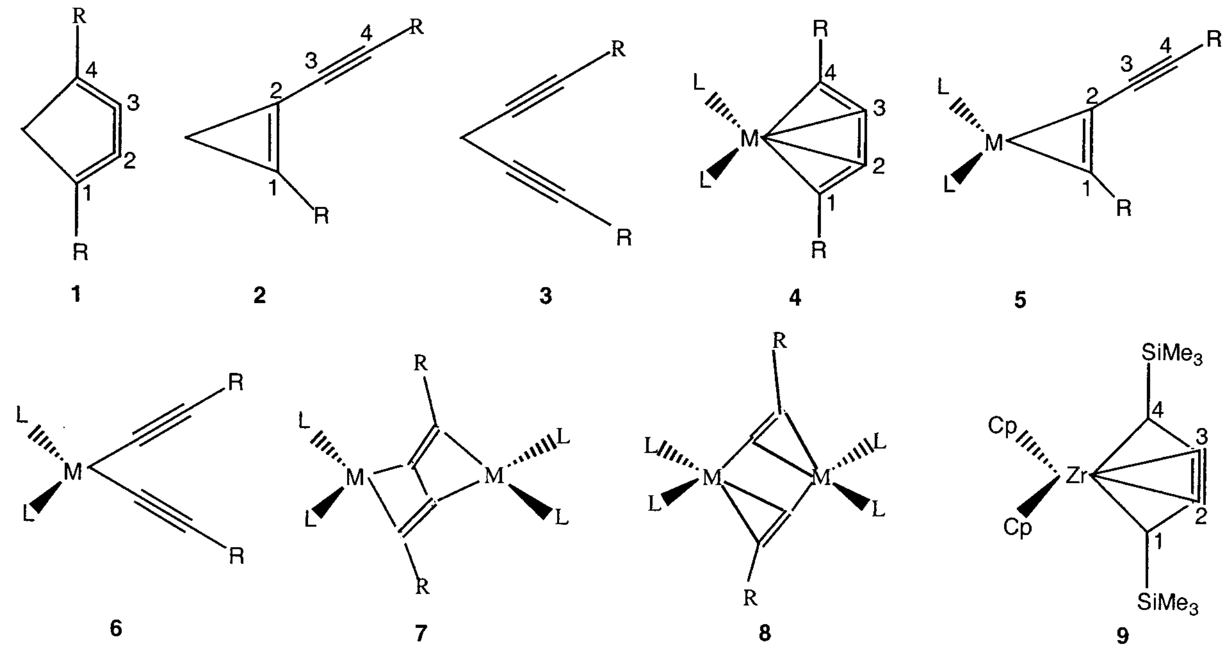
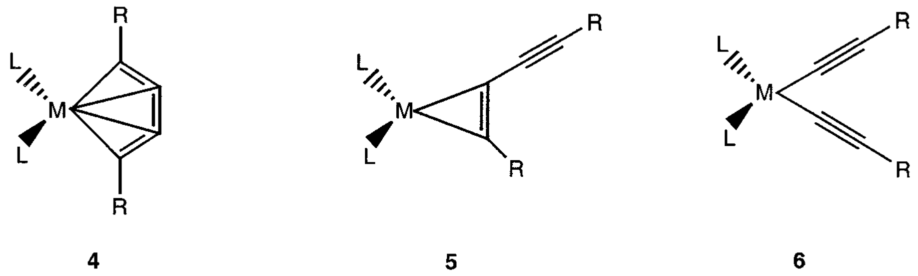


Chart 2



	M	L	R	4	5	6	ref.
i)	Ti	Cp	^{t}Bu	4			7
ii)	Ti	Cp*	$SiMe_3$		5		5
iii)	Ti	$C_5H_4(SiMe_3)$	$SiMe_3$			6	9b
iv)	Zr	Cp	^{t}Bu	4			6
v)	Zr	Cp*	Ph	4			5
vi)	Zr	Cp*	$SiMe_3$	4			5
vii)	Zr	Cp*	Ph			6	9c
viii)	Zr	Cp	CH_3			6	9a
ix)	Zr	$C_5(Me)_4H$	$SiMe_3$			6	9d

theoretical studies are unraveling the details of these intricate sets of reactions.[2,4,6,7] In this paper, we concentrate on the relative stabilities of the cyclopropene, cumulene, and bis(acetylide) structures and their dependence on substituents. A comparison will also be made between the zirconacyclopentyne complex **9** and its cumulenic counterpart. While the relative energies of the organic isomers are part of general knowledge in organic chemistry, a similar understanding is only beginning to take shape in transition-metal organometallics. Our attempt is to contribute to this increasing body of understanding.

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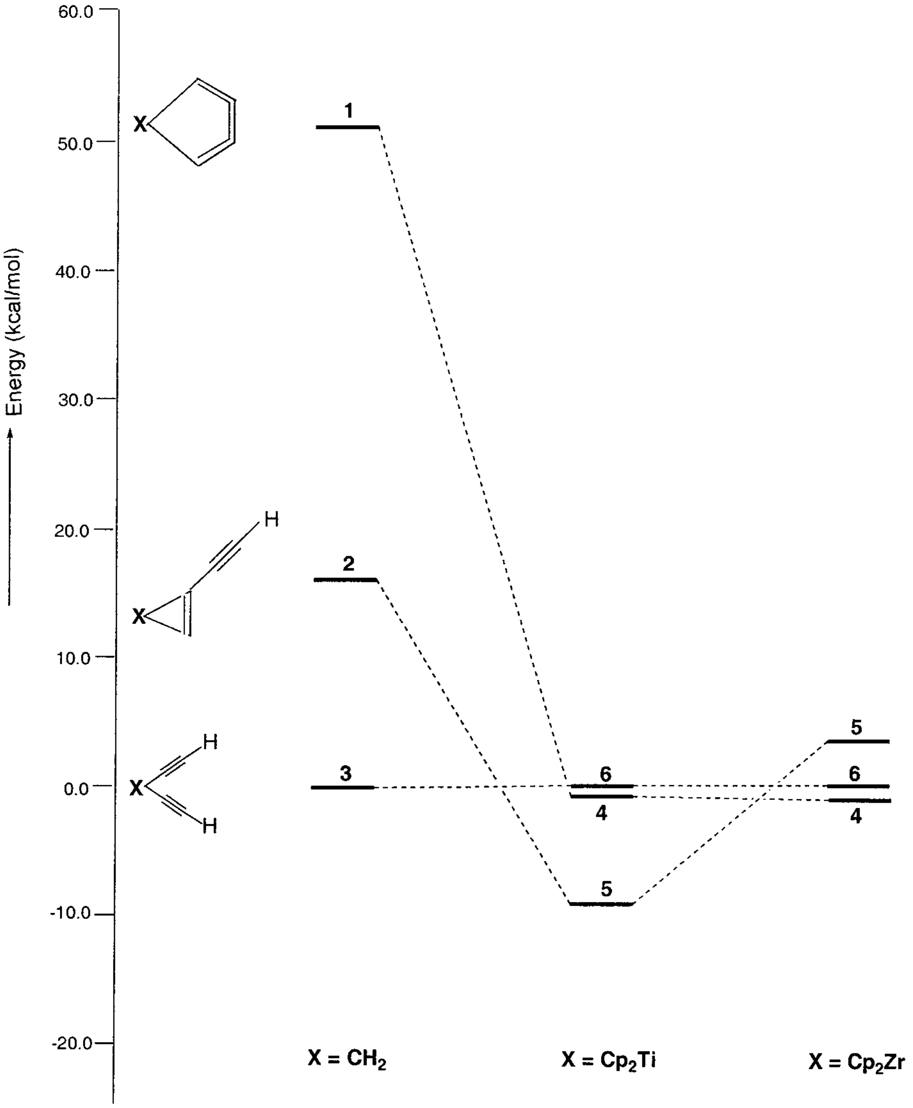
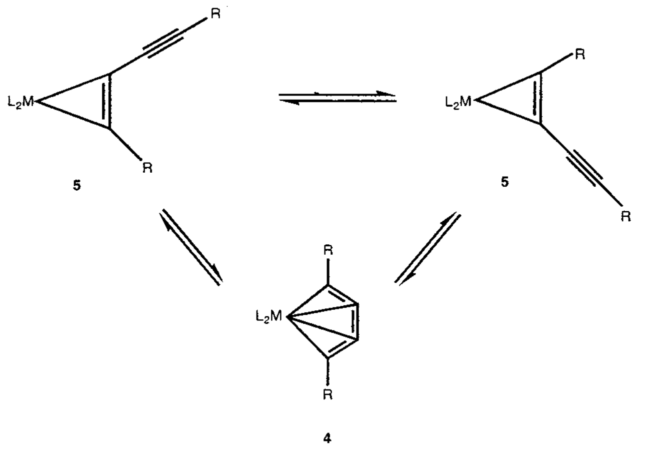


Figure 1. Comparison of relative energies (kcal/mol) of **1**−**3** with that of **4**−**6**, respectively, at the B3LYP level. The structures of **3** and **6** are kept at the reference value of 0.0.

Scheme 1



Computational Details

All the structures were completely optimized using the hybrid HF-DFT method, labeled as B3LYP.[14] This is based on Becke's three-parameter functional[14a] including Hartree−Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke[14b] together with the nonlocal correction for the correlation energy suggested by Lee et al.[14c] We used the LANL2DZ basis set with the effective core potentials (ECP) of Hay and Wadt.[15] Calculations were performed for the complexes **4** and **5** and the transition state connecting **4** and **5** with L = Cp. On the basis of earlier studies, we used H, F, and CN as the butadiyne substituents.[2] All the stationary points (**1**−**9**) and transition states (**TS**) were characterized by vibrational frequency analysis. The nature of bonding was studied through NBO analysis.[16] The Gaussian 94 suite of programs was used for all the calculations.[17]

Results and Discussion

(a) Relative Stabilities of 1−6 and TS Connecting 4 and 5. The relative energies of the organic molecules are as anticipated. When a zero value is

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Scheme 2

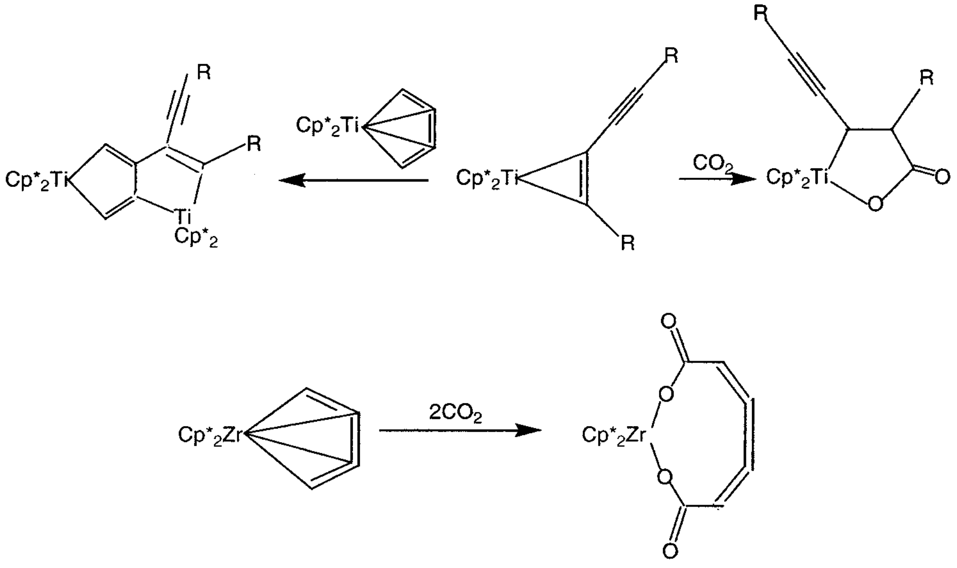

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Table 1. Relative Energies (in kcal/mol) for the Cumulene 4, Cyclopropene 5, Bis(acetylide) 6, and Transition State TS Connecting 4 and 5 at the B3LYP/LANL2DZ Level Including ZPVE[a]

metal	ligand	substituent (R)	4	5	6	TS
Ti	Cp	H	0.0	−8.1	0.93	6.2
		F	0.0	3.3	22.5	15.3
		CN	0.0	−10.3	0.16	1.9
Zr	Cp	H	0.0	4.7	1.1	16.8
		F	0.0	14.8	22.8	24.7
		CN	0.0	1.5	1.9	12.2
	C_5H_4[b]		0.0 (**1**)	−34.9 (**2**)	−51.6 (**3**)	

[a] The energies of cyclocumulene (**1**), alkynylcyclopropene (**2**), and dialkynylmethane (**3**) are given for comparison. [b] Hydrocarbon equivalent.

assigned for the least strained acyclic species **3**,[18] the cyclocumulene derivative **1** is higher in energy by 51.6 kcal/mol and the cyclopropene derivative **2** is higher in energy by 16.7 kcal/mol. Such a clear spread of energy between the three structures vanishes with the Cp_2Ti and Cp_2Zr analogues (Table 1 and Figure 1). The introduction of a metal brings a dramatic change in the stability of these molecules. The three cumulative double bonds are highly strained in the organic structure **1**. In the metallacyclocumulene **4**, the in-plane π orbitals are stabilized by their interaction with the in-plane orbitals of the metal atom (Figure 1, **5**). Such a stabilization in the cyclopropene derivative **2** corresponds to the Dewar−Chatt−Duncanson description of the ethylene π donation and back-bonding. Another component of the reduction in strain in going from the organic molecules to the metal-substituted ones arises from the longer M−C bonds as opposed to the corresponding C−C bonds. The C1−C2−C3 angle in **1** of 114.7° is far away from the ideal linearity anticipated for cumulenes. The complexation with metal increases this to 145.1° in **4** (with M = Ti and R = H). Calculations indicate that the cyclocumulene **4** and the bis(acetylide) **6** are comparable in energy for both Ti and Zr. The difference between Ti and Zr is shown in the relative energies of the metallacyclopropene derivative. The titanacyclopropene is lower in energy than the other two isomers, while the zirconacyclopropene is higher in energy. How do these relate to energies found by experiments? The in situ generated metallocene fragment reacts with butadiyne to give either a metallacyclocumulene (**4**) or a metallacyclopropene (**5**). It also forms the isomeric bis(acetylide) complex (**6**). It is clearly seen from the experiments so far that the Cp_2Ti fragment prefers a metallacyclopropene structure. Several products implied in reactions (Scheme 2) indicate the presence of **5** with Ti as the metal.[6,19] On the other hand, similar experiments with Zr give no indication of products arising from **5**; structure **10**, which may be derived from **4**, is observed instead.[5,19] For M = Ti and R = H, CN, the structure **5** is lower in energy than **4** by 8.2 and 10.3 kcal/mol, respectively (Figure 2). Substitution of the R group by F increases the energy of **5** for both Ti and Zr. The higher stability of the CN-substituted η^2 complexes **5** may come from extended conjugation of the CN group with the MC_4 skeleton.

We located a transition state (**TS**) connecting **4** and **5** (Figure 3) and the magnitude of the barrier height, which dictates the ease of interconversion of these complexes. The barrier for the process **4** → **5** with different butadiyne substituents increases in the order CN < H < F for both Ti and Zr. The relatively low barrier height of the complexes with M = Ti enables them to exist in a dynamic equilibrium, as is found experimentally. It should be possible to shift the equilibrium by fine-tuning the substituents. The computed

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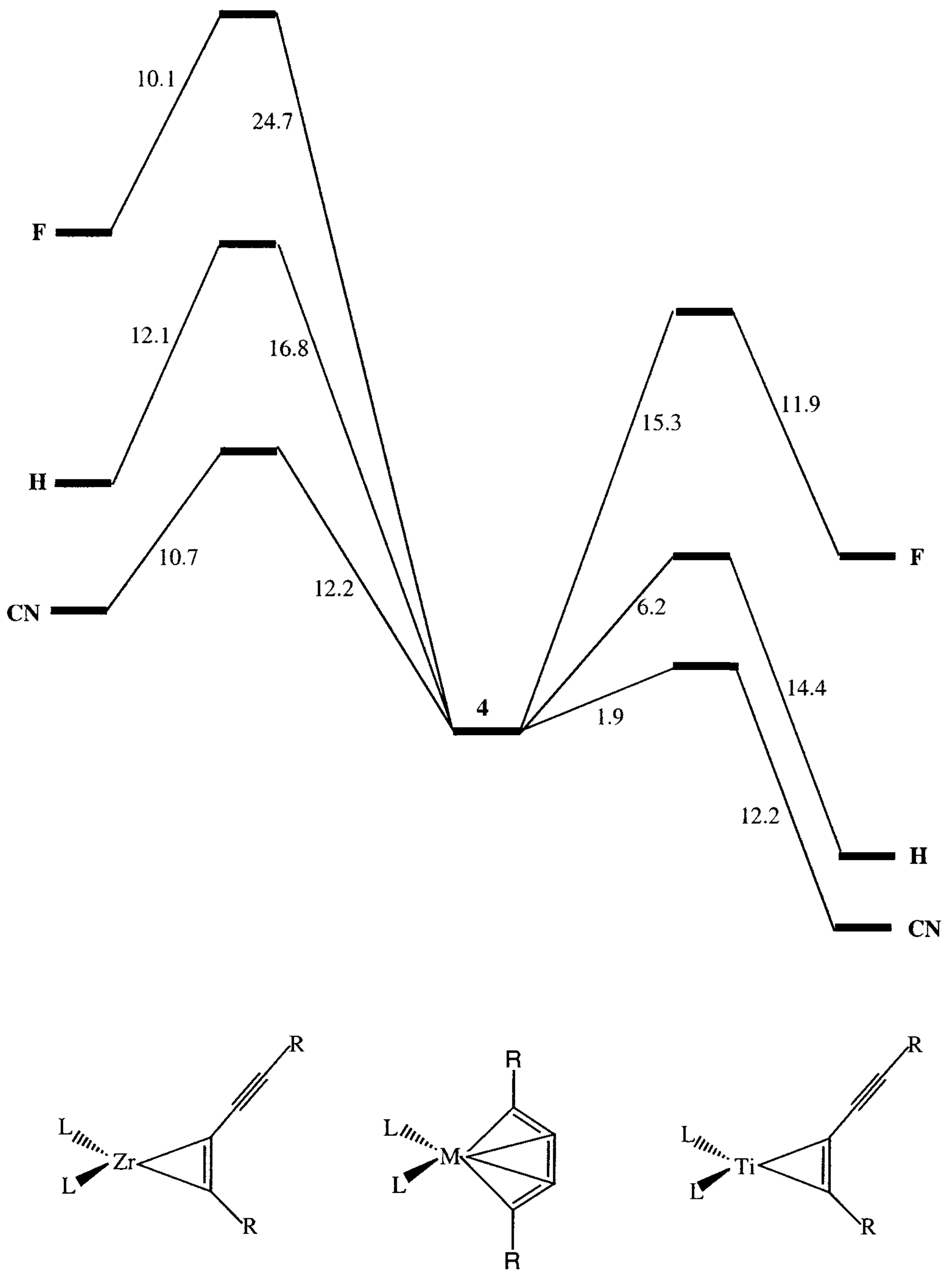

5 5

Figure 2. Potential energy diagram for the isomerization of **4** → **5** at the B3LYP level. Structure **5** is kept at the reference value of 0.0. The labels at the extreme right- and left-hand sides of the figure indicate the butadiyne substituents: viz., **H**, **F**, and **CN**.

barrier height for the process **4** → **5** is much lower than what is known experimentally. For Ti, the experimental barrier height is found to be approximately 10.7 kcal/mol, while the computed values are 6.2 and 1.9 kcal/mol with R = H, CN, respectively. This difference may come from the change in ligand and the butadiyne substituent in our calculations compared to those in the experimental system. The structure **5** can also be stabilized for Zr by choosing the proper butadiyne substituents. The calculations show that this can be achieved by using cyanide (CN) as the substituent. The unusual stability of **5** is the result of the well-known Dewar–Chatt–Duncanson model of π bonding and metal back-bonding.[20] This is reflected in the longer C–C bond length as well as in the C–C stretching frequency of the three-membered ring (ν_{C-C} 1683 cm^{-1} (H) and 1753 cm^{-1} (CN) for M = Ti; ν_{C-C} 1587 cm^{-1} (H) and 1664 cm^{-1} (CN) for M = Zr). The lower frequencies for the Zr complex indicate the strong back-bonding and consequently greater stability.

(b) Structure and Bonding Analysis of 4, 5, and the TS Connecting 4 and 5. The geometrical parameters for all the complexes are given in Table 2. The metal–carbon and the carbon–carbon distances obtained for these models are comparable to those found

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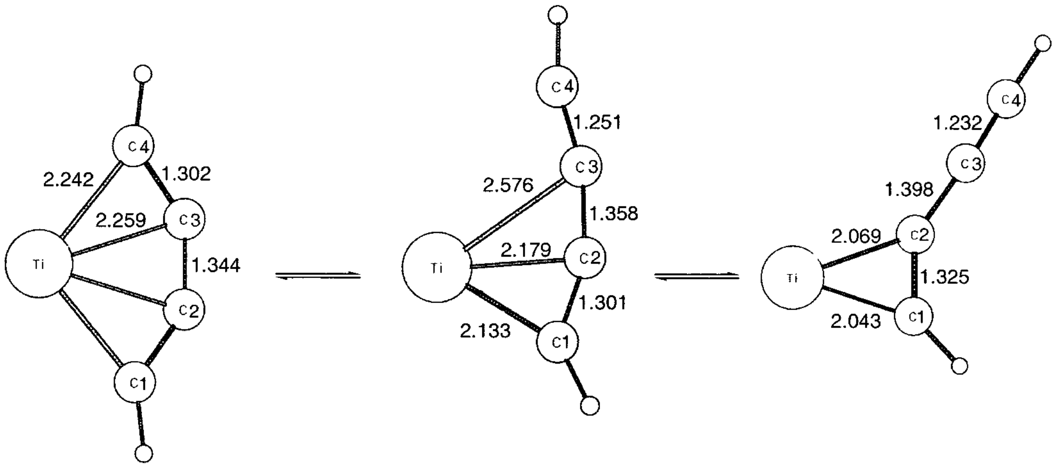

Figure 3. Transition state (**TS**) connecting **4** and **5**. The bond lengths (in Å) are given for M = Ti, L = Cp, and R = H. The Cp rings are omitted for clarity.

Table 2. Important Geometric Parameters of the Structures at the B3LYP/LANL2DZ Level[a]

				distance (Å)							angle (deg)			
molecule	M	L	R	M−Cp	M−C1	M−C2	M−C3	C1−C2	C2−C3	C3−C4	L−M−L	M−C1−C2	C1−C2−C3	C2−C3−C4
4	Ti	Cp	H	2.144	2.242	2.259		1.302	1.344		130.9	73.9	145.1	
					0.663	*0.338*		*2.047*	*1.467*					
			F	2.126	2.153	2.337		1.318	1.337		132.1	80.7	138.8	
					0.698	*0.305*		*1.871*	*1.574*					
			CN	2.118	2.267	2.284		1.308	1.327		132.1	74.0	145.7	
					0.549	*0.314*		*1.858*	*1.559*					
	Zr	Cp	H	2.292	2.353	2.373		1.316	1.342		130.3	74.7	146.6	
					0.624	*0.294*		*1.992*	*1.554*					
			F	2.276	2.30	2.450		1.327	1.335		131.6	80.1	141.8	
					0.647	*0.261*		*1.861*	*1.637*					
			CN	2.268	2.379	2.40		1.320	1.325		131.7	74.8	147.1	
					0.519	*0.265*		*1.820*	*1.644*					
5	Ti	Cp	H	2.124	2.043	2.069	3.312	1.325	1.398	1.232	134.9		144.8	176.2
					0.792	*0.692*	*0.030*	*1.837*	*1.205*	*2.722*				
			F	2.115	2.010	2.092	3.339	1.319	1.396	1.221	134.8		146.3	176.3
					0.822	*0.692*	*0.029*	*1.769*	*1.194*	*2.623*				
			CN	2.097	2.064	2.085	3.320	1.332	1.381	1.238	136.3		143.7	175.1
					0.676	*0.643*	*0.029*	*1.694*	*1.265*	*2.437*				
	Zr	Cp	H	2.295	2.179	2.197	3.484	1.349	1.405	1.232	134.1		138.8	176.1
					0.784	*0.704*	*0.028*	*1.783*	*1.194*	*2.733*				
			F	2.288	2.159	2.227	3.517	1.339	1.404	1.221	134.0		140.1	176.2
					0.796	*0.669*	*0.027*	*1.758*	*1.179*	*2.639*				
			CN	2.271	2.203	2.221	3.492	1.353	1.388	1.237	135.8		138.6	174.9
					0.654	*0.626*	*0.027*	*1.664*	*1.253*	*2.447*				
TS	Ti	Cp	H	2.116	2.133	2.179	2.576	1.301	1.358	1.251	133.8		160.9	165.0
					0.682	*0.476*	*0.144*	*1.995*	*1.322*	*2.448*				
			F	2.103	2.036	2.196	2.767	1.305	1.350	1.267	134.6		165.3	157.2
					0.784	*0.466*	*0.119*	*1.826*	*1.387*	*2.316*				
			CN	2.084	2.112	2.255	2.709	1.309	1.343	1.252	136.3		160.9	176.9
					0.606	*0.424*	*0.114*	*1.817*	*1.406*	*2.216*				
	Zr	Cp	H	2.275	2.256	2.240	2.860	1.316	1.362	1.251	133.9		175.9	164.0
					0.712	*0.514*	*0.104*	*1.913*	*1.330*	*2.480*				
			F	2.269	2.183	2.272	3.0	1.318	1.355	1.265	133.9		178.6	156.9
					0.767	*0.480*	*0.093*	*1.804*	*1.383*	*2.347*				
			CN	2.253	2.262	2.289	2.844	1.320	1.338	1.259	134.6		171.9	166.8
					0.608	*0.429*	*0.108*	*1.754*	*1.447*	*2.181*				

[a] The numbers in italics indicate the Wiberg bond index (WBI).

experimentally. The three C−C bond lengths are almost equal, indicating that even the middle in-plane π-bond is delocalized to the metal. All the M−C bonds are within the bonding range, and the middle M−C bonds are marginally longer than the end ones. The bite angle, i.e., the angle between the geometrical center point of the Cp rings and the metal, is about 132°. The M−C1−C2 angle does not vary much with a change in the metal. However, when the substituent is F, it increases from 74 to 80°. The M−C1 and M−C4 bonds are more polarized toward the carbon atom, more so when M = Zr, having a weightage of more than 72% on the carbon atom as opposed to 60% when M = Ti. This polarization of the M−C bonds increases with different butadiyne substituent in the order H < F < CN. An analysis of the natural charge obtained from the NBO indicates the

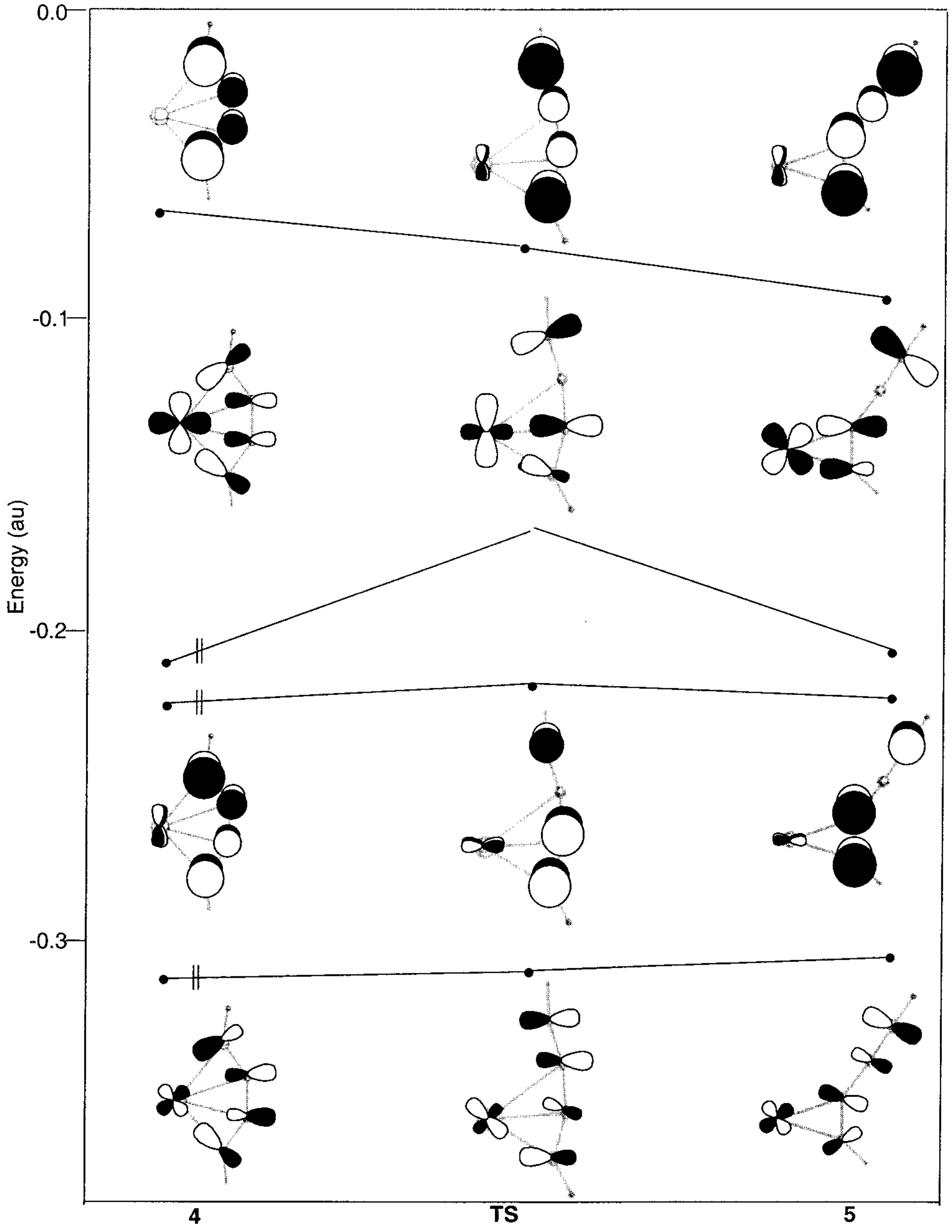

Figure 4. Correlation diagram for the conversion of **4** to **5** via the transition state (**TS**). The ligands (Cp) are omitted for clarity.

same. The positive charge on the Zr atom (1.2) is more than that in Ti (0.2), indicating greater Zr to C4 back-bonding.

A better understanding of the structure **4** is obtained from a fragment molecular orbital approach.[21] The metal fragment Cp_2M is in the formal oxidation state of +2 with two valence electrons and three frontier orbitals, all of which are in the MC4 plane. The in-plane frontier orbitals of the HCCCCH fragment are formed from the sp hybrid orbitals on the end carbon atoms, C1 and C4, and the two in-plane p orbitals on the two middle carbon atoms. These form four linear combinations, much the same in symmetry as the π orbitals of butadiene. The lowest two orbitals among these are filled. The next MO, the LUMO of the C_4H_2 fragment, corresponds to the LUMO of the butadiene in symmetry and is bonding between C2 and C3. The strongest stabilizing interaction between the Cp_2M fragment and C_4H_2 takes place between this LUMO of C_4H_2 and the HOMO of Cp_2M. This interaction stabilizes the C2−C3 bond. This is in contrast with the familiar Dewar−Chatt−Duncanson model of metal to π^* back-bonding, which decreases C2−C3 bonding, elongating the C2−C3 distance.[20] The consequence of this bonding is tempered by the two π MOs perpendicular to the MC4 plane, typical of butadiene.

All the C−C bond lengths in **5** are within the expected range. Both of the M−C bonds are of almost equal order, as evident from the Wiberg bond indexes (WBI). There is a marked reduction in the bite angle from the experimental value of 141.4°; the calculated bite angle is 135.0°. This reduction in the bite angle may arise because the experiments were done with Cp*. There is

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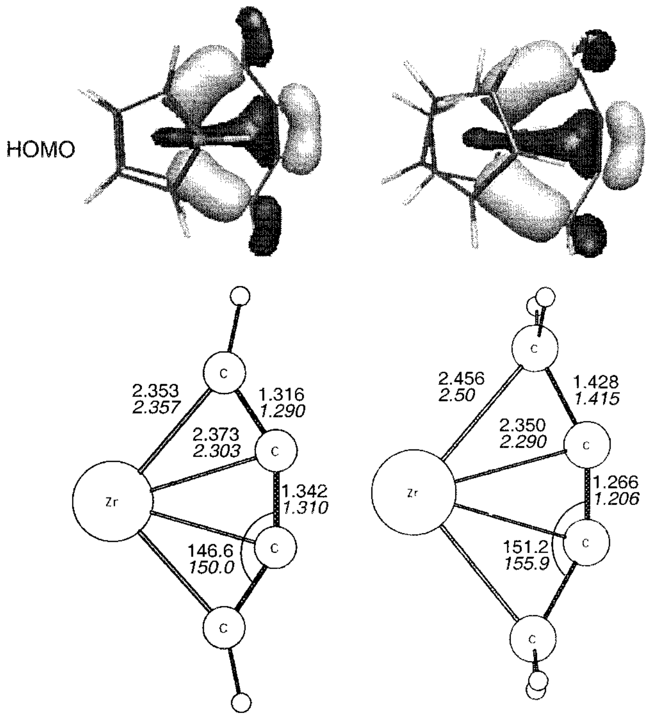
(21) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179. (c) Fujimoto, H.; Hoffmann, R. *J. Phys. Chem.* **1974**, *78*, 1167.



4 **9**

Figure 5. Structures of $Cp_2ZrC_4H_2$ (**4**) and $Cp_2ZrC_4H_4$ (**9**) calculated at the B3LYP/LANL2DZ level of theory. The bond lengths (Å) and angles (deg) are given for comparison. The numbers given in italics are the related experimental values. The Cp rings are omitted for clarity.

no interaction between the C3−C4 bond and the metal in **5**, as is evident from the near-linearity of the C2−C3−C4 angle of 176.0°. The natural charge analysis computes a higher positive charge on the metal than in the η^4 complexes. The total charge on the Cp ligand is identical with that in **4**: viz., about 0.0 in Ti complexes and −0.3 in Zr complexes.

In going from **4** to **5** through the transition state, the following changes take place in the M−C and C−C distances (Figure 3). For example, when M = Ti and R = H, the M−C3 bond changes from 2.259 Å (**4**) to 2.576 Å (**TS**) to 3.312 Å (**5**), the C2−C3 bond goes from 1.344 Å (**4**) to 1.358 Å (**TS**) to 1.398 Å (**5**), and the C1−C2−C3 angle changes from 145.1° (**4**) to 160.9° (**TS**) to 144.8° (**5**). Even though the M−C3 bond is somewhat elongated, it is still within the bonding distance, as indicated by the WBI of 0.114 (Table 2). Similar changes were noticed with the other substituents (F and CN) for both Ti and Zr. The Cp ligand shows electronic effects similar to those in **4**−**6**. We constructed a correlation diagram to understand the changes in the frontier orbitals in going from **4** to **5** via the transition state (**TS**), as shown in Figure 4. Even though many bonds appear to be breaking and many are formed, the overall $M-C_4H_2$ bonding is not affected considerably. The only orbital that goes up substantially during the reaction is the HOMO. Even this MO is stabilized by the incipient C3−C4 triple-bond formation (see the decrease in this bond length in Figure 3). Similarly, there is a weak M−C4 bonding interaction even in the **TS**. The retention of major bonding interactions in the **TS** explains the low barrier for the transformation.

The recently reported zirconacyclopentyne complex **9** has a structure remarkably similar to that of the zirconacyclocumulene **4** (Figure 5). All four carbon atoms and the metal atom of the five-membered ring in **9** are in the same plane. The M−C bond lengths in **4** and **9** are comparable. The similarity in bonding of **4** and **9** is exemplified by the HOMO (Figure 5). The power of bis(cyclopentadienyl)titanium and -zirconium in stabilizing strained π bonds is remarkable.

Conclusions

A comparison of the energetics of metallacyclocumulene (**4**), metallacyclopropene (**5**), and bis(acetylide) (**6**) with their hydrocarbon analogues (**1**−**3**) shows that the metal fragment has a dramatic impact on the relative energies. The replacement of the CH_2 group by Cp_2M (M = Ti, Zr) makes structures **4**−**6** comparable in energy. Our calculations support the experimental observation that the metallacyclopropene **5** is more favorable for the Ti complex. Under similar reaction conditions, Ti reacts through the cyclopropene structure **4**, whereas Zr reacts through the cumulenic structure **5**.[11] However, it should be possible to obtain both the cyclocumulene (**4**) and cyclopropene (**5**) type complexes for Ti and Zr by using the proper substituent on the carbon skeleton. The transition state connecting **4** and **5** retains most of the M−C bonding interactions, leading to a low barrier for conversion. Comparison of the structures of **4** with Zr as the metal and **9** shows similar structural patterns.

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Supporting Information Available: Tables giving coordinates for the B3LYP/LANL2DZ optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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