

# Reactions of Group 4 Metallocene Alkyne Complexes with Carbodiimides: Experimental and Theoretical Studies of the Structure and Bonding of Five-Membered Hetero-Metallacycloallenes

Katharina Kaleta,<sup>†</sup> Martin Ruhmann,<sup>†,‡</sup> Oliver Theilmann,<sup>†,‡</sup> Torsten Beweries,<sup>†</sup> Subhendu Roy,<sup>§</sup> Perdita Arndt,<sup>†</sup> Alexander Villinger,<sup>‡</sup> Eluvathingal D. Jemmis,<sup>\*,§,⊥</sup> Axel Schulz,<sup>\*,†,‡</sup> and Uwe Rosenthal<sup>\*,†</sup>

<sup>†</sup>Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany

<sup>‡</sup>Abteilung Anorganische Chemie, Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, D-18059 Rostock, Germany

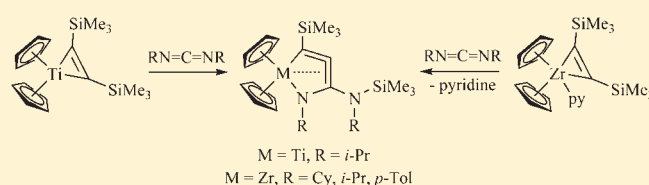
<sup>§</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

<sup>⊥</sup>Indian Institute of Science Education and Research Thiruvananthapuram, CET campus, Thiruvananthapuram 695016, India

**S** Supporting Information

**ABSTRACT:** The reaction of the low-valent metallocene(II) sources  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  (**7**) and  $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  (**11**, Cp =  $\eta^5$ -cyclopentadienyl, py = pyridine) with carbodiimides  $\text{RN}=\text{C}=\text{NR}$  (R = Cy, *i*-Pr, *p*-Tol) leads to the formation of five membered hetero-metallacycloallenes  $\text{Cp}_2\text{M}\{\text{Me}_3\text{SiC}=\text{C}=\text{C}[\text{N}(\text{SiMe}_3)(\text{R})]-\text{N}(\text{R})\}$  (**9M-R**) (M = Ti, R = *i*-Pr; M = Zr, R = Cy, *i*-Pr, *p*-Tol).

Elimination of the alkyne (as the hitherto known reactivity of titanocene and zirconocene alkyne complexes would suggest) was not observed. The molecular structures of the obtained complexes were confirmed by X-ray studies. Moreover, the structure and bonding of the complexes **9Zr-Cy** and **9Zr-*p*-Tol** was investigated by DFT calculations.



## 1. INTRODUCTION

Metallacycles (cycloallenes, dienes, alkynes, cumulenes, etc.) are an important class of organometallic compounds. Their importance for various catalytic applications was demonstrated on several occasions,<sup>1</sup> e.g. in the chromium mediated tetramerization of ethylene to 1-octene.<sup>2</sup> In our group we focused on the synthesis, formation, reaction, and computational studies of three-, four-, and five-membered titana-, zircona-, and hafnacycles.<sup>3</sup> For these purposes, bis(trimethylsilyl)acetylene containing group 4 metallocene complexes of the type  $\text{Cp}'_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  (Cp' = Cp, Cp\*, etc.; M = Ti, Zr, Hf; L = pyridine, THF, acetone) were found to be excellent starting materials due to their ability to release the alkyne under generation of the “free” metallocene fragment under mild conditions. The formation of saturated and unsaturated metallacycles from these precursor complexes was widely investigated in the past. Especially the unsaturated, highly strained metallacycles are unusual because the corresponding carbocyclic analogues, i.e. cyclic cumulene **1** and alkyne **2**, are unstable due to the angle strain on incorporation of linear unsaturated units, i.e.  $\text{C}=\text{C}=\text{C}=\text{C}$  and  $\text{C}-\text{C}\equiv\text{C}-\text{C}$  into the small ring systems.<sup>4,5</sup> As shown recently for metallacyclopenta-2,3,4-trienes (**3M**)<sup>6</sup> and metallacyclopentynes (**4M**),<sup>7</sup> replacing the  $\text{CH}_2$  group by the isolobal  $\text{Cp}_2\text{M}$  (M = Ti, Zr, and Hf) moiety in these molecules results in a decrease of the ring strain to give stable, isolable metallocene complexes (Scheme 1), which could be fully characterized; their reactivity, e.g. toward Lewis acids or other metal

fragments, was studied in detail.<sup>8</sup> Moreover, these complexes have shown to be relevant for stoichiometric and catalytic C–C coupling and cleavage reactions of unsaturated molecules such as alkynes, olefins, acetylides, and vinylides.<sup>3a,3c,9</sup>

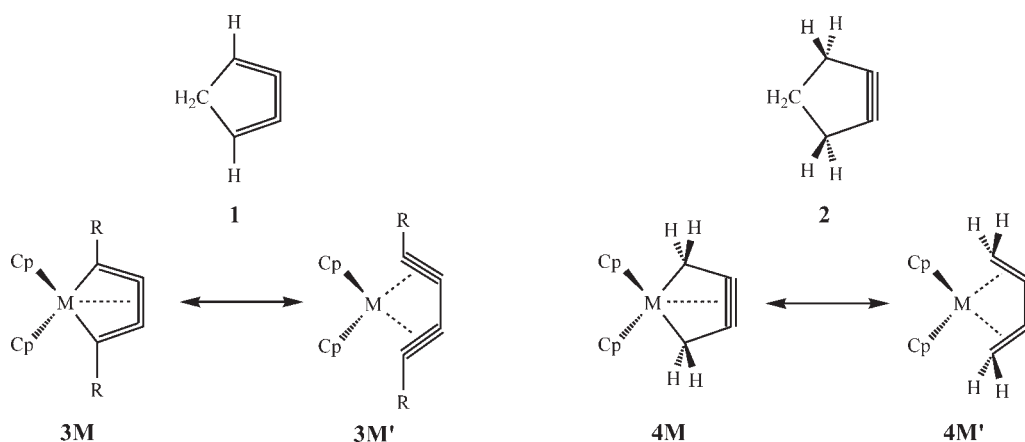
Both metallacyclocumulenes and metallacyclopentynes display strongly bent geometries at the  $\text{sp}$ -hybridized central carbon atoms, which would not be stable in the corresponding hydrocarbon analogues.<sup>4,5</sup> The remarkable stability of these complexes (both metallacycles can be kept at room temperature under argon) is attributed to the in-plane interaction of the bent metallocene unit with the central unsaturated C–C bond involving the vacant acceptor orbitals of the  $\text{Cp}_2\text{M}$  moiety and the filled orbitals of the  $\text{C}_4$  ligands. Alternatively, these complexes can be described in an  $\eta^4\text{-}\pi,\pi$ -coordination mode (**3M'** and **4M'**, Scheme 1); these mesomeric forms also contribute to the resonance hybrid of these systems.

As an extension to these unique bonding strategies, very recently, Suzuki and co-workers and Erker et al. have isolated and characterized the first examples for five-membered all-carbon zircona- and hafnacycloallenes (**6**, Scheme 2) spectroscopically, by X-ray diffraction and also by DFT computations.<sup>10,11</sup> Similarly as for the above-mentioned species **1** and **2**, the carbocyclic analogue of a five-membered metallacycloallene (**5**) would also not be stable due to the angle strain.<sup>5</sup>

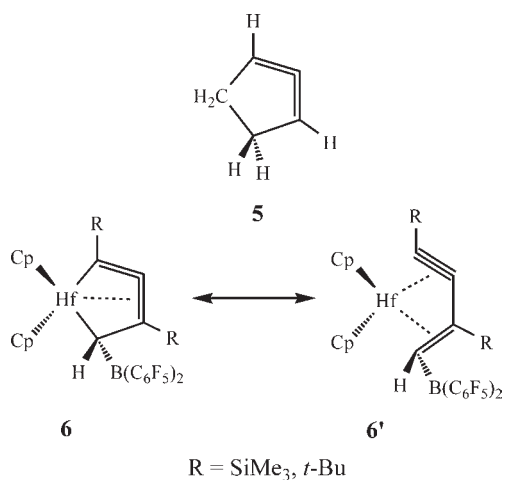
Received: December 21, 2010

Published: March 17, 2011

**Scheme 1. Schematic Representation of Cyclocumulene 1, Cyclopentyne 2, Metallacyclocumulene 3M and Metallacyclopentyne 4M and Their Mesomeric Forms (3M' and 4M', Respectively)**



**Scheme 2. Schematic Representation of Cycloallene 5, Erker's Five-Membered Hafnacycloallene 6 and Its Mesomeric Form 6'**<sup>11a</sup>



As shown recently by our group for the synthesis of a 1-zircona-2,5-disilacyclopent-3-yne,<sup>12</sup> insertion of another heteroatom such as silicon, nitrogen, oxygen, or sulfur into the metallacycle can be another elegant way to increase the stability of such highly strained systems. This approach was discussed in the past,<sup>3f</sup> however, experimental support for this concept was rare. Very recently, we reported on the reaction of the well-known titanocene alkyne complex  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  (7) with 1,3-*N,N'*-dicyclohexylcarbodiimide (8-Cy),<sup>13</sup> yielding two different dinuclear titanocene species (Scheme 3).<sup>13</sup> Most interestingly, one of these complexes can be referred to as a transient titanocene carbene-like complex, which can be regarded as an intermediate for the formation of the final reduction-coupling product.

The first examples for well-defined seven-membered aza-zirconacycloallenes were presented by Xi et al.<sup>14</sup> The authors showed that insertion of a variety of organic nitriles into the Zr–C bond of a zirconacyclopentene followed by intramolecular coupling of the two cyclic moieties of the intermediate results in ring enlargement to yield a seven-membered metallacycle.

In this contribution we present the synthesis of the first examples for five-membered hetero-metallacycloallenes as well as theoretical studies on the structure and bonding of these complexes.

## 2. RESULTS AND DISCUSSION

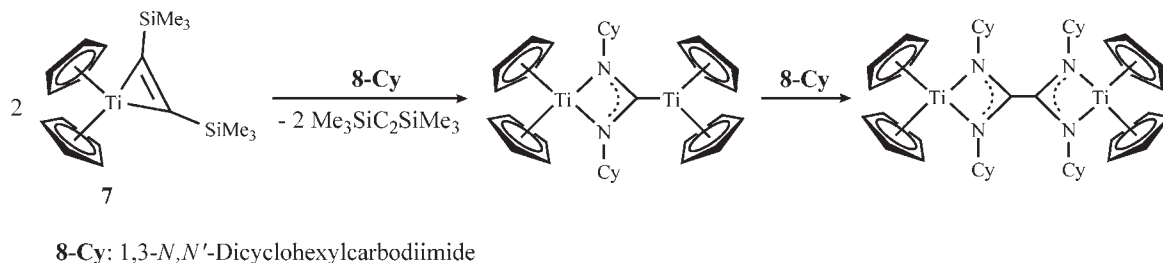
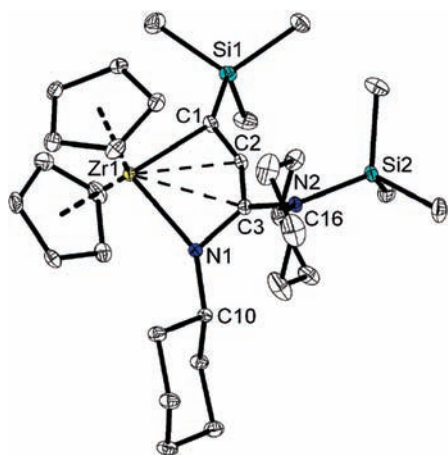
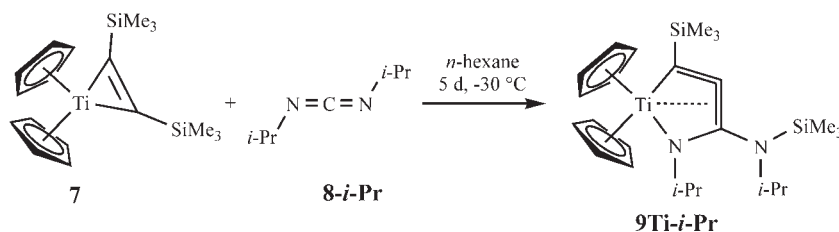
The reaction of the titanocene alkyne complex  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  (7) with 1,3-*N,N'*-diisopropylcarbodiimide (8-*i*-Pr) at low temperatures revealed the formation of a hitherto unknown hetero-metallacycloallene 9Ti-*i*-Pr (Scheme 4). Performing the reaction at ambient temperature results in the formation of a dinuclear titanocene complex; details on this reaction will be published in due course.

Dark red crystals of compound 9Ti-*i*-Pr suitable for X-ray analysis were obtained from concentrated *n*-hexane solutions in moderate yields (50%); the molecular structure and structural parameters are depicted in the Supporting Information. The structural motif is similar to the corresponding zirconocene complexes 9Zr-Cy and 9Zr-*p*-Tol (cf. Figure 1) showing a five-membered nonplanar metallacycle with the ring nitrogen being bent out of the plane formed by the metal atom and the ring carbon atoms. NMR spectroscopic data reveal the presence of a hetero-metallacycloallene unit. In the <sup>13</sup>C NMR spectrum resonances due to the allene scaffold can be found at 110.6, 117.9, and 145.9 ppm. Moreover, loss of symmetry in the molecule can be derived from the nonequivalent signals for the SiMe<sub>3</sub> protons in the <sup>1</sup>H NMR spectra ( $\delta = 0.39$  and 0.42 ppm). Further details referring to chemical shifts in <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR experiments can be found in the Experimental Section (vide infra).

Most surprisingly and in contrast to the reaction of the alkyne complex 7 with 8-*i*-Pr, under similar reaction conditions the use of 1,3-*N,N'*-di-*p*-tolylcarbodiimide 8-*p*-Tol results in the formation of a dinuclear complex 10 bridged by a tetraaminate ligand (Scheme 5). This complex was described before by Floriani et al.<sup>15</sup>

The synthesis of compound 10 was successfully carried out in a one-pot reaction. A solution of 1,3-*N,N'*-di-*p*-tolylcarbodiimide (8-*p*-Tol) dissolved in *n*-hexane was added to a solution of alkyne complex 7 also dissolved in *n*-hexane resulting in a deep-red solution. Crystallization at low temperature led to the formation of red crystals (yield 58%) which were characterized as complex 10 by X-ray studies. X-ray analysis and properties of the isolated

## Scheme 3. Reaction of the Titanocene Alkyne Complex 7 with a Carbodiimide

Scheme 4. Formation of the Hetero-titanacycloallene 9Ti-*i*-Pr

**Figure 1.** Molecular structure of **9Zr-Cy**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zr1–N1 2.183(1), N1–C3 1.361(2), C2–C3 1.395(2), C1–C2 1.290(2), Zr1–C1 2.301(1), Zr1–C2 2.333(1), Zr1–C3 2.529(1), N1–C10 1.466(2), N2–C3 1.420(2), Si1–C1 1.856(1), Si2–N2 1.764(1), N2–C16 1.486(2); N1–Zr1–C1 91.88(5), C3–N1–Zr1 87.87(8), N1–C3–C2 114.0(1), C1–C2–C3 153.6(1), C2–C1–Zr1 75.22(8), C10–N1–Zr1 149.35(8), C3–N1–C10 122.1(1), N1–C3–N2 126.3(1), C2–C3–N2 119.8(1), C2–C1–Si1 138.6(1), Si1–C1–Zr1 144.72(7), C3–N2–Si2 117.16(9), C16–N2–Si2 123.72(9), C3–N2–C16 118.1(1).

crystals of **10** have already been published by Floriani and co-workers.<sup>15</sup> This complex displays a different structural motif than **9Ti-*i*-Pr**, which could be attributed to the presence of alkyl vs aryl substituents at the substrate. The scope of carbodiimide substituents in this respect is under investigation; details will be published in due course.

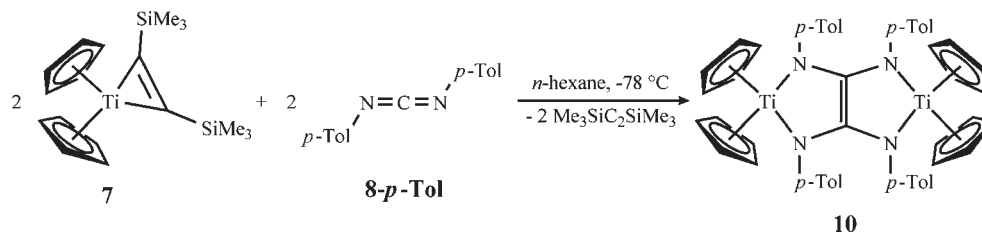
Similarly, the reaction of the zirconocene precursor  $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  (**11**, py = pyridine) with the carbodiimides  $\text{RN}=\text{C}=\text{NR}$  **8-R** (R = Cy, *i*-Pr and *p*-Tol) resulted in the formation of the hetero-zirconacycloallenes **9Zr-R** (R = Cy,

*i*-Pr and *p*-Tol). If performed with stoichiometrically equal amounts of metallocene source **11** and heteroallene substrate **8-Cy** in *n*-hexane for 12 h, the mixture showed a red color. After the solvent was removed, a red, oily product was isolated. This crude product was purified by sublimation at elevated temperatures (120 °C;  $10^{-3}$  mbar). During sublimation the pure reaction product **9Zr-Cy** condensed in pale-yellow crystals which appeared to be suitable for X-ray analysis. Compound **9Zr-*i*-Pr** was obtained as a yellow powder after recrystallization from mixtures of *n*-hexane, ether, and THF at  $-78$  °C. Similarly, the reaction of the zirconocene complex **11** and the carbodiimide **8-*p*-Tol** in THF for 6 h yields an orange reaction mixture, from which the yellow crystalline product **9Zr-*p*-Tol** can be isolated at  $-40$  °C. Crystals suitable for X-ray analysis were obtained from THF- $d_8$  (Scheme 6). It is noteworthy, that for all reactions described here, the THF stabilized zirconocene alkyne complex  $\text{Cp}_2\text{Zr}(\text{thf})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  can also be used as a metallocene source with THF as solvent. Moreover, monitoring of the reactions by means of NMR techniques has shown that almost no byproducts are formed in the reactions of the alkyne complexes with the corresponding carbodiimides.

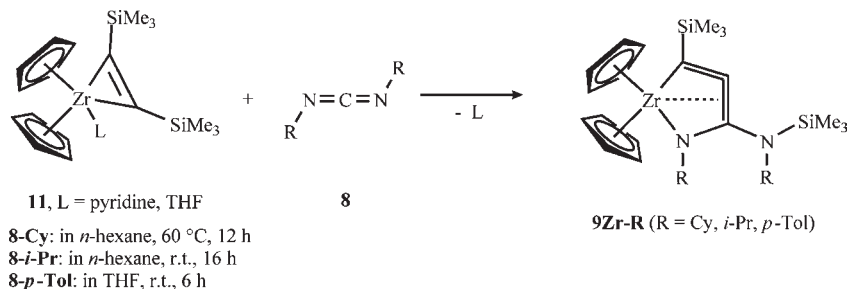
NMR data closely resemble those of the titanocene complex described above; however, the  $^{13}\text{C}$  resonance due to the central carbon atom C2 is found to be slightly shifted downfield (e.g., 134.8 ppm for complex **9Zr-Cy**). A detailed compilation of the data from  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR experiments is depicted in the Experimental Section (vide infra). In mass spectrometry experiments (CI, isobutane) characteristic signals for the molecular ions were observed at 596 (**9Zr-Cy**), 516 (**9Zr-*i*-Pr**) and 612 (**9Zr-*p*-Tol**). Moreover, for complexes **9Zr-Cy** and **9Zr-*p*-Tol**, the free ligand could be detected at 377 [ $\text{Me}_3\text{SiC}\equiv\text{C}(\text{N}(\text{Me}_3\text{Si})(\text{Cy}))=\text{N}(\text{Cy}) + \text{H}$ ] $^+$  (**9Zr-Cy**) and 395 [ $\text{Me}_3\text{SiC}\equiv\text{C}(\text{N}(\text{Me}_3\text{Si})(\text{p-Tol}))=\text{N}(\text{p-Tol}) + \text{H}_2 + \text{H}$ ] $^+$  (**9Zr-*p*-Tol**), respectively.

The mononuclear complex **9Zr-Cy** crystallizes in the triclinic space group  $\text{P}\bar{1}$  with two molecules per unit cell, whereas

Scheme 5. Formation of the Dinuclear Complex 10



Scheme 6. Formation of the Hetero-zirconacycloallenes 9Zr-R



compound **9Zr-*p*-Tol** crystallizes in the orthorhombic space group *Pccn* with eight molecules per unit cell. The molecular structures are shown in Figures 1 and S1 (Supporting Information). The bond lengths and angles of the two complexes are comparable. Small deviations can be found in the bond angles due to the different electronic and steric properties of the Cy and *p*-Tol substituents. Especially the most interesting structural features of the metallacycle such as the conformation along the C–C–C–N unit or the metal ligand distances and C–C and C–N are almost identical. Due to these observations the molecular structure of **9Zr-Cy** is discussed exemplarily for both compounds.

In compound **9Zr-Cy** the zirconium center adopts a strongly distorted tetrahedral geometry (Ct1–Zr1–Ct2 125.65(6)°, N1–Zr1–C1 91.88(5)°; Ct = centroid of the Cp fragment). This is in agreement with other zirconocene-containing complexes with highly unsaturated ligands.<sup>3d,3f,7a,7d,10,11b</sup> The Zr1–N1 bond (2.183(1) Å) is distinctly shorter than the Zr1–C1 bond (2.301(1) Å). The metallacycle Zr1–C1–C2–C3–N1 does not appear planar but shows an envelope conformation in which the nitrogen atom is bent out of the plane (Zr1–N1–C3–C2 38.9°). On the contrary, Zr1, C1, C2, and C3 form a plane with a deviation from planarity smaller than 2° (Zr1–C1–C2–C3 1.85°). Furthermore, in this metallacycle unit the found C1–C2 bond length is the shortest with 1.290(2) Å and concerns more to a double bond in an allene unit (1.307 Å<sup>17</sup>) than to an elongated C–C triple bond ( $\Sigma r_{\text{cov}}$  for a triple bond: 1.20 Å<sup>16</sup>). The N1–C3 bond is somewhat longer (1.361(2) Å) and can be referred to as a typical C<sub>sp</sub><sup>2</sup>–N<sub>sp</sub><sup>2</sup> single bond (1.336 Å) or a weak C–N double bond (1.279 Å).<sup>17</sup> The central C2–C3 bond displays a double bond rather than single bond character (1.395(2) Å); however, this distance is elongated compared to literature values (1.34 Å<sup>16</sup>). In principle, two mesomeric Lewis formulas may be mainly involved to characterize this compound, namely a zirconocene(II)-bis- $\pi$ -complex (**F**) and a zirconocene(IV)-metallacycloallene (**G**) (Scheme 8). However, the data from X-ray analysis suggest the presence of

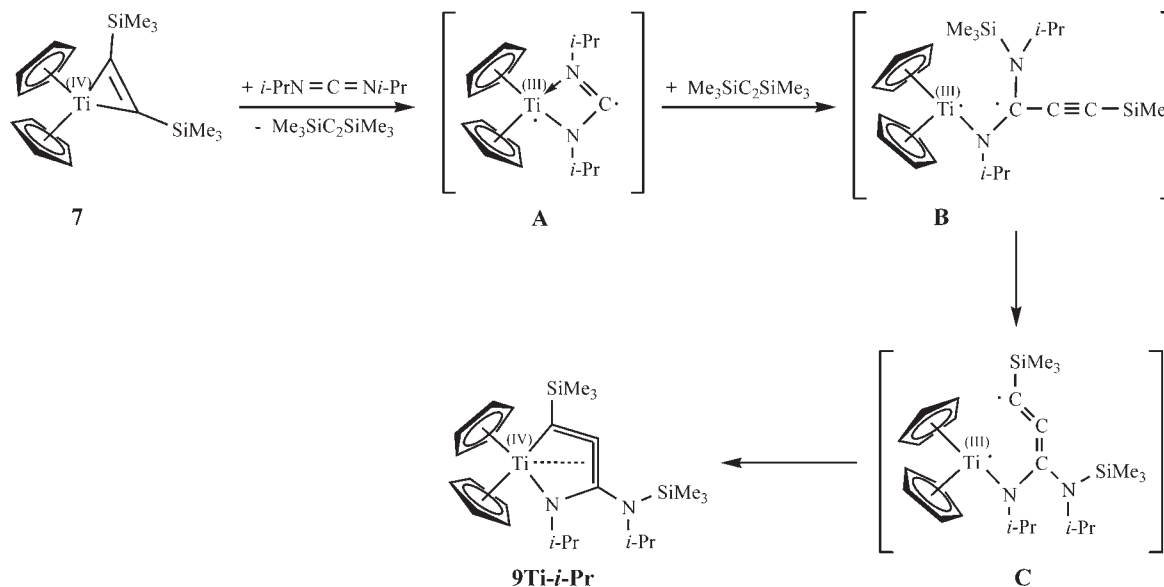
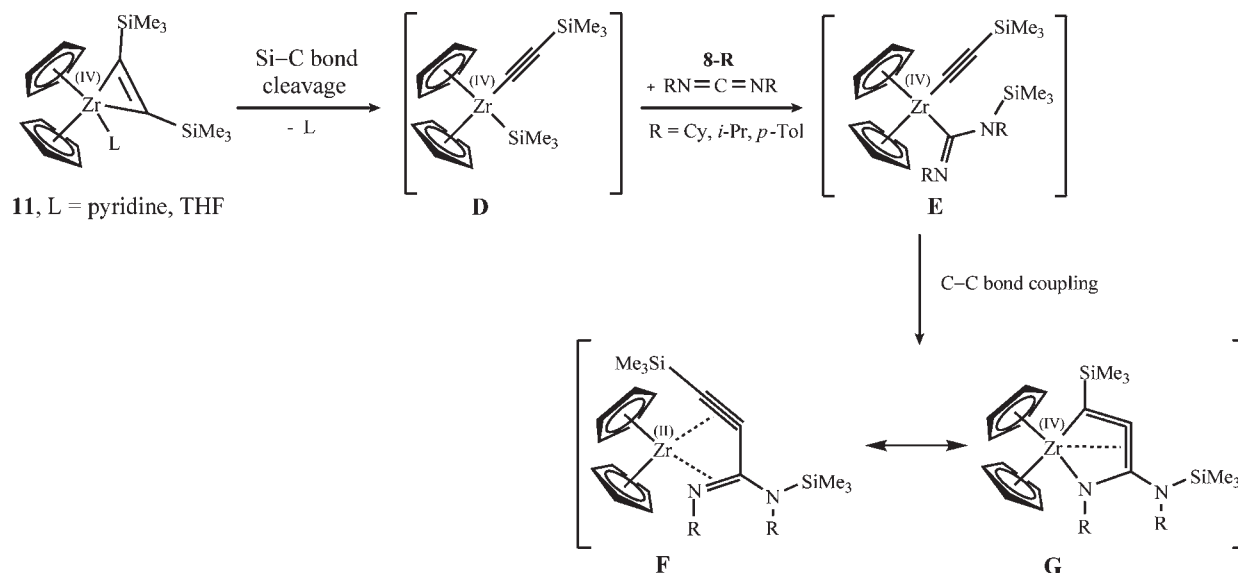
a mesomeric form which corresponds more to the description as a metallacycloallene with the metal center in the oxidation state +4 (**G**). The complex is stabilized by means of intramolecular coordination, which can be derived from the relatively short Zr1–C2 bond (2.333(1) Å).

The mechanism of the formation of the titanium complex **9Ti-*i*-Pr** is unclear; however, it is known that in the first reaction step the titanocene fragment [Cp<sub>2</sub>Ti] is formed by dissociation of the alkyne.<sup>3b</sup> This can then react with one molecule of a 1,3-carbodiimide to yield a Ti(III) radical species (**A**), which should be capable of cleaving the Si–C bond of the free alkyne. Such formal insertions of carbenes into Si–C bonds are known in literature.<sup>18</sup> Subsequently, the newly formed radical intermediate (**B** and **C**, respectively) can form the isolated product by recombination of the radical moieties and ring closure (Scheme 7).

In contrast, the mechanism of the formation of hetero-zirconacycloallenes **9Zr-R** should include a Si–C bond cleavage and a C–C bond-coupling step. Most likely, loss of the stabilizing ligand L is accompanied with a Si–C bond rupture to form a zirconocene silyl-alkynyl species (**D**). Precedent for this reaction motif was reported on several occasions, e.g. for nickel and platinum compounds<sup>19</sup> as well as for hafnocene complexes.<sup>20</sup> Subsequently, the carbodiimide inserts into the Zr–Si bond by forming a zirconocene heteroene-alkynyl (**E**). Finally, this intermediate experiences an intramolecular C–C coupling by generating a heteroene-yne ligand coordinated to the zirconocene fragment. This product is supposed to be a zirconocene(II) bis- $\pi$ -complex **F** or, in another mesomeric description, a zirconocene(IV) metallacycloallene **G** (Scheme 8).

This structural motif was predicted to be existent earlier;<sup>3c</sup> the synthesis of compounds **9M-R** (M = Ti, R = *i*-Pr; M = Zr, R = Cy, *i*-Pr, *p*-Tol), which closely resemble the so-called 1-metallacyclopenta-2,3-dienes follows the results published by Erker et al. for Zr and Hf<sup>1</sup> and by Suzuki and co-workers for Zr.<sup>10</sup> In principle, there are two reaction pathways possible to obtain such 1-metallacyclopenta-2,3-dienes: mixed  $\sigma$ -bonded alkynyl-alkenyl



Scheme 7. Proposed Mechanism for the Formation of the Hetero-Titanacycloallene **9Ti-*i*-Pr**Scheme 8. Proposed Mechanism for the Formation of Hetero-Zirconacycloallenes **9Zr-R**

complexes  $[\text{Cp}'_2\text{M}(-\text{C}\equiv\text{CR})(-\text{CR}=\text{CR}_2)]$  form metal-coordinated but-1-ene-3-yne ( $\text{R}_2\text{C}=\text{CR}(-\text{C}\equiv\text{CR})$ ). The zirconocene forces the 1-ene-3-yne ligand into two mesomeric coordination modes, the first one being a  $\eta^4$ - $\pi$ -attachment (**F'**) of the unsaturated ligand, the second mode being an asymmetric 1-zirconacyclopenta-2,3-diene (**G'**) (Scheme 9).

In contrast to this, for the lighter congener titanium, Mach and co-workers suggest a coordination of exclusively the alkyne moiety to the smaller titanocene fragment resulting in a  $\eta^2$ - $\pi$ -coordination mode.<sup>21</sup>

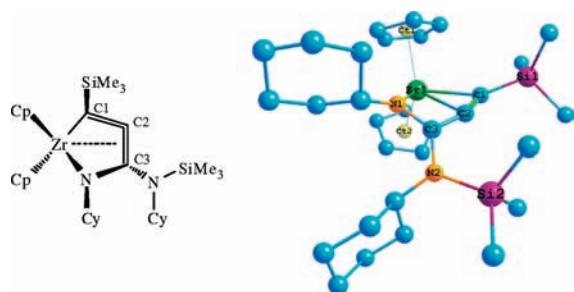
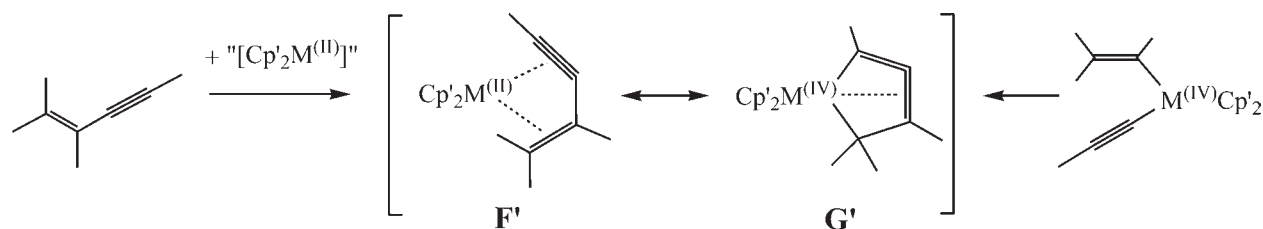
### 3. STRUCTURE AND BONDING ANALYSIS OF THE FIVE-MEMBERED HETERO-METALLACYCLOALLENE

Our experimental observations prompted us to investigate the structure and bonding of the five-membered hetero-metallacycloallene

in more detail by theoretical methods. The results described here are from BP86 calculations with a BS2 basis set (see Computational Details in the Experimental Section). The nature of bonding of complexes **9Zr-Cy** and **9Zr-*p*-Tol** is studied using NBO analysis.<sup>22</sup> Nucleus-independent chemical shifts (NICS)<sup>23</sup> are calculated at the geometrical center point of the ring to get an understanding of the extent of cyclic delocalization of electrons in the complexes. This also gives an idea about the possible interaction between the Zr center and the C-C-C-N moiety in complexes **9Zr-Cy** and **9Zr-*p*-Tol**. The correlation diagram in Figure 4 is drawn from single-point calculations of the structures. The results of the analysis for complexes **9Zr-Cy** and **9Zr-*p*-Tol** are similar in nature. Thus, only the analysis of complex **9Zr-Cy** is described here in detail.

The computed structure of complex **9Zr-Cy** is in excellent agreement with the data obtained from X-ray crystal structure

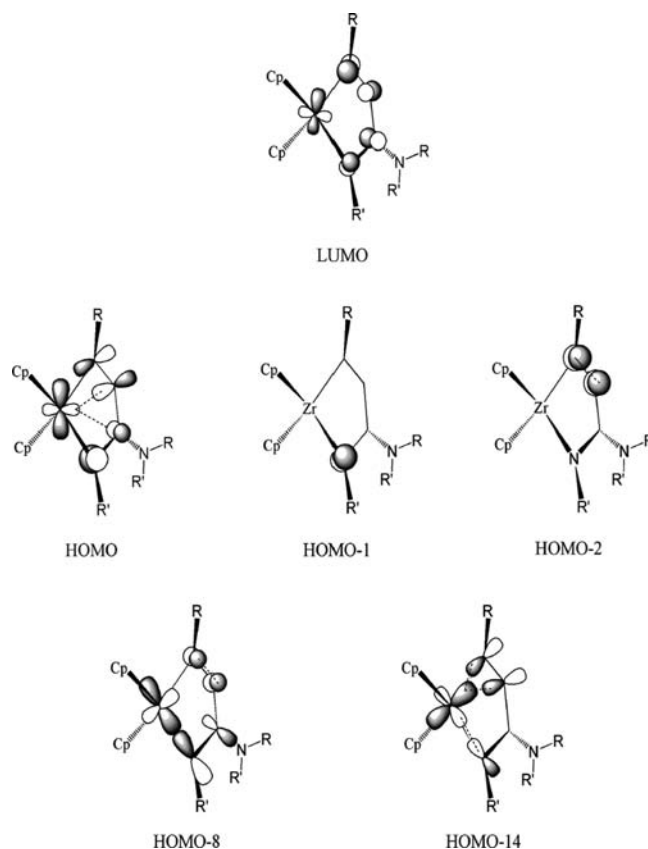
## Scheme 9. Coordination of a 1-Ene-3-Yne to a Metallocene Fragment



**Figure 2.** Schematic representation (left) and calculated structure (right) of complex **9Zr-Cy**.

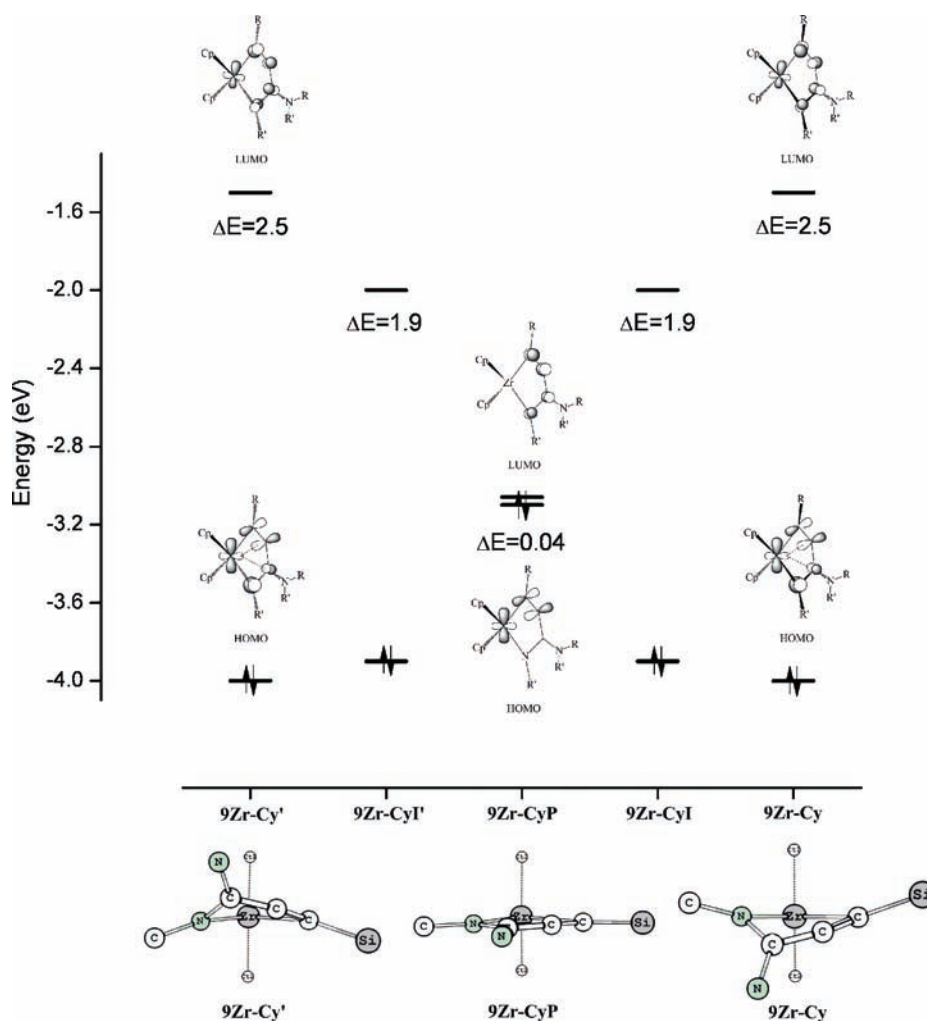
elucidation (Table S1 and Figures 1 and 2, respectively). It shows the characteristic nonplanarity of the metallacyclic unit of complex **9Zr-Cy**. The deviation from planarity (angle  $\text{N1-C3}\cdots\text{C1-Zr1} = 33.0^\circ$ ) matches well with the calculated deviation ( $\text{N1-C3}\cdots\text{C1-Zr1} = 32.0^\circ$ ). The  $\text{Zr1-C1}$  bond length is 2.319 Å which is close to the experimental value of 2.301(1) Å and in the same range as found in other compounds with  $\text{Zr-C}$   $\sigma$ -bonds (e.g., 2.277 Å in  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ ).<sup>24</sup> The  $\text{Zr1-C2}$  bond length is 2.359 Å, which is only slightly longer than the  $\text{Zr1-C1}$  bond (2.319 Å). This might indicate the presence of a strong interaction between the metal center and C2. The  $\text{Zr1-N1}$  bond length is 2.241 Å which is longer than the experimental value of 2.183(1) Å. The  $\text{C1-C2}$  bond length is 1.309 Å which is very close to the  $\text{C-C}$  bond length of a typical allene ( $\text{C-C} = 1.307$  Å).<sup>17</sup> The larger bond length of the  $\text{C2-C3}$  bond (1.404 Å) than the  $\text{C1-C2}$  bond is attributed to the ineffective interaction between the C2 and C3 carbon p-orbitals because of orthogonal orientation. The  $\text{C3-N1}$  bond length is 1.365 Å and it is close to a typical  $\text{C}_{\text{sp}^2}\text{-N}_{\text{sp}^2}$  bond (1.336 Å<sup>17</sup>). The Wiberg bond indices of  $\text{C1-C2}$  and  $\text{C2-C3}$  are 2.041 and 1.287, respectively (Table S2), which also supports the cycloallenic character of complex **9Zr-Cy**. The lower value of the Wiberg bond index for the  $\text{C2-C3}$  bond is already explained in terms of ineffective  $\pi$ -orbital interaction between the C2 and C3 carbon atoms. It is worthwhile to note that the  $\text{Zr1-C3}$  distance is 2.607 Å, which is somewhat larger than those found for  $\text{Zr1-C1}$  and  $\text{Zr1-C2}$ . However, it is not far from the  $\text{Zr-C}$  distance in the complex  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  (vide supra)<sup>24</sup> and thus indicates the existence of an interaction between the metal center and the carbon atom C3.

Moreover, we have carried out the molecular orbital (MO) analysis of bonding of complex **9Zr-Cy**. In the isolated  $\text{Cp}_2\text{Zr}$  fragment the metal is in the formal oxidation state +2 with two valence electrons. The HOMO of complex **9Zr-Cy**, which involves donation of electrons from the metal orbital (HOMO) to the vacant ligand orbital (LUMO), is bonding



**Figure 3.** Important MOs of complex **9Zr-Cy** ( $\text{R} = \text{SiMe}_3$ ,  $\text{R}' = \text{Cy}$ ).

between the C2 and C3 carbon atoms. Thus, the metal is in the formal oxidation state of +4 in complex **9Zr-Cy**. The orthogonal orientation of the C2 and C3 carbon orbital makes the  $\pi$ -bonding interaction between the C2 and C3 carbon atoms less effective. As a result, the  $\text{C2-C3}$  bond does not shorten as much as expected. This is reflected in the relatively larger bond length of the  $\text{C2-C3}$  bond compared to that of the  $\text{C1-C2}$  bond. The substituents,  $\text{SiMe}_3$  (R) and Cy ( $\text{R}'$ ) at the C1 and N1 atoms, respectively, are tilted in a way to make the C1 and N1 orbitals interact more effectively with the metal orbitals. The other stabilizing interaction (HOMO-14) involves donation of electrons from the ligand orbital to the vacant metal orbital. It is important to note that the metal center interacts effectively with both the C1 and C2 carbon atoms (HOMO and HOMO-14) and this is supported by the existence of a 3c-2e bond among the  $\text{Zr1-C1-C2}$  unit of complex **9Zr-Cy** in the NBO analysis. This is also indicated by the strong  $\text{Zr1-C1}$  and  $\text{Zr1-C2}$  interactions, which lie in the range of a typical  $\text{Zr-C}$  single bond.<sup>24</sup> The



**Figure 4.** Correlation diagram between the planar structure and the nonplanar structure of complex **9Zr-Cy**. The variation of the HOMO and LUMO of complex **9Zr-Cy** ( $\text{Cy} = \text{R}'$ ) is plotted as a function of the nonplanarity of complex **9Zr-Cy** (on both sides).

relatively weak interaction between Zr1 and C3 results indirectly from the strong interaction of C3 and N2. There is one localized perpendicular  $\pi$ -bond on the C1 and C2 (HOMO-2) carbon atoms. The short C1-C2 bond length displays the existence of a  $\pi$ -bond. The metal does not have any significant interaction with this perpendicular  $\pi$ -orbital. So, the orbital is available for a further interaction with another moiety. The HOMO-1 is a perpendicular p-orbital localized on N1 carrying the lone pair of the nitrogen atom. So, the molecular orbital analysis supports a cycloallenic electronic structure for complex **9Zr-Cy**. The HOMO, LUMO, HOMO-1, HOMO-2, HOMO-8, and HOMO-14 of complex **9Zr-Cy** are shown in Figure 3.

A correlation diagram between the planar structure and nonplanar structure of complex **9Zr-Cy** is drawn in Figure 4 in order to understand why the complex adopts a nonplanar structure. The HOMO and LUMO of the planar complex (**9Zr-CyP**, Figure 4) are very close in energy ( $\Delta E = 0.04$  eV). As a result, the planar complex (**9Zr-CyP**) undergoes structural distortion, allowing mixing of HOMO and LUMO and thus stabilizes the nonplanar complex **9Zr-Cy** to a greater extent. The HOMO-LUMO gap increases with the increase in the extent of nonplanarity as can be seen from the correlation diagram (from  $\Delta E = 0.04$  eV to  $\Delta E = 2.5$  eV, Figure 4). The

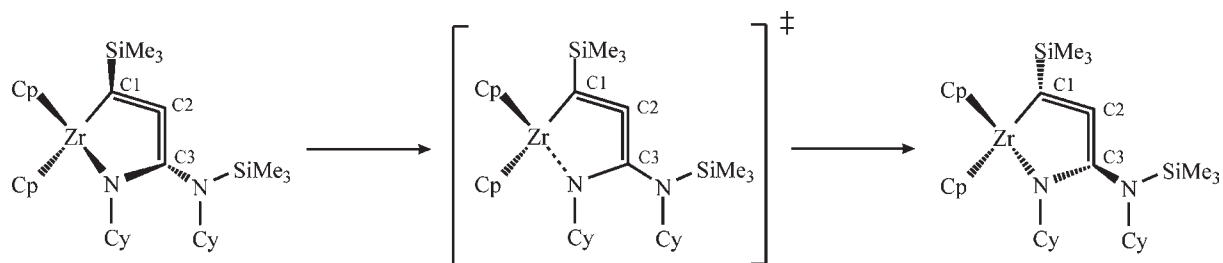
structural distortion takes place due to a second-order energy change in the HOMO. So, this is a second-order or pseudo-Jahn-Teller distortion.<sup>25</sup>

Thus, the near-planar structure (**9Zr-CyTS**, Scheme 10) of complex **9Zr-Cy** turns out to be the transition state with a barrier of 18.3 kcal/mol for the conformational isomerism of complex **9Zr-Cy**, where the C3 carbon atom moves up and down to get to the nonplanar geometry as the stable structure.

The C1-C2-C3 allene arrangement ( $\angle \text{C1-C2-C3} = 155.7^\circ$ ) in complex **9Zr-Cy** falls in the category of a bent allene.<sup>26</sup> This moiety is effectively stabilized by the  $\text{Cp}_2\text{Zr}$  fragment, thus reconfirming the tendency of the bent metallocene ( $\text{Cp}_2\text{Zr}$ ) unit to internally stabilize strained  $\pi$  systems.

The complex **9Zr-Cy** may be described as shown before in Scheme 9. It is a long-standing question of whether to describe a system such as complex **9Zr-Cy** as a coordinated ene-yne complex (F) or a cycloallene complex (G). The NICS values of the isolated ligand and the complex are shown in Table 1. The increase in the negative NICS values, when the isolated ligand forms the complex, implies a significant interaction between the  $\text{Cp}_2\text{Zr}$  moiety and the allenic ligand moiety. In a similar way, complex **9Zr-*p*-Tol** is also shown to have a good interaction between the  $\text{Cp}_2\text{Zr}$  moiety and the allenic ligand moiety. The

Scheme 10. Schematic Representation of the Transition State of Complex 9Zr-Cy

Table 1. Calculated NICS ( $x$ ) Values (in ppm) for Complexes 9Zr-Cy and 9Zr-*p*-Tol (at the BP86/BS2 level of theory)

| NICS( $x$ ) <sup>a</sup> | 9Zr-Cy       |             | (bent-[Me <sub>3</sub> SiHCCC(NSiMe <sub>3</sub> (Cy)NHCy]) <sup>b</sup> |             |
|--------------------------|--------------|-------------|--|-------------|
|                          | concave side | convex side | concave side   | convex side |
| NICS (0)                 |              | -19.7       |  | -9.5        |
| NICS (0.5)               | -16.6        | -19.5       | -7.4   | -9.9        |
| NICS (1.0)               | -12.0        | -12.5       | -4.0   | -5.9        |
| NICS (1.5)               | -8.0         | -7.2        | -1.7   | -2.4        |

| NICS( $x$ ) <sup>a</sup> | 9Zr- <i>p</i> -Tol |             | (bent-[Me <sub>3</sub> SiCCC(NSiMe <sub>3</sub> ( <i>p</i> -Tol)NH <i>p</i> -Tol]) <sup>b</sup> |             |
|--------------------------|--------------------|-------------|---|-------------|
|                          | concave side       | convex side | concave side  | convex side |
| NICS (0)                 | -21.5              | -9.7        |   |             |
| NICS (0.5)               | -17.4              | -20.9       | -6.8  | -10.2       |
| NICS (1.0)               | -12.2              | -12.8       | -3.2  | -5.5        |
| NICS (1.5)               | -8.0               | -7.0        | -1.1  | -1.8        |

<sup>a</sup> Calculated at the ring center (0) and above the ring center (0.5 to 1.5 Å). <sup>b</sup> Using the same structure by deleting Cp<sub>2</sub>Zr and satisfying the two dangling valencies of the bent-[Me<sub>3</sub>SiHCCC(NSiMe<sub>3</sub>(R)NHR] (R = Cy, 9Zr-Cy; R = *p*-Tol, 9Zr-*p*-Tol) by two H atoms.

stabilization of a bent allene unit, as mentioned above, by the Cp<sub>2</sub>Zr moiety in complex 9Zr-Cy also supports this.

Thus, from MO and NBO analysis as well as NICS calculations, the complex 9Zr-Cy is better described as a  $\sigma$ -complex with cycloallenic character (G, Scheme 9) rather than a coordinated ene-yne complex (F). Pseudo-Jahn-Teller distortion plays a major role in stabilizing the nonplanar structure of the complex.

#### 4. CONCLUSION

The reaction of group 4 titanocene and zirconocene alkyne complexes 7 and 11 with cyclohexyl-, isopropyl-, or *p*-tolyl-substituted carbodiimides revealed the formation of five-membered metalla(IV)cycles exhibiting allene moieties. These metallacycles may be also described as metallocene(II) bis- $\pi$ -complexes. In each case, a Si-C bond-cleavage step forming a metallocene silyl-alkynyl compound has to be supposed. Subsequently, insertion of the hetero-allene substrate into the newly formed Si-Zr bond with a following intramolecular C-C coupling was expected. The molecular structures of these complexes confirmed a contribution of both mesomeric structures (metallacycle and bis- $\pi$ -complex). Interestingly, theoretical studies show the hetero-metallacycloallene form of complex 9Zr-Cy to be the major contributor to the resonance hybrid of the complex. The herein described complexes are the first examples for heteroatom-containing metallacyclopenta-2,3-dienes. In respect to the described reactions, the choice of metallocene source, allene substrate, and further substituents plays an

important role. Further studies on the reactivity of these complexes in ring-opening and insertion reactions as well as coordination of Lewis acidic fragments to the metallacycle are currently undertaken and will provide useful insights regarding the role of the ring heteroatom.

#### 5. EXPERIMENTAL SECTION

**General Information.** All manipulations were carried out in an oxygen- and moisture-free argon atmosphere using standard Schlenk and drybox techniques. Nonhalogenated solvents were dried over sodium/benzophenone and freshly distilled prior to use. The carbodiimides were purchased from Sigma-Aldrich and sublimed or distilled prior to use. The alkyne complexes Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) (7) and Cp<sub>2</sub>Zr( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) (11) were synthesized as described in literature previously.<sup>3b,27,28</sup> <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded on Bruker AV250, AV300, and AV400 instruments, respectively. The <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to the solvent signals: benzene-*d*<sub>6</sub> ( $\delta_{\text{H}}$  7.16,  $\delta_{\text{C}}$  128.0), CDCl<sub>3</sub> ( $\delta_{\text{H}}$  7.26,  $\delta_{\text{C}}$  77.2), and THF-*d*<sub>8</sub> ( $\delta_{\text{H}}$  3.58 and 1.73,  $\delta_{\text{C}}$  67.4 and 25.2). IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a smart endurance attenuated total reflection (ATR) device. Mass spectra were recorded on a Finnigan MAT 95-XP (Thermo-Electron). Elemental analysis were performed on a Leco CHNS-932 elemental analyzer. Melting points are uncorrected and were measured in sealed capillaries using an E/Z-Melt, Standford Research Systems.

**Computational Details.** The complexes 9Zr-Cy and 9Zr-*p*-Tol were optimized at the BP86 level of theory using Gaussian 03 and



Gaussian 09 program packages.<sup>29</sup> BP86 includes the exchange function of Becke<sup>30,31a,31b</sup> and the correlation functional of Perdew.<sup>30,32</sup> For the calculations, two types of basis sets were used: (i) BS1: LANL2DZ for all the atoms and (ii) BS2: the 6-311+G(d,p) basis set for C, H, N, Si atoms, and the LANL2DZ basis set for the Zr atom. The LANL2DZ basis set uses the effective core potentials (ECP) of Hay and Wadt.<sup>33</sup> Both the complexes are found to be minima on the potential energy surface.

**Synthesis of Complex 9Ti-*i*-Pr.** The titanocene complex 7 (0.300 g, 0.861 mmol) was dissolved in 5 mL of *n*-hexane and cooled to  $-30\text{ }^{\circ}\text{C}$ . To this solution was added 1,3-*N,N'*-diisopropylcarbodiimide (**8-*i*-Pr**) (0.110 g, 0.861 mmol). The solution was kept at  $-30\text{ }^{\circ}\text{C}$  for five days. During this time the color of the reaction mixture changed from light brown to dark red. The solution was concentrated in vacuum and stored at  $-30\text{ }^{\circ}\text{C}$ . The product crystallized at this temperature and was isolated by decanting of the mother liquor. Yield: 0.185 g (50%). Anal. Calcd for  $\text{C}_{25}\text{H}_{42}\text{N}_2\text{Si}_2\text{Ti}$  (474.65  $\text{g}\cdot\text{mol}^{-1}$ ): C, 63.26; H, 8.92; N, 5.90. Found: C, 63.16; H, 8.80; N, 5.77.  $^1\text{H}$  NMR (benzene- $d_6$ , 300 MHz, 298 K):  $\delta = 0.39$  (s, 9H, SiMe<sub>3</sub>), 0.42 (s, 9H, SiMe<sub>3</sub>), 1.15 (d, 6H, CH<sub>3</sub>, *i*-Pr-N-Si), 1.26 (d, 6H, CH<sub>3</sub>, *i*-Pr-N-Ti), 3.07 (m, 1H, CH-N-Si), 3.97 (m, 1H, CH-N-Ti), 5.25 (s, 10H, Cp).  $^{13}\text{C}$  NMR (benzene- $d_6$ , 75 MHz, 297 K):  $\delta = -0.6$  (Me<sub>3</sub>Si-C-Ti), 0.6 (Me<sub>3</sub>Si-N), 25.0 ((CH<sub>3</sub>)<sub>2</sub>CH-N-Si), 25.3 ((CH<sub>3</sub>)<sub>2</sub>CH-N-Ti), 49.3 (CH-N-Si), 50.2 (CH-N-Ti), 104.0 (Cp), 110.6 (Ti-C-Si), 117.9 (C=C-N<sub>2</sub>), 145.9 (C=C=C).  $^{29}\text{Si}$  NMR (benzene- $d_6$ , 60 MHz, 297 K):  $\delta = -7.88$  (SiMe<sub>3</sub>), 4.34 (SiMe<sub>3</sub>). MS (CI, *i*-butane):  $m/z$  (%) 474 (37) [ $\text{C}_{25}\text{H}_{42}\text{N}_2\text{Si}_2\text{Ti}^+$ ], 344 (13) [ $\text{C}_{19}\text{H}_{26}\text{NSiTi}^+$ ], 279 (13) [ $\text{C}_{14}\text{H}_{21}\text{NSiTi}^+$ ], 167 (42) [ $\text{C}_9\text{H}_{19}\text{NSi}_2^+$ ].

**Synthesis of Complex 10<sup>15</sup>.** 1,3-*N,N'*-Di-*p*-tolylcarbodiimide (**8-*p*-Tol**) (0.063 g, 0.287 mmol) was dissolved in 10 mL of *n*-hexane. The solution was cooled to  $-78\text{ }^{\circ}\text{C}$  and a solution of the titanocene complex 7 (0.100 g, 0.287 mmol) in 10 mL of *n*-hexane was added. The color of the reaction mixture changed from light brown to red, and after several minutes a red precipitate was formed, which was isolated by filtration. Crystals suitable for X-ray analysis were obtained from saturated *n*-hexane solutions. Yield 0.130 g (58%). Mp: 115  $^{\circ}\text{C}$  dec. Due to the paramagnetic properties of this titanocene(III) complex (**10**), no NMR data could be obtained. IR (ATR 16 scans,  $\text{cm}^{-1}$ ): 3021 (w), 2952 (m), 2919 (w), 2895 (w), 1814 (m), 1573 (s), 1504 (s), 1441 (w), 1405 (w), 1313 (m), 1303 (w), 1243 (s), 1213 (w), 1172 (w), 1104 (m), 1014 (m), 951 (m), 922 (m), 833 (s), 790 (m), 750 (m), 716 (w) 681 (m), 630 (m).

**Synthesis of Complex 9Zr-Cy.** 1,3-*N,N'*-Dicyclohexylcarbodiimide (**8-Cy**) (0.044 g, 0.213 mmol) was dissolved in 5 mL of *n*-hexane. This solution was added to a suspension of the zirconocene complex **11** (0.100 g, 0.213 mmol) and 15 mL of *n*-hexane. After addition, the color of the reaction mixture turned from dark violet to orange, and the mixture was stored overnight (12 h) at  $60\text{ }^{\circ}\text{C}$  to complete the reaction. After cooling to room temperature the solvent was removed and a deep red, oily solid was obtained. As attempts of recrystallization failed due to the high solubility of the product, the complex was sublimed under reduced pressure ( $10^{-3}$  mbar) at  $120\text{ }^{\circ}\text{C}$ . During the sublimation the pure reaction product condensed in yellow crystals and appeared to be suitable for X-ray analysis. Yield: 0.102 g (80%). Mp: 157  $^{\circ}\text{C}$  dec. Anal. Calcd for  $\text{C}_{31}\text{H}_{50}\text{N}_2\text{Si}_2\text{Zr}$  (598.14  $\text{g}\cdot\text{mol}^{-1}$ ): C, 62.25; H, 8.34; N, 4.68. Found: C, 55.13; H, 8.29; N, 4.68. Despite the use of  $\text{V}_2\text{O}_5$  no accurate carbon content could be detected.  $^1\text{H}$  NMR (benzene- $d_6$ , 300 MHz, 300 K):  $\delta = 0.46$  (s, 9H, SiMe<sub>3</sub>), 0.48 (s, 9H, SiMe<sub>3</sub>), 1.81–0.85 (m, 22H, Cy), 5.42 (s, 5H, Cp), 5.61 (s, 5H, Cp).  $^{13}\text{C}$  NMR (benzene- $d_6$ , 75 MHz, 300 K):  $\delta = 1.4$  (N-Me<sub>3</sub>Si), 1.9 (C-Me<sub>3</sub>Si), 26.2 (CH<sub>2</sub>, Cy), 26.6 (CH<sub>2</sub>, Cy), 26.8 (CH<sub>2</sub>, Cy), 27.2 (CH<sub>2</sub>, Cy), 27.4 (CH<sub>2</sub>, Cy), 27.9 (CH<sub>2</sub>, Cy), 35.9 (CH, Cy), 37.4 (CH, Cy), 103.5 (Cp), 105.5 (Cp), 109.4 (Zr-C(Me<sub>3</sub>Si)=), 112.4 (=C-N<sub>2</sub>), 134.8 (=C=).  $^{29}\text{Si}$  NMR (benzene- $d_6$ , 60 MHz, 300 K)  $\delta = -8.07$  (SiMe<sub>3</sub>),  $-3.50$  (SiMe<sub>3</sub>). IR

(ATR 16 scans,  $\text{cm}^{-1}$ ): 3097 (w), 2958 (w), 2923 (m), 2849 (m), 2664 (w), 1766 (m), 1586 (m), 1463 (w), 1446 (m), 1358 (w), 1338 (m), 1257 (s), 1245 (w), 1234 (w), 1181 (m), 1094 (s), 1011 (s), 979 (w), 938 (m), 882 (m), 837 (m), 780 (s), 752 (w), 685 (m), 648 (m), 623 (w), 595 (w), 532 (w). MS (CI, *i*-butane):  $m/z$  (%) 596 (100) [ $\text{C}_{31}\text{H}_{50}\text{N}_2\text{Si}_2\text{Zr}^+$ ], 427 (9) [ $\text{C}_{23}\text{H}_{32}\text{N}_2\text{Zr} + \text{H}^+$ ], 377 (83) [ $\text{C}_{21}\text{H}_{40}\text{N}_2\text{Si}_2 + \text{H}^+$ ], 303 (17) [ $\text{C}_{18}\text{H}_{31}\text{N}_2\text{Si} + \text{H}^+$ ], 207 (14) [ $\text{C}_{13}\text{H}_{22}\text{N}_2 + \text{H}^+$ ], 171 (29) [ $\text{C}_8\text{H}_{18}\text{Si}_2 + \text{H}^+$ ], 73 (9) [ $\text{C}_3\text{H}_9\text{Si}^+$ ].

**Synthesis of Complex 9Zr-*i*-Pr.** To a solution of the zirconocene complex **11** (0.235 g, 0.500 mmol) in 10 mL of *n*-hexane was added dropwise 1,3-*N,N'*-diisopropylcarbodiimide (**8-*i*-Pr**) (0.063 g, 0.500 mmol). After addition, the reaction mixture turned from dark violet to orange and was allowed to stand for 16 h to complete the reaction. The solution was filtered and the solvent was removed in vacuum. By recrystallization from a mixture of *n*-hexane, ether, and THF at  $-78\text{ }^{\circ}\text{C}$  a yellow powder was obtained which was isolated, washed with cold *n*-hexane, and dried in vacuum. Yield: 0.224 g (86%). Mp: 109  $^{\circ}\text{C}$  dec. Anal. Calcd for  $\text{C}_{25}\text{H}_{42}\text{N}_2\text{Si}_2\text{Zr}$  (518.01  $\text{g}\cdot\text{mol}^{-1}$ ): C, 57.97; H, 8.17; N, 5.41. Found: C, 58.28; H, 8.12; N, 5.34.  $^1\text{H}$  NMR (benzene- $d_6$ , 300 MHz, 297 K):  $\delta = 0.44$  (s, 9H, SiMe<sub>3</sub>), 0.45 (s, 9H, SiMe<sub>3</sub>), 1.04–1.12 (m, 9H, CH<sub>3</sub>), 1.40 (m, 3H, CH<sub>3</sub>), 3.07 (m, 1H, CH), 3.97 (m, 1H, CH), 5.37 (s, 5H, Cp), 5.59 (s, 5H, Cp).  $^{13}\text{C}$  NMR (benzene- $d_6$ , 75 MHz, 297 K):  $\delta = 1.8$  (SiMe<sub>3</sub>), 4.1 (SiMe<sub>3</sub>), 24.6 (CH<sub>3</sub>, *i*-Pr), 24.7 (CH<sub>3</sub>, *i*-Pr), 25.8 (CH<sub>3</sub>, *i*-Pr), 26.0 (CH<sub>3</sub>, *i*-Pr), 47.4 (CH, *i*-Pr), 48.8 (CH, *i*-Pr), 103.5 (Cp), 105.5 (Cp), 106.8 (Zr-C(Me<sub>3</sub>Si)=), 111.0 (=C-N<sub>2</sub>), 134.2 (=C=).  $^{29}\text{Si}$  NMR (benzene- $d_6$ , 80 MHz, 297 K)  $\delta = -7.92$  (SiMe<sub>3</sub>), 3.16 (SiMe<sub>3</sub>). IR (Nujol mull,  $\text{cm}^{-1}$ ): 3103 (w), 2959 (m), 1770 (m), 1578 (w), 1306 (m), 1264 (m), 1174 (m), 1152 (m), 1020 (m), 841 (m), 784 (m). MS (EI, 70 eV):  $m/z$  (%) 516 (36) [ $\text{M}^+$ ], 473 (21) [ $\text{M} - \text{C}_3\text{H}_7^+$ ], 289 (24) [( $\text{C}_5\text{H}_5$ )<sub>2</sub>Zr(CN<sup>*i*</sup>Pr)]<sup>+</sup>, 220 (100) [( $\text{C}_5\text{H}_5$ )<sub>2</sub>Zr]<sup>+</sup>, 155 (91) [( $\text{C}_5\text{H}_5$ )Zr]<sup>+</sup>.

**Synthesis of Complex 9Zr-*p*-Tol.** 1,3-*N,N'*-Di-*p*-tolylcarbodiimide (**8-*p*-Tol**) (0.111 g, 0.500 mmol) was dissolved in 5 mL of THF. This solution was added to a solution of the zirconocene complex **11** (0.232 g, 0.500 mmol) in 5 mL of THF. After addition, the reaction mixture turned from dark violet to orange and was allowed to stand for 6 h to complete the reaction. The solution was filtered and cooled to  $-40\text{ }^{\circ}\text{C}$ . The resulting yellow precipitate was isolated and washed with cold THF. Recrystallization from THF gave yellow crystals which were isolated and dried in vacuum. Crystals suitable for X-ray analysis were obtained from THF- $d_8$ . Yield: 0.198 g (65%). Mp: 217  $^{\circ}\text{C}$  dec. Anal. Calcd for  $\text{C}_{33}\text{H}_{42}\text{N}_2\text{Si}_2\text{Zr}$  (614.09  $\text{g}\cdot\text{mol}^{-1}$ ): C, 64.54; H, 6.89; N, 4.56. Found: C, 61.13; H, 6.94; N, 4.52. Despite the use of  $\text{V}_2\text{O}_5$  no accurate carbon content could be detected.  $^1\text{H}$  NMR (THF- $d_8$ , 300 MHz, 300 K):  $\delta = 0.26$  (s, 9H, C-Me<sub>3</sub>Si), 0.33 (s, 9H, N-Me<sub>3</sub>Si), 2.19 (s, 3H, CH<sub>3</sub>, *p*-Tol), 2.34 (s, 3H, CH<sub>3</sub>, *p*-Tol), 5.36 (s, 5H, Cp), 5.47 (s, 5H, Cp), 6.68 (m, 2H, CH, *p*-Tol), 6.82 (m, 2H, CH, *p*-Tol), 6.95 (m, 2H, CH, *p*-Tol), 7.10 (m, 2H, CH, *p*-Tol).  $^{13}\text{C}$  NMR (THF- $d_8$ , 75 MHz, 300 K):  $\delta = 1.5$  (C-Me<sub>3</sub>Si), 1.9 (N-Me<sub>3</sub>Si), 20.8 (CH<sub>3</sub>, *p*-Tol), 20.8 (CH<sub>3</sub>, *p*-Tol), 105.1 (Cp), 106.2 (Cp), 114.6 ( $^{\circ}\text{C}$ ), 121.9 (CH, *p*-Tol), 129.0 (CH, *p*-Tol), 129.8 (CH, *p*-Tol), 130.5 ( $^{\circ}\text{C}$ ), 131.4 (CH, *p*-Tol), 133.3 ( $^{\circ}\text{C}$ ), 135.3 ( $^{\circ}\text{C}$ ), 141.8 ( $^{\circ}\text{C}$ ), 143.9 ( $^{\circ}\text{C}$ ), 150.4 ( $^{\circ}\text{C}$ ).  $^{29}\text{Si}$  NMR (THF- $d_8$ , 80 MHz, 300 K):  $\delta = -7.13$  (SiMe<sub>3</sub>), 7.04 (SiMe<sub>3</sub>). IR (ATR 16 scans,  $\text{cm}^{-1}$ ): 3020 (w), 2960 (m), 2919 (w), 2897 (w), 2860 (w), 2728 (w), 1775 (m), 1726 (m), 1588 (m), 1549 (m), 1502 (s), 1440 (m), 1408 (w), 1357 (m), 1302 (w), 1282 (w), 1258 (s), 1203 (w), 1168 (w), 1091 (m), 1012 (s), 833 (w), 786 (s), 751 (w), 719 (w), 687 (m), 631 (m), 615 (m). MS (CI, *i*-butane):  $m/z$  (%) 612 (11) [ $\text{C}_{33}\text{H}_{42}\text{N}_2\text{Si}_2\text{Zr}^+$ ], 395 (100) [ $\text{C}_{23}\text{H}_{32}\text{N}_2\text{Si}_2 + \text{H}_2 + \text{H}^+$ ], 393 (73) [ $\text{C}_{23}\text{H}_{32}\text{N}_2\text{Si}_2 + \text{H}^+$ ], 323 (15) [ $\text{C}_{20}\text{H}_{24}\text{N}_2\text{Si} + \text{H}_2 + \text{H}^+$ ], 321 (9) [ $\text{C}_{20}\text{H}_{24}\text{N}_2\text{Si} + \text{H}^+$ ], 297 (11) [ $\text{C}_{18}\text{H}_{24}\text{N}_2\text{Si} + \text{H}^+$ ], 225 (41) [ $\text{C}_{15}\text{H}_{16}\text{N}_2 + \text{H}^+$ ].

**Structure Elucidation.** Crystals of the complexes **9Ti-*i*-Pr**, **10**, **9Zr-Cy**, and **9Zr-*p*-Tol** suitable for X-ray determination (Table 2), were

Table 2. Crystal Structure Data

|   | 9Ti- <i>i</i> -Pr   | 10   | 9Zr-Cy  | 9Zr- <i>p</i> -Tol  |
|---|---|--|---|---|
| chem. formula                                       | C <sub>25</sub> H <sub>42</sub> N <sub>2</sub> Si <sub>2</sub> Ti | C <sub>50</sub> H <sub>48</sub> N <sub>4</sub> Ti <sub>2</sub> | C <sub>31</sub> H <sub>50</sub> N <sub>2</sub> Si <sub>2</sub> Zr | C <sub>33</sub> H <sub>42</sub> N <sub>2</sub> Si <sub>2</sub> Zr |
| form. weight [g·mol <sup>-1</sup> ]                 | 474.69  | 800.72   | 598.13  | 614.09  |
| color   | dark red  | brown  | yellow  | yellow  |
| crystal system                                      | triclinic   | triclinic  | triclinic   | orthorhombic  |
| space group   | $P\bar{1}$  | $P\bar{1}$   | $P\bar{1}$  | <i>Pccn</i>   |
| <i>a</i> [Å]  | 10.3611(11)   | 8.1040(6)  | 10.4688(3)  | 16.8952(6)  |
| <i>b</i> [Å]  | 11.5566(13)   | 10.3858(7)   | 12.2660(4)  | 31.7271(9)  |
| <i>c</i> [Å]  | 13.457(2)   | 12.3515(9)   | 13.3377(4)  | 11.7933(3)  |
| $\alpha$ [deg]                                      | 96.926(6)   | 94.436(3)  | 78.808(1)   | 90.00   |
| $\beta$ [deg]                                       | 106.836(6)  | 94.238(3)  | 85.741(1)   | 90.00   |
| $\gamma$ [deg]                                      | 116.529(4)  | 103.346(3)   | 69.627(1)   | 90.00   |
| <i>V</i> [Å <sup>3</sup> ]                          | 1319.8(3)   | 1003.96(12)  | 1574.99(8)  | 6321.6(3)   |
| <i>Z</i>  | 2   | 1  | 2   | 8   |
| $\rho_{\text{calc.}}$ [g·cm <sup>-3</sup> ]         | 1.194   | 1.324  | 1.261   | 1.290   |
| $\mu$ [mm <sup>-1</sup> ]                           | 0.429   | 0.439  | 0.447   | 0.447   |
| $\lambda_{\text{Mo K}\alpha}$ [Å]                   | 0.71073   | 0.71073  | 0.71073   | 0.71073   |
| <i>T</i> [K]  | 173(2)  | 173(2)   | 133(2)  | 200(2)  |
| no. of rflns collected                              | 19446   | 12735  | 15194   | 32846   |
| no. of indep. rflns                                 | 5665  | 4905   | 8866  | 6193  |
| no. of rflns with $I > 2\sigma(I)$                  | 3678  | 2644   | 7837  | 4174  |
| <i>R</i> <sub>int.</sub>                            | 0.0613  | 0.0491   | 0.0189  | 0.0330  |
| <i>F</i> (000)                                      | 512   | 420  | 636   | 2576  |
| <i>R</i> <sub>1</sub> ( $R [F^2 > \sigma_2(F^2)]$ ) | 0.0504  | 0.0536   | 0.0713  | 0.0255  |
| $wR_2(F^2)$   | 0.1076  | 0.1328   | 0.0740  | 0.0506  |
| GooF  | 0.989   | 0.907  | 1.043   | 0.825   |
| parameters  | 281   | 283  | 331   | 351   |

selected in Fomblin YR-1800 oil (Alfa Aesar) at room temperature. All samples were cooled during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer (9Ti-*i*-Pr, 10 and 9Zr-Cy) and a STOE IPDS II diffractometer (9Zr-*p*-Tol). The radiation was graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  nm). The structures were solved by direct methods and refined by least-squares full matrix methods.<sup>34</sup> For compounds 9Ti-*i*-Pr, 10, and 9Zr-Cy semiempirical absorption corrections (SADABS)<sup>35</sup> were utilized; complex 9Zr-*p*-Tol was treated with numerical absorption correction (X-Shape and X-Red32).<sup>36</sup> All non-hydrogen atoms were refined anisotropically, all H atoms were positioned geometrically and refined using a riding model. Diamond was used for graphical representations.<sup>37</sup>

## ■ ASSOCIATED CONTENT

**S** Supporting Information. Crystallographic details of complexes 9Ti-*i*-Pr, 10, 9Zr-Cy, and 9Zr-*p*-Tol; details of the DFT calculations on complexes 9Zr-Cy and 9Zr-*p*-Tol as well as the full reference 29. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

jemmis@iisertvm.ac.in; axel.schulz@uni-rostock.de; uwe.rosenthal@catalysis.de

## ■ ACKNOWLEDGMENT

We thank our technical and analytical staff for assistance, in particular Dr. Anke Spannenberg for X-ray analysis of compound

9Zr-*p*-Tol. Financial support by the DFG (RO 1269/7-2) is gratefully acknowledged. E.D.J. and S.R. acknowledge the SERC of IISc and CMSD of UoH for computations. The Department of Science and Technology, New Delhi, is thanked for funding this research (J. C. Bose Fellowship).

## ■ REFERENCES

- (1) (a) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. *J. Am. Chem. Soc.* **2005**, *127*, 10166. (b) Köhn, R. D. *Angew. Chem., Int. Ed.* **2008**, *47*, 245.
- (2) (a) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Haasbroek, D.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H. *J. Am. Chem. Soc.* **2005**, *127*, 10723. (b) Peitz, S.; Aluri, B. R.; Peulecke, N.; Müller, B. H.; Wöhl, A.; Müller, W.; Al-Hazmi, M. H.; Mosa, F. M.; Rosenthal, U. *Chem.—Eur. J.* **2010**, *16*, 7670.
- (3) (a) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119. (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884. (c) Rosenthal, U. *Angew. Chem., Int. Ed.* **2004**, *43*, 3882. (d) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2005**, *24*, 456. (e) Rosenthal, U. In *Acetylene Chemistry*; Diederich, F., Stang, P. J., Tykwinski, R. R., Eds.; VCH: Weinheim, 2005; p 139. (f) Rosenthal, U.; Burlakov, V. V.; Bach, M. A.; Beweries, T. *Chem. Soc. Rev.* **2007**, *36*, 719. (g) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Spannenberg, A.; Jäger-Fiedler, U.; Klahn, M.; Hapke, M. In *Activating Unreactive Substrates*; Bolm, C., Hahn, E., Eds.; VCH: Weinheim, 2009; p 165. (h) Jemmis, E. D.; Phukan, A. K.; Giju, K. T. *Organometallics* **2002**, *21*, 2254. (i) Jemmis, E. D.; Phukan, A. K.; Jiao, H.; Rosenthal, U. *Organometallics* **2003**, *22*, 4958. (j) Jemmis, E. D.; Parameswaran, P.; Phukan, A. K. *Mol. Phys.* **2005**, *103*, 897. (k) Bach, M. A.; Parameswaran, P.; Jemmis, E. D.; Rosenthal, U. *Organometallics*

- 2007, 26, 2149. (l) Jemmis, E. D.; Roy, S.; Burlakov, V. V.; Jiao, H.; Klahn, M.; Hansen, S.; Rosenthal, U. *Organometallics* **2010**, 29, 76.
- (4) For reviews, see: (a) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, 109, 189. (b) Gleiter, R.; Merger, R. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; p 285. (c) Meier, H. *Adv. Strain Org. Chem.* **1991**, 1, 215.
- (5) For reviews, see: (a) Johnson, R. P. *Chem. Rev.* **1989**, 89, 1111. (b) Balci, M.; Taskesenligil, Y. *Adv. Strained Interesting Org. Mol.* **2000**, 8, 43. (c) Christl, M. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; VCH: Weinheim, 2004; pp 243, and references cited therein.
- (6) (a) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1605. (b) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1112. (c) Burlakov, V. V.; Beweries, T.; Bogdanov, V. S.; Arndt, P.; Baumann, W.; Petrovskii, P. V.; Spannenberg, A.; Lyssenko, K. A.; Shur, V. B.; Rosenthal, U. *Organometallics* **2009**, 28, 2864.
- (7) (a) Suzuki, N.; Nishiura, M.; Wakatsuki, Y. *Science* **2002**, 295, 660. (b) Suzuki, N.; Aihara, N.; Takahara, H.; Watanabe, T.; Iwasaki, M.; Saburi, M.; Hashizume, D.; Chihara, T. *J. Am. Chem. Soc.* **2004**, 126, 60. (c) Suzuki, N.; Watanabe, T.; Hirose, T.; Chihara, T. *Chem. Lett.* **2004**, 33, 1488. (d) Suzuki, N.; Watanabe, T.; Iwasaki, M.; Chihara, T. *Organometallics* **2005**, 24, 2065. (e) Suzuki, N.; Watanabe, T.; Yoshida, H.; Iwasaki, M.; Saburi, M.; Tezuka, M.; Hirose, T.; Hashizume, D.; Chihara, T. *J. Organomet. Chem.* **2006**, 691, 1175.
- (8) (a) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Parameswaran, P.; Jemmis, E. D. *Chem. Commun.* **2004**, 2074. (b) Bach, M. A.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2005**, 24, 3047. (c) Bach, M. A.; Beweries, T.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Bonrath, W. *Organometallics* **2005**, 24, 5916. (d) Beweries, T.; Bach, M. A.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, 26, 241.
- (9) (a) Ohff, A.; Pulst, S.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. *Synlett* **1996**, 111. (b) Togni, A.; Halterman, R. L., Eds.; *Metalloenes: Synthesis, Reactivity, Applications*; VCH: Weinheim, 1998; Vols. 1 and 2 and references therein. (c) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, 100, 2835.
- (10) (a) Suzuki, N.; Hashizume, D.; Koshino, H.; Chihara, T. *Angew. Chem., Int. Ed.* **2008**, 47, 5198. (b) Suzuki, N.; Hashizume, D. *Coord. Chem. Rev.* **2010**, 254, 1307.
- (11) (a) Ugolotti, J.; Dierker, G.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, 47, 2622. (b) Ugolotti, J.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, 131, 1996. (c) Ugolotti, J.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *Chem. Commun.* **2009**, 6572.
- (12) Lamac, M.; Spannenberg, A.; Jiao, H.; Hansen, S.; Baumann, W.; Arndt, P.; Rosenthal, U. *Angew. Chem., Int. Ed.* **2010**, 49, 2937.
- (13) Theilmann, O.; Ruhmann, M.; Villinger, A.; Schulz, A.; Seidel, W. W.; Kaleta, K.; Beweries, T.; Arndt, P.; Rosenthal, U. *Angew. Chem., Int. Ed.* **2010**, 49, 9282.
- (14) Zhang, S.; Zhang, W.-X.; Zhao, J.; Xi, Z. *J. Am. Chem. Soc.* **2010**, 132, 14042.
- (15) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, 20, 349.
- (16) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Principles of Structure and Reactivity*, 4th ed.; Prentice Hall: New York, 1995.
- (17) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
- (18) Kirmse, W.; Konrad, W. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 661.
- (19) (a) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, 18, 4660. (b) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, 21, 1190.
- (20) Beweries, T.; Burlakov, V. V.; Bach, M. A.; Peitz, S.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Pathak, B.; Jemmis, E. D. *Angew. Chem., Int. Ed.* **2007**, 46, 6907.
- (21) Stepnicka, P.; Gyepes, R.; Cisarova, I.; Horacek, M.; Kubista, J.; Mach, K. *Organometallics* **1999**, 18, 4869.
- (22) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899.
- (23) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, 118, 6317. (b) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, G. V.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, 119, 12669. (c) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, 3, 2465.
- (24) Hunter, W. E.; Hrcir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, 2, 750.
- (25) (a) Jahn, H. A.; Teller, E. *Proc. R. Soc.* **1937**, A161, 220. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; Part 1, p 95.
- (26) (a) Dyker, C. A.; Lavallo, V.; Donnadiu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, 47, 3206. (b) Lavallo, V.; Dyker, C. A.; Donnadiu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, 47, S411.
- (27) Burlakov, V. V.; Rosenthal, U.; Petrovskii, P. V.; Shur, V. B.; Volpin, M. E. *Organomet. Chem. USSR* **1988**, 1, 953.
- (28) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Z. Anorg. Allg. Chem.* **1995**, 621, 77.
- (29) Frisch, M. J.; et al. *Gaussian 03*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2004. Frisch, M. J.; et al. *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
- (30) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
- (31) (a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (b) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
- (32) Perdew, P. *Phys. Rev. B* **1986**, 33, 8822.
- (33) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, 82, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 299.
- (34) Sheldrick, G. M. *Acta Crystallogr.* **2008**, A64, 112.
- (35) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 2004.
- (36) *X-SHAPE and X-RED32*; STOE & Cie GmbH: Darmstadt, Germany, 2005.
- (37) Brandenburg, K. *DIAMOND*, Version 3.1e; Crystal Impact GbR: Bonn, Germany, 2007.