ACCOUNTS of chemical research

Article

pubs.acs.org/accounts

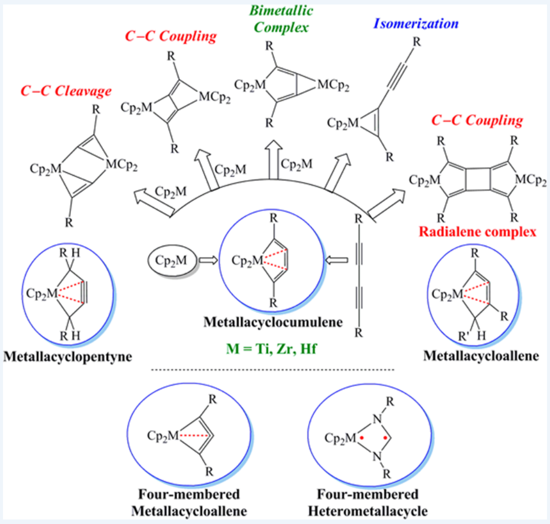
Metallacyclocumulenes: A Theoretical Perspective on the Structure, Bonding, and Reactivity

Subhendu Roy,[†] Uwe Rosenthal,[‡] and Eluvathingal D. Jemmis*,[†]

[†]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, 560012, India

[‡]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Strasse 29a, D-18059 Rostock, Germany

S *Supporting Information*



CONSPECTUS: Transition metals help to stabilize highly strained organic fragments. Metallacycles, especially unsaturated ones, provide much variety in this area. We had a sustained interest in understanding new C–C bond formation reactions affected by binuclear transition metal fragments Cp_2M. One such study led to the exploration of the bimetallic C–C cleavage and coupled complexes, where the acetylide ligands bridge two metal atoms. The underlying M–C interaction in these complexes inspired the synthesis of a five-membered cyclocumulene complex, which opened a new phase in organometallic chemistry. The metallacyclocumulene produces a variety of C–C cleavage and coupled products including a radialene complex. Group 4 metallocenes have thus unlocked a fascinating chemistry by stabilizing strained unsaturated C_4 organic fragments in the form of five-membered metallacyclocumulenes, metallacyclopentynes, and metallacycloallenes. Over the years, we have carried out a comprehensive theoretical study to understand the unusual stability and reactivity of these metallacycles.

The unique ($M-C_\beta$) interaction of the internal carbon atoms with the metal atom is the reason for unusual stability of the metallacycles. We have also shown that there is a definite dependence of the C–C coupling and cleavage reactions on the metal of metallacyclocumulenes. It demonstrates unexpected reaction pathways for these reactions. Based on this understanding, we have predicted and unraveled the stabilization factors of an unusual four-membered metallacycloallene complex. Indeed, our prediction about a four-membered heterometallacycle has led to an interesting bonding situation, which is experimentally realized. This type of M–C bonding is intriguing from a fundamental perspective and has great relevance in synthesizing unusual structures with interesting properties.

In this Account, we first give a short prologue of what led to the present study and describe the salient features of the structure and bonding of the metallacyclocumulenes. The unusual reaction pathway of this metallacycle is explored next. Similar features of the metallacyclopentynes and metallacycloallenes are briefly mentioned. Then, we discuss the exploitation of the unique M–C bonding to design some exotic molecules such as a four-membered metallacycloallene complex. Our efforts to build a conceptual framework to understand these metallacycles and to exploit their chemistry continue.

INTRODUCTION

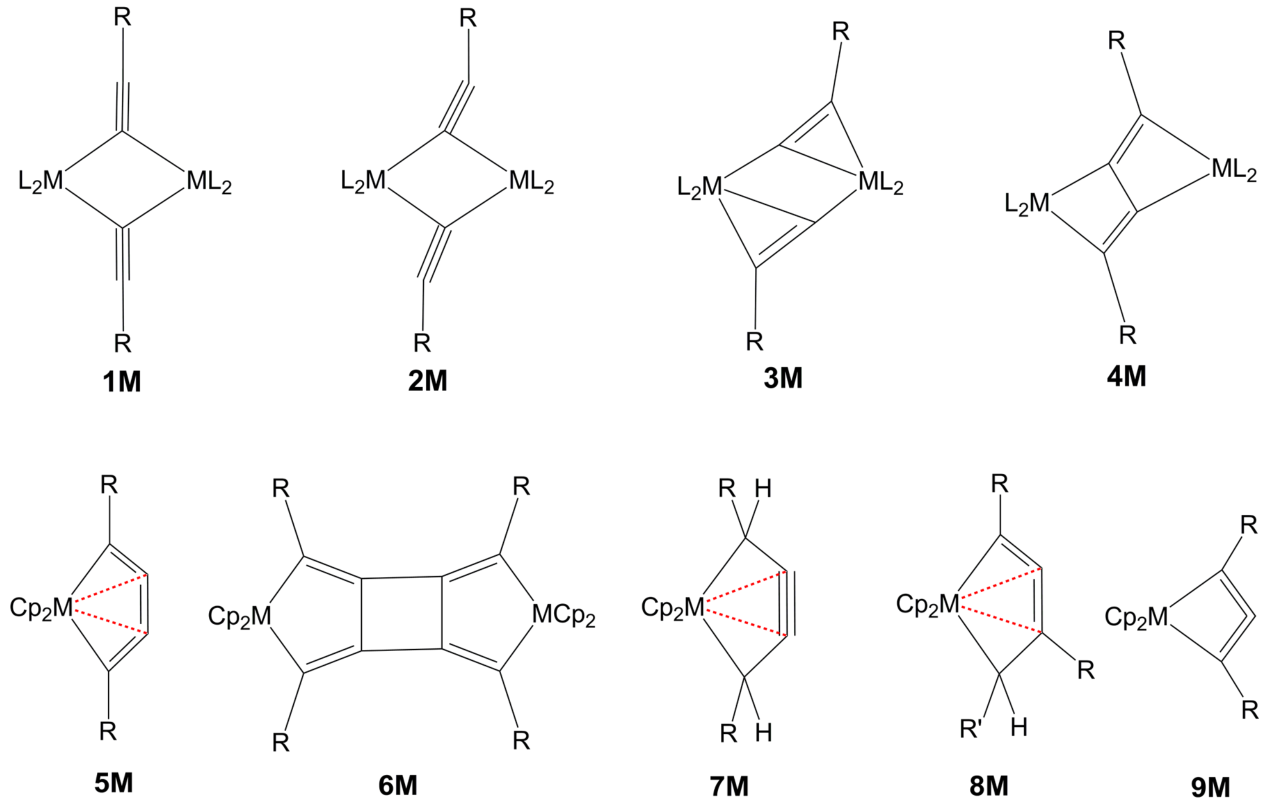
Transition metals have attained superstar status for making seemingly impossible transformations possible under normal conditions and for providing unprecedented bonding situations that expand our understanding of the chemical bond.[1] Metallacycles provide much variety in this area. The involvement of metallacyclic intermediates, such as metallacyclobutane and metallacyclobutadiene in olefin and alkyne metathesis is well-known.[2−4] Metallacyclopentane and metallacyclopentadiene with no direct metal–C_β bonding interactions are well documented.[5] The *in situ* generated metallocenes (Cp_2M) of group 4 metals (M = Ti and Zr) have a special position in this chemistry because of their capability in forming several unsaturated metallacycles on reactions with unsaturated hydrocarbons.[6] Nugent, Negishi, Nakamura, and Buchwald, among others, have pioneered the use of group 4 metals in the synthesis of important and complex organic molecules through the involvement of metallacycles.[7] Here we focus on unsaturated metallacycles generated from the Cp_2M ($Cp = C_5H_5$) fragments and hydrocarbons such as RCCCCR, RHCCCCHR, RCCCRCHR′, RCCCR, and their heteroanalogues (Scheme 1). We have used in this study computational methods that over the years evolved as a powerful technique not only to complement experimental studies but also to design new experiments and develop novel concepts.

Group 4 metallocenes (Cp_2M) with their 14e configuration are both coordinatively and electronically unsaturated. The

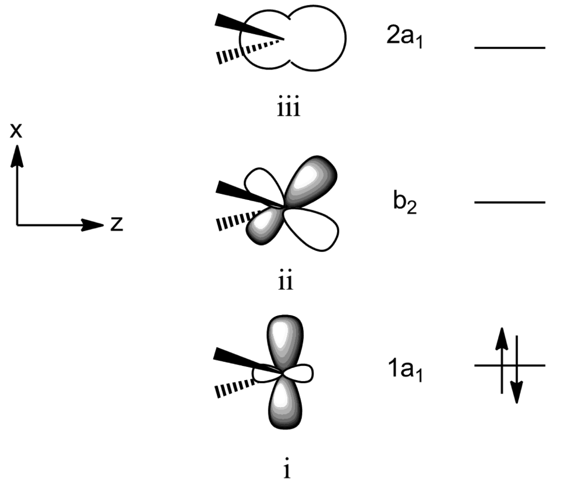
Received: April 19, 2014
Published: August 29, 2014

dx.doi.org/10.1021/ar5001567 | *Acc. Chem. Res.* 2014, 47, 2917−2930

Scheme 1. Schematic Representations of Various Metallacycles



Scheme 2. Frontier Molecular Orbitals of a Bent Metallocene (Cp_2M, M = Ti, Zr, or Hf) Unit



bent group 4 metallocene, with a d^2 configuration (M^{+2}), has three in-plane frontier molecular orbitals in the equatorial plane bisecting the CpMCp angle (i−iii, Scheme 2) with two valence electrons.[8] Thus, Cp_2M is isolobal to carbene because both have two electrons in a set of a_1 and b_2 orbitals. However, carbene cannot stabilize the strained organic fragments as the Cp_2M fragment does with its more diffuse orbitals having more varied extensions in space under the same symmetry. This is why replacement of CH_2 fragments in organic molecules by isolobal Cp_2M (M = Ti, Zr and Hf) fragments brings dramatic changes in the structure, bonding, and reactivity of the organometallic complexes in comparison to the organic counterpart.[5]

Our interest in Cp_2M fragments started with a search for new C−C bond forming reactions. One such study[9] led to the analysis of structural variations in the complexes where the acetylide ligands (−C≡CR) bridge two metal atoms (Scheme 1). The bimetallic complexes of Li, Be, Na, and Al have the structures **1M** or **2M** with very little involvement of the π MOs of the acetylide in M−C bonding.[9] In contrast, Cp_2M fragments prefer structures **3M** where in-plane π and π^* orbitals of the acetylides interact strongly with the metal orbitals and **4M** with a new C−C bond. The Cp_2Zr fragment prefers the acetylide structure **3M**, and Cp_2Ti prefers the **4M**. The preference for **3M** or **4M** also depends on the substituent R (Table 1).

These observations inspired many chemists[9] and led one of us to isolate the structure **5M** (M = Ti or Zr, Scheme 3).[10] This is the smallest cyclocumulene to be isolated and characterized. The metallacyclocumulene **5M** also produces a radialene complex **6M**, a formal [2 + 2] cycloaddition product, but only for M = Ti (Scheme 3).[11] Surprisingly for M = Zr, only the C−C cleavage product **3Zr** is obtained (Table 1).[12] Earlier, Buchwald and co-workers also tried to synthesize such a complex **6Zr** with $SiMe_3$ substituents[13] but were unsuccessful. However, the synthesis of metallacyclocumulene led chemists to the isolation of two related structures, metallacyclopentyne[14] and metallacycloallene,[15] as well as four-membered metallacycloallenes and heteroallenes (**7M**, **8M**, and **9M**, Scheme 1). The status of these attempts forms the subject of this Account.

■ METALLACYCLOCUMULENES

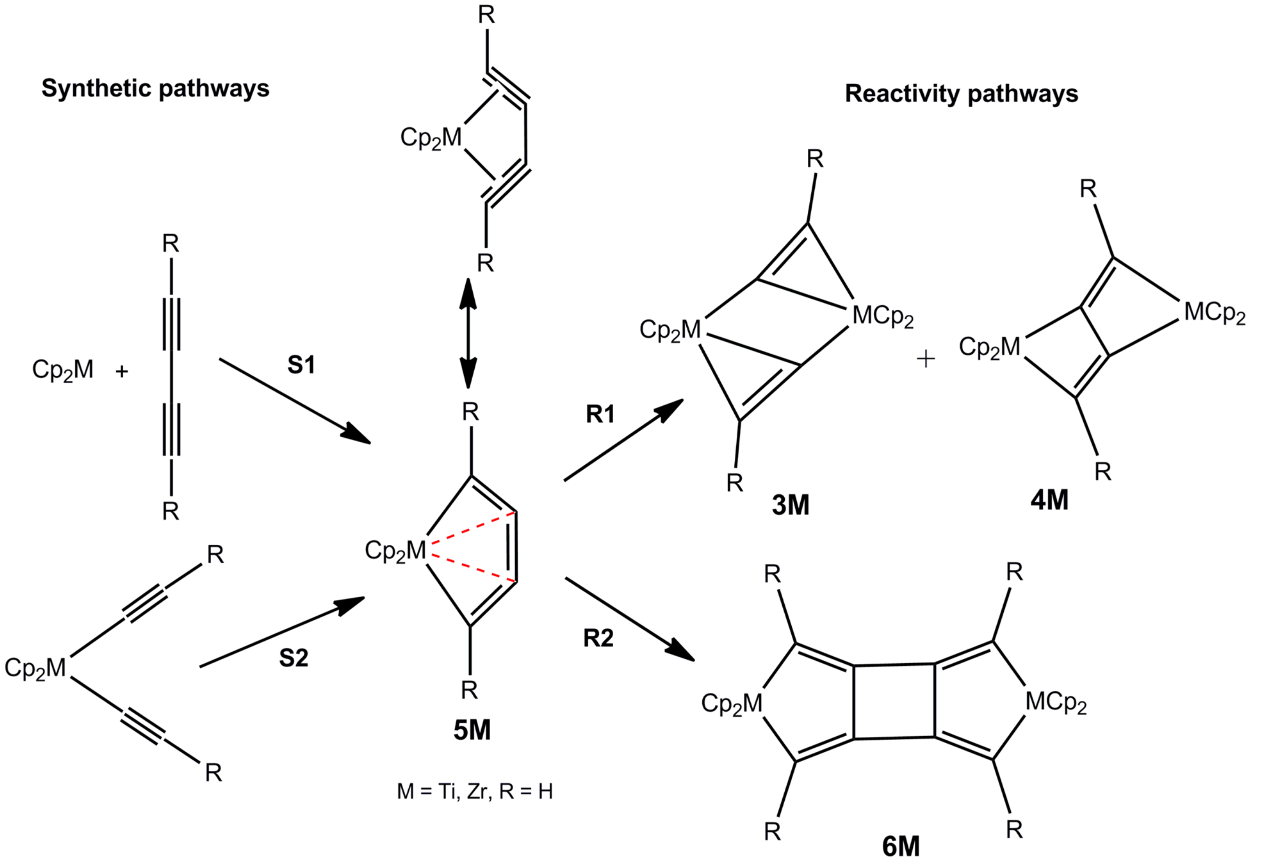
Many derivatives of metallacyclocumulenes (**5M**) are known experimentally for metals Ti, Zr, and Hf.[10,16] Calculations show that all M−C bonds are within the bonding range with significant internal M−C_β interactions (Figure 1a; Table S1,

Table 1. Known Structures of 1M−8M (Scheme 1)

metallacycle	M	ligand (L_2)	substituent R[a]	metallacycle	M	ligand (L_2)	substituent R[a]
1	Li	Tmpda	Ph (9)	**3**	Zr	$(C_5H_4Me)_2$	Ph (20)
1	Be	$(NMe_3)(C{\equiv}CMe)$	Me (9)	**3**	Zr	Cp ($\mu-\eta^5$-C_5H_4)	Ph (20)
1	Be	$(NMe_3)(Me)$	Me (9)	**3**	Zr	Cp ($\mu-\eta^5$-C_5H_4)	$SiMe_3$ (20)
1	Ti	$(C_5H_4)_2SiMe_2$	Ph (20)	**3**	Zr	($\mu-\eta^5$-C_5H_4) (η^5-$C_5H_3SiMe_3$) $SiMe_2$	$SiMe_3$ (20)
2	Be	$(NMe_3)(C{\equiv}CMe)$	Me (9)	**4**	Ti	Cp_2	Ph, *t*Bu, $SiMe_3$ (20)
2	Al	Ph_2	Ph (9)	**4**	Ti	$(C_5H_4Me)_2$	Ph (20)
2	Al	Me_2	Me (9)	**5**	Ti,Zr	Cp_2	*t*Bu (6)
2	Ga, In	Me_2	Me (9)	**5**	Zr	Cp^*_2	Ph or $SiMe_3$ (6)
2	Er	Cp_2	CMe_3 (9)	**6**	Ti	Cp_2	Ph (11)
2	Cu,Ag	$(Me_3P)_2$	Ph (9)	**7**	Ti	Cp_2	H, $SiMe_3$ (26)
2	Sm	$(C_5H_4Me)_2$	CMe_3 (9)	**7**	Zr	Cp_2	$SiMe_3$, *t*Bu (14)
3	Ti	$(C_5H_4)_2SiMe_2$	Ph (20)	**7**	Zr	Cp^*_2	H (26)
3	Ti	$(C_5H_3Me_2)_2$	$SnMe_3$ (20)	**7**	Hf	Cp_2	$SiMe_3$ (26)
3	Zr	Cp_2	$SiMe_3$, *n*Bu (20)	**8**	Zr,Hf	Cp_2	*t*Bu, $SiMe_3$ (15)

[a] References for the corresponding structures are given in parentheses after the substituents.

Scheme 3. Schematic Representation of Synthetic and Reactivity Pathways for Five-Membered Metallacyclocumulene 5M



Supporting Information). The analysis of computed C−C bond length and bond indices and population analysis (NBO) suggests cumulenic nature for **5M**.[5] The metal atom and the four carbon atoms of the MC_4 ring in **5M** are coplanar, and there is a strong bonding interaction between the metal and all four carbon atoms orbitals (HOMO, HOMO − 6 in Figure 1b).

The bonding of **5M** can be best analyzed from a fragment molecular orbital approach.[17] The three frontier orbitals of the Cp_2M fragment (Scheme 2) are in the MC_4 plane. The in-plane frontier orbitals of the RCCCCR fragment are very similar to the π MOs of butadiyne or butadiene. These are constructed from the two in-plane p orbitals on the two central carbon atoms (C2 and C3) and the sp^2 hybrid orbitals on the terminal carbon atoms (C1 and C4). Out of the four resulting MOs, the lowest two MOs are occupied.[17] The LUMO of the C_4H_2 fragment, which is bonding between C2 and C3, is similar to the in-plane equivalent of the LUMO of butadiene π-orbitals. The strongest stabilizing interaction is between this LUMO of the C_4H_2 fragment and the HOMO of the Cp_2M fragment strengthening the C2−C3 bond (HOMO, Figure 1b).[17] The other stabilizing interaction is the donation of electrons from the HOMO − 1 of C_4H_2 into the LUMO + 1 of the metal to form HOMO − 6. The bonding is similar to the ligand to metal

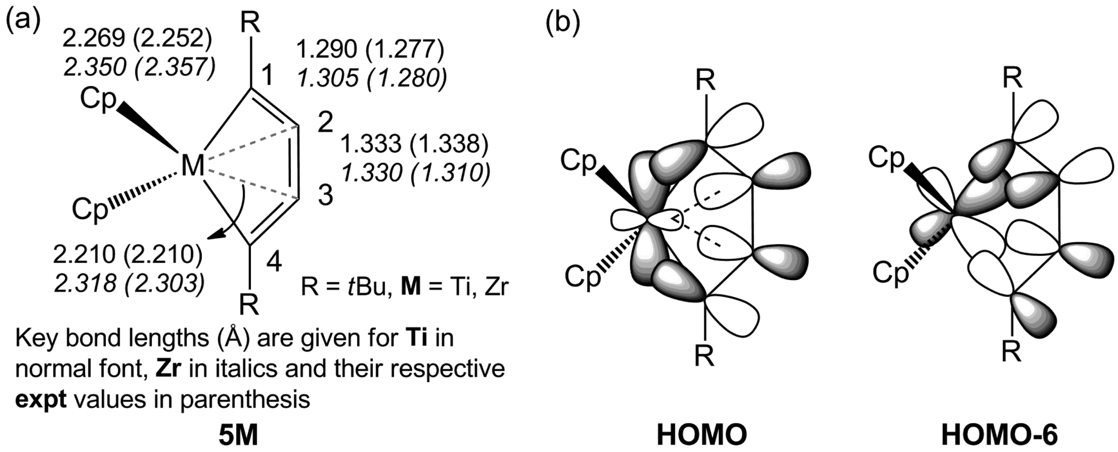
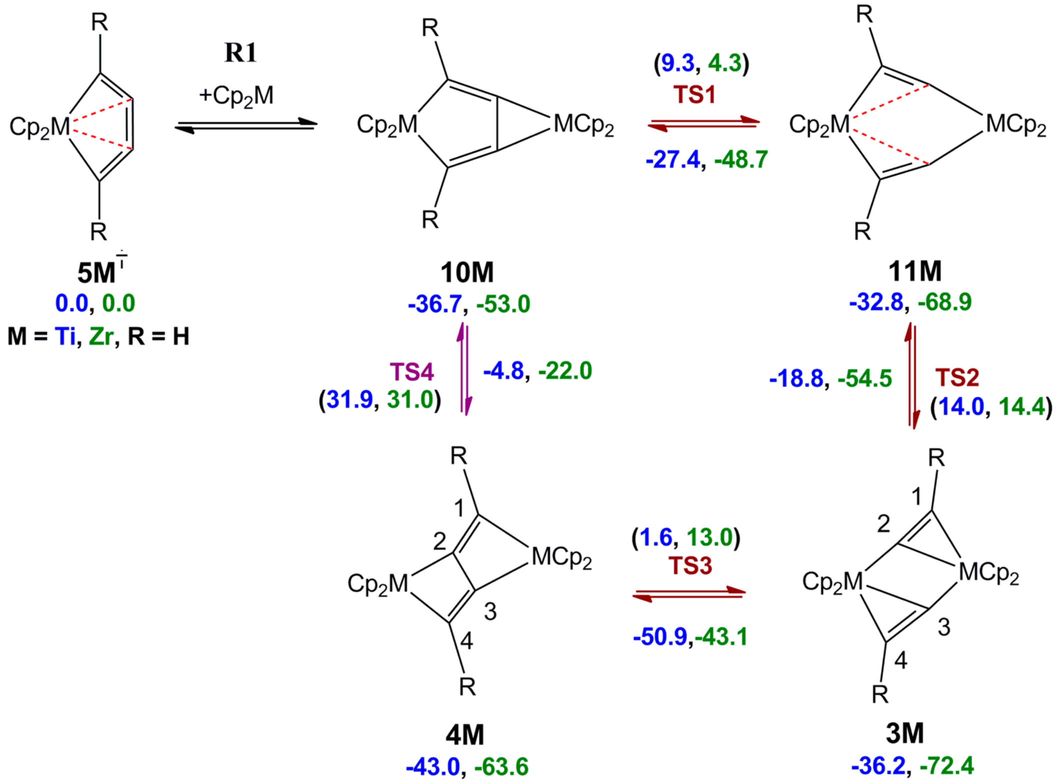


Figure 1. Optimized geometrical parameters of **5M** (a) and its important MOs (b).

Scheme 4. Reaction Pathways for the C−C Coupling and Cleavage Reactions of Metallacyclocumulene 5M (R1, Scheme 3)[a]



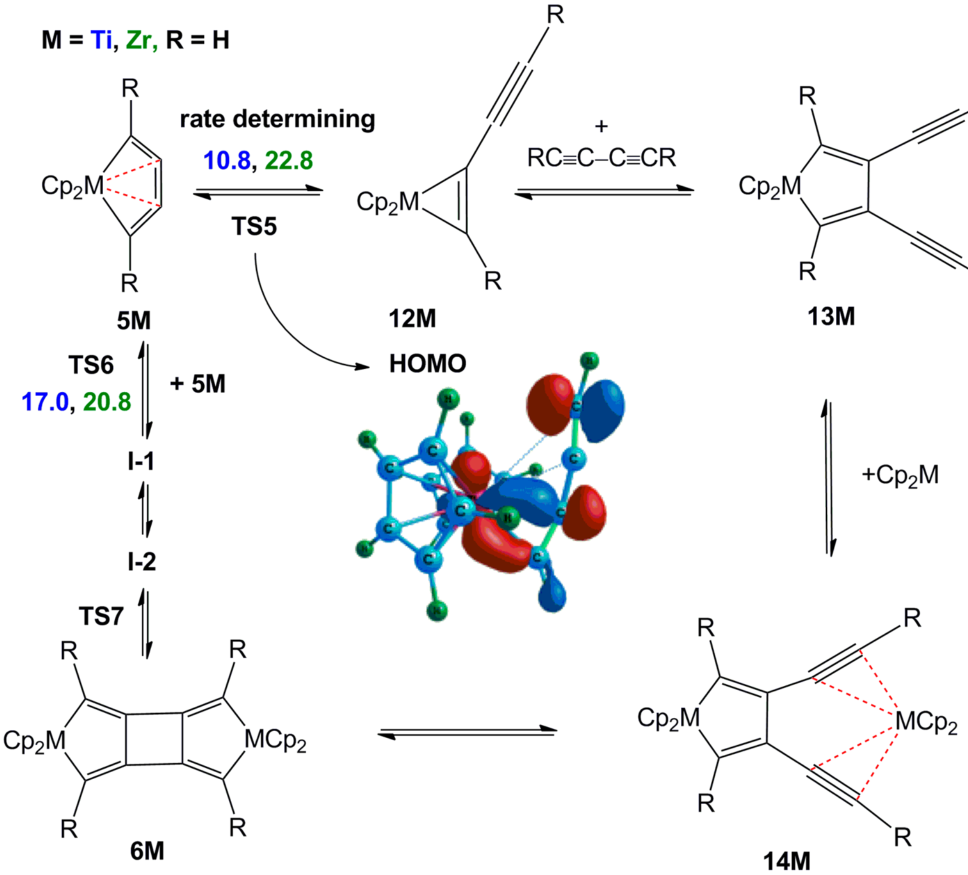
[a] Relative energies (kcal/mol) are calculated with respect to **5M** at B3LYP/def2-SVP level of theory for M = Ti (blue) or Zr(green). Energy barriers for each step are given in parentheses. Energy of the **5M** and the isolated Cp_2M are taken as reference.

donation and metal to ligand back bonding observed in the Dewar−Chat−Duncanson model, except for the C2−C3 bonding nature of the acceptor orbital on C_4H_2. The analysis suggests the metallacyclic structure **5M** to be the major descriptor of the complex.[5,18] The calculated nucleus-independent chemical shift (NICS) values for **5Zr** (R = H) are −30.41 and −14.37 at the ring center and 1 Å above the ring center. Obviously, there is cyclic delocalization of electrons in the complex. Thus, NICS calculations and other analysis reveal **5M** to be neutral in-plane aromatic.[5] Aromaticity plays an important role in stabilizing such strained systems as was recently observed in the reported osmapentalenes,[19] where an unsaturated C_7 fragment interacts with a metal.

■ REACTIVITY OF METALLACYCLOCUMULENES

Generally the metallacyclocumulene **5M**, formed from the reaction of Cp_2M with butadiyne (RC≡C−C≡CR), reacts with another mole of Cp_2M to produce the C−C cleavage product **3M** or the C−C coupled product **4M** depending on the metal and the substituents (Table 1).[6] We had established the mechanism of these reactions and unraveled the reason for the different preferences of Ti (**4Ti**) and Zr metals (**3Zr**).[20] We present very briefly the pathway for formation of the complexes **3M** and **4M** and also show how radialene **6Ti** is formed through an unusual mechanism.

Scheme 5. Plausible Reaction Pathways for the Formation of Radialene Complex 6M



C–C CLEAVAGE AND COUPLING REACTIONS

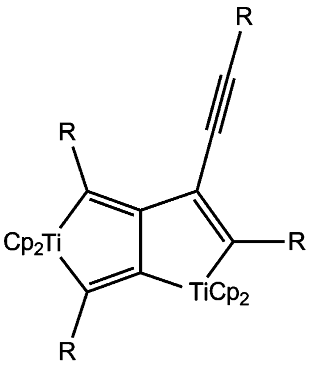
The formation of the C–C coupled product **4M** via intermediates **10M**, **11M**, and **3M** is found to be the most favorable pathway.[20,21] Direct conversion of **10M** to **4M** is not feasible due to the higher reaction energy barrier of 31.9 kcal/mol associated with this step, in comparison to 14.4 kcal/mol calculated as the highest barrier for the favorable pathway (Scheme 4).[20,21] The isomeric **3M**–**4M** transformation is the important step that differentiates between Ti and Zr in the mechanistic scheme.

The unusual C–C coupling that led to the Ti complex (**4M**) and the absence of it in the corresponding Zr complex (**3M**) is attributed to the thermodynamic energy difference between the two isomers. The C–C coupled product **4Ti** is calculated to be lower in energy by 6.8 kcal mol^{-1} compared with **3Ti** (R = H). But the C–C cleavage product **3Zr** is lower in energy than the C–C coupled product **4Zr** by 8.8 kcal mol^{-1}. The difference in the diffuse nature of the valence atomic orbitals of the two metals suggests an explanation. The more diffuse orbitals of Zr lead to longer Zr–acetylide σ-ligand distance, which in turn causes longer C2–C3 distance (2.993 Å) in **3Zr**. Simultaneously the orbitals of the same Zr interact strongly with the π MOs of the other acetylide. The similar interaction is not as strong with Ti with its less diffuse orbitals. In addition, the C3 unit in **4M** interacts better with Ti, bringing **4Ti** lower in energy than **3Ti**. These are reflected in the exothermicity of the equation **3Ti** + **4Zr** → **4Ti** + **3Zr** of 15.6 kcal/mol at B3LYP/def2-SVP.[20,21] The energy barrier and the extent of movement of atoms required in the reaction follow the Evan Polyani's and Hammond's postulates.[22] However, the energy differences involved are not very large. Calculations reveal that electron withdrawing substituents such as R = F could draw the acetylides closer to the metal, thereby bringing the two C atoms closer to drive the **3M**–**4M** equilibrium to the C–C coupled product **4M** for both Ti and Zr metals.[20]

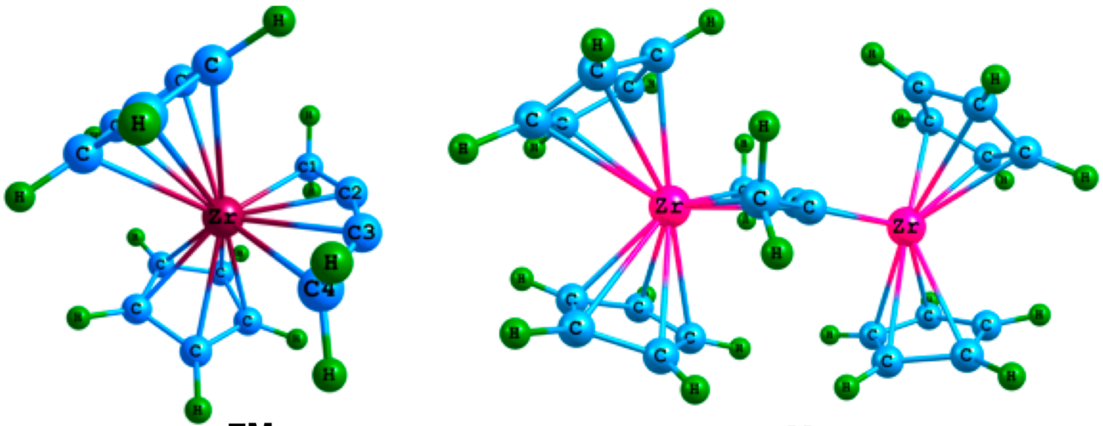
DIMERIZATION OF METALLACYCLOCUMULENES

Dimerization of **5M** to give radialene **6M** is exothermic by 18.9 and 18.6 kcal mol^{-1} (dimerization energy; basis set superposition error (bsse) corrected) for Ti and Zr metals, respectively, but only **6Ti** is known.[21] The direct [2 + 2] cycloaddition pathway is not symmetry allowed. A stepwise

Scheme 6. Titanacyclopentadiene–Titanacyclopentene Complex



R = Ph, Me



7M

15M

Figure 2. Optimized structure of **7Zr** and bimetallic complex **15M**.

mechanism also did not distinguish between Ti and Zr analogs; the calculated barrier for the first step in the dimerization of **5M** is 17.0 kcal mol^{-1} for Ti and 20.8 kcal mol^{-1} for Zr (Scheme 5).[21] The absence of the formation of **6Zr** requires another mechanistic explanation.[11]

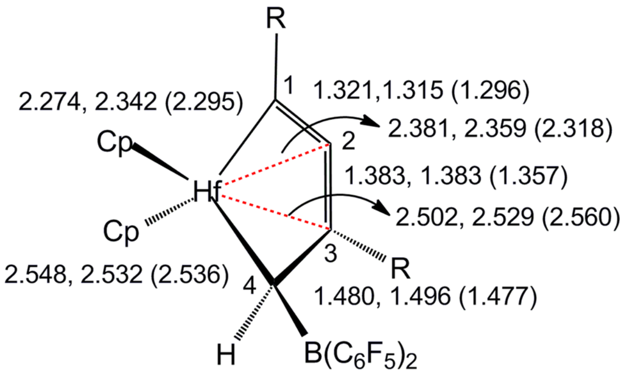
The η^4-metallacyclocumulene **5M** is observed to exist in equilibrium with its isomeric three-membered η^2-metallacyclopropene **12M**.[23] The barrier for the **5M**−**12M** isomerization via **TS5** is calculated to be 10.8 kcal mol^{-1} for Ti and 22.8 kcal mol^{-1} for Zr. The HOMO of the transition state **TS5** indicates the M−C bond breaking (Scheme 5). This barrier difference of isomerization reflects the two metals' ability to interact with the carbon atoms of the C_4 π-ligand. With its more contracted orbitals, the Ti interacts effectively with a C_2 ligand in **12Ti**, while the larger Zr binds better with the C_4 ligand in **5Zr**. This trend holds true for all the substituents as is evident from the free energy difference of the two complexes **5M** and **12M** for the two metals (Table S3, Supporting Information). The stability of the η^2-alkyne π-complex increases with increasing electron-donating substituents on carbon for both Ti and Zr complexes. The Cp^*_2Zr fragment ($Cp^* = C_5Me_5$) reacts with $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ to form the η^4-complex, $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}Me_3SiC_4SiMe_3)$, while smaller Cp^*_2Ti generates the three-membered η^2-complex, $Cp^*_2Ti(\eta^2\text{-}1,2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)$.[16] Generally Zr forms the η^2-complex with an additional ligand.

Indeed, the titanacyclopentadiene−titanacyclopentene complex (Scheme 6), which was isolated during the formation of **6M**, supports the existence of **12Ti**.[11] The metallacyclopropene **12M**, on reductive coupling with another molecule of 1,3-butadiyne ($RC{\equiv}C{-}C{\equiv}CR$), can form the bis(alkynyl)-metallacyclopentadiene **13M** with low barrier height (Scheme 5). Bis(alkynyl)metallacyclopentadienes are known. Coordination of **13M** with Cp_2M to give **14M** is significantly exothermic. The reaction of bis-alkyne complex **14Ti** to the radialene complex **6Ti** is nearly barrierless. Thus, the decisive step is the **5M**−**12M** isomerization. This kind of reaction path was suggested for the reaction of $Me_3SiC{\equiv}C{-}CH_2{-}C{\equiv}CSiMe_3$ with zirconocene.[24] The preference of Zr for **5M**, rather than **12M**, is evident from the structural features as well (Table S1, Supporting Information). There are several products observed that support that Zr prefers **5Zr** while Ti tends to choose **12Ti**.[16] Additionally formation of **6Hf** from **5Hf** at higher temperature, which may allow the conversion to **12Hf**, reinforces this mechanistic proposal.[25]

■ METALLACYCLOPENTYNES AND METALLACYCLOALLENES

The stabilization of **5M** led to the anticipation of metallacyclopentyne **7M** and metallacycloallene **8M**. Suzuki et al. synthesized **7Zr**,[14,26] which contains a strained alkyne unit (Figure 2). Molecular orbital analysis suggests that the strong interaction between the metal and C_β atoms stabilize this system.[5,18,26] All five atoms of the MC_4 ring are coplanar in **7Zr**. A detailed analysis of the calculated NICS values at the ring center and 1 Å above the ring center (−44.76 and −18.44, respectively, for **7Zr**, R = H) shows it to be a neutral bishomoaromatic[5] with both in-plane and out-of-plane delocalization. However, there is a perpendicular π-orbital (HOMO − 1) in **7Zr**, which is mainly localized on the C_β atoms (C2 and C3). These π-orbitals can interact with a second metal.[27] This proposition is exemplified by the existence of $Cp_2M(\mu{-}\eta{:}\eta\text{-}H_2C_4H_2)M'L_2$[27] (**15M**, Figure 2) where M = Zr and $M'L_2 = ZrCp_2$ or $Ni(PR_3)_2$.

Scheme 7. Optimized Geometrical Parameters of Metallacycloallene 8Hf (*anti*)



Key bond lengths (Å) are given for R = H, SiH_3 in normal font and for experimental structure R = *t*Bu in parenthesis

8Hf (*anti*)

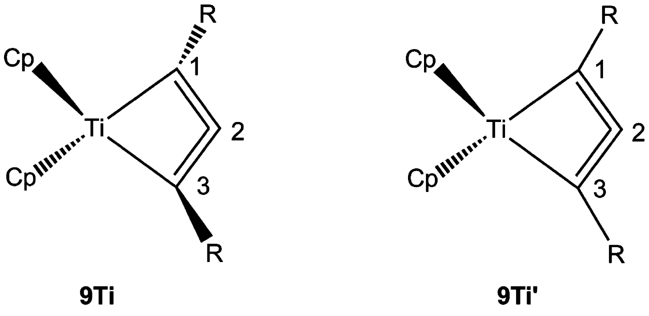
Erker et al. synthesized the five-membered metallacycloallene **8M** containing a strained allene unit with R = $SiMe_3$ or *t*Bu (Table 1 and Scheme 7).[15] The MC_4 unit in **8M**, unlike in **5M** or **7M**, is not planar. We have analyzed the structure and bonding of **8Hf**; the calculated structural parameters are in good agreement with the values from the X-ray crystal structure (Scheme 7).[17]

The structure **8Hf** (*anti*) with a near-planar HfC_4 unit turns out to be the transition state, and the barrier for conformational isomerism of **8Hf** (*anti*, R in opposite site w.r.t. $B(C_6F_5)_2$ in the nonplanar ring) to **8Hf** (*syn*) with R = $SiMe_3$ is calculated to be 28.2 kcal/mol, which is somewhat higher than the experimental value of 14.4 ± 0.3 kcal/mol.[15] The similarity of Hf−C1 and Hf−C2 bond lengths indicates that there is a strong interaction between the metal atom and the internal carbon atom C2 along with a distinct Hf−C1 bond. The interaction between the metal atom and the carbon atom C3 is not as strong compared with that of Hf−C1 and Hf−C2 bonds. Naturally the Hf−C3/C4 bonds are relatively longer than the Hf−C1/C2 bonds (Scheme 7). The NBO analysis suggests an allenic arrangement in **8M**. In essence, M−C bonding as in **5M** and **7M** stabilizes **8M**.

■ FOUR-MEMBERED METALLACYCLOALLENES

The study of metallacyclocumulenes, metallacyclopentynes, and metallacycloallenes led us to four-membered metallacycloallene complexes **9M** (Scheme 1).[28] The carbocyclic analogue 1,2-cyclobutadiene is too strained to be isolated. It may be noted that there are many reports on metallacyclobutadienes (MC_3R_3).[29] Schrock et al. had described two complexes with similar structural skeleton to **9M**, "deprotiometallacyclobutadienes" $[Mo\{C_3(tBu)_2\}\{OCH(CF_3)_2\}_2(py)_2]$ (**16Mo**) and $[CpW\{C_3(tBu)_2\}Cl]$, during the metathesis of terminal alkynes.[30] Herein, we present an analysis of bonding in **9Ti** (Scheme 8) and suggest synthetic approaches.

Scheme 8. Schematic Representations of a Four Membered Metallocycloallene 9Ti and the Planar Complex 9Ti′



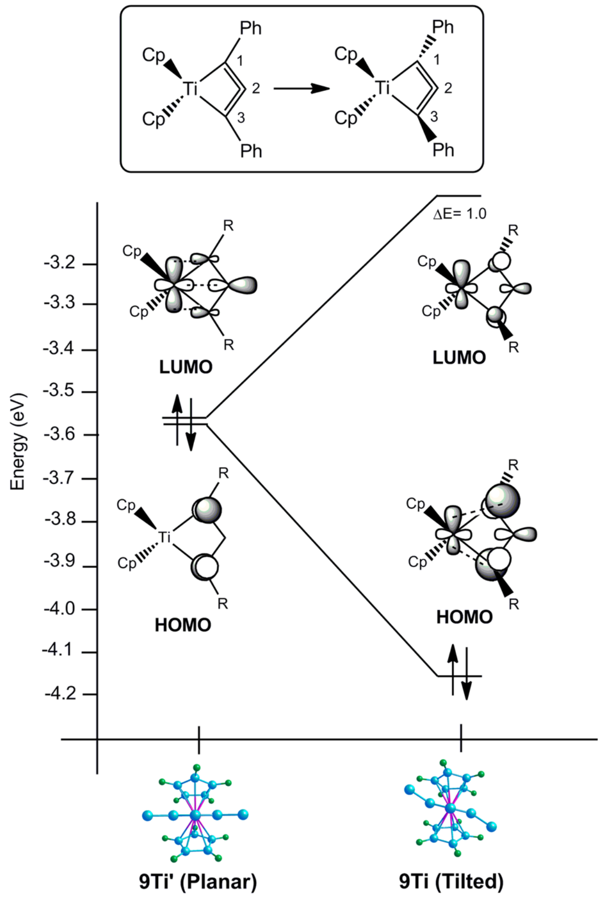
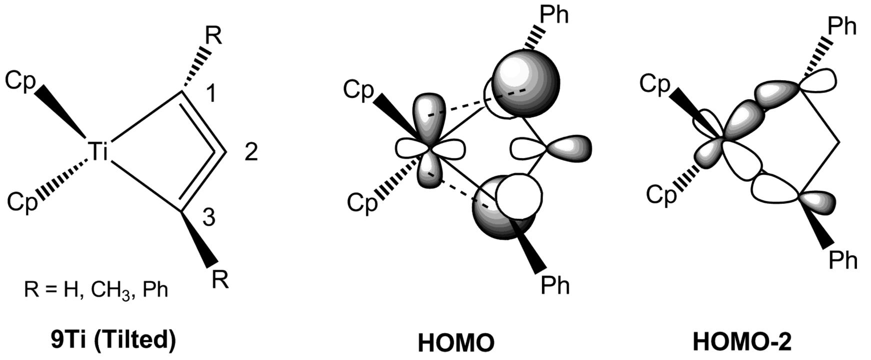


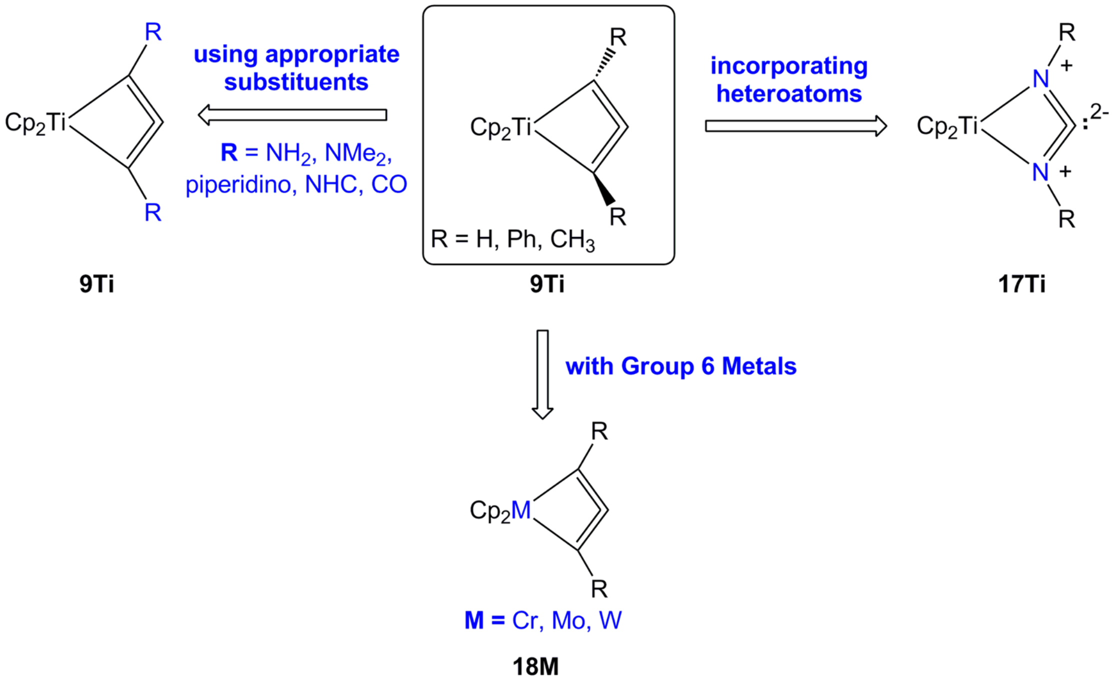
Figure 3. Correlation diagram between the planar structure **9Ti′** and the tilted structure **9Ti** (R = Ph). The energy change of the HOMO and LUMO is plotted as a function of distortion in **9Ti**.

The optimized structure of **9Ti** with R = H, CH_3, and Ph has a tilted geometry. The MC_3 ring deviates from the plane (equatorial plane) that bisects the CpMCp angle. In addition, the substituents (R) are out of the M−C1−C2−C3 plane to a significant extent (Scheme 9). The planar structure **9Ti′** (R = H) with constrained geometry turns out to be a first-order saddle point, which is 20.0 kcal/mol higher in energy than the optimized complex **9Ti** (R = H). The HOMO and HOMO − 2 (Scheme 9) are two MOs of **9Ti** (R = Ph) that predominantly constitute the Ti−C bonds of 2.202 Å (cf. calculated Ti−C σ bond length of 2.168 Å in $[Cp_2TiMe_2]$). Although the Ti−C1/C3 bonds (2.202 Å) and Ti···C2 (2.211 Å) have close

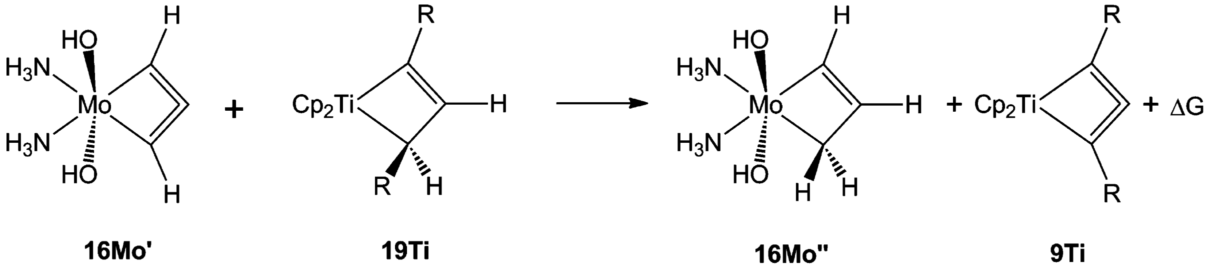
Scheme 9. Schematic Representations of the Optimized Structure of 9Ti and Its Important MOs



Scheme 10. Strategies for Transformation of the Tilted Complex 9Ti to Various Planar Systems

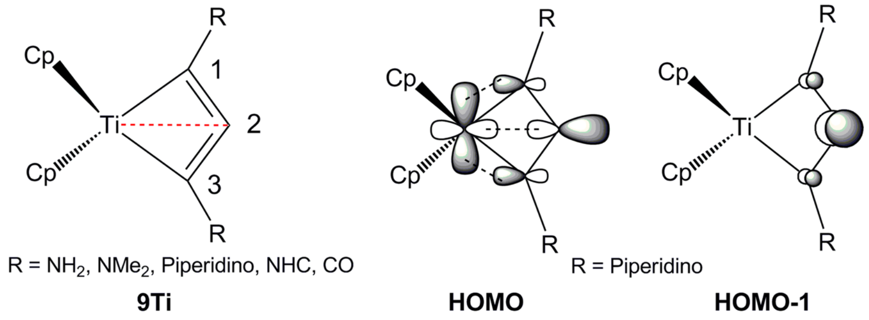


Scheme 11. Δ*G* (kcal/mol) for the Isodesmic Equation at the BP86/def2-SVP Level



R	H	Ph	CH_3	NH_2	NMe_2	Piperidino	NHC	CO
ΔG	17.2	9.7	13.8	-0.6	-8.4	-8.6	-3.7	-6.6

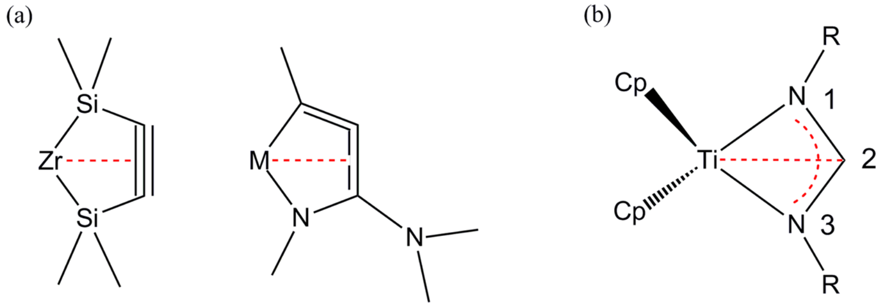
Scheme 12. Schematic Representations of the Optimized Planar Structure of 9Ti and Important MOs of 9Ti



interatomic distances, there is no MO indicating a strong Ti···C2 interaction. Besides, no lone pair is noticed on C2 in **9Ti** (R = Ph).

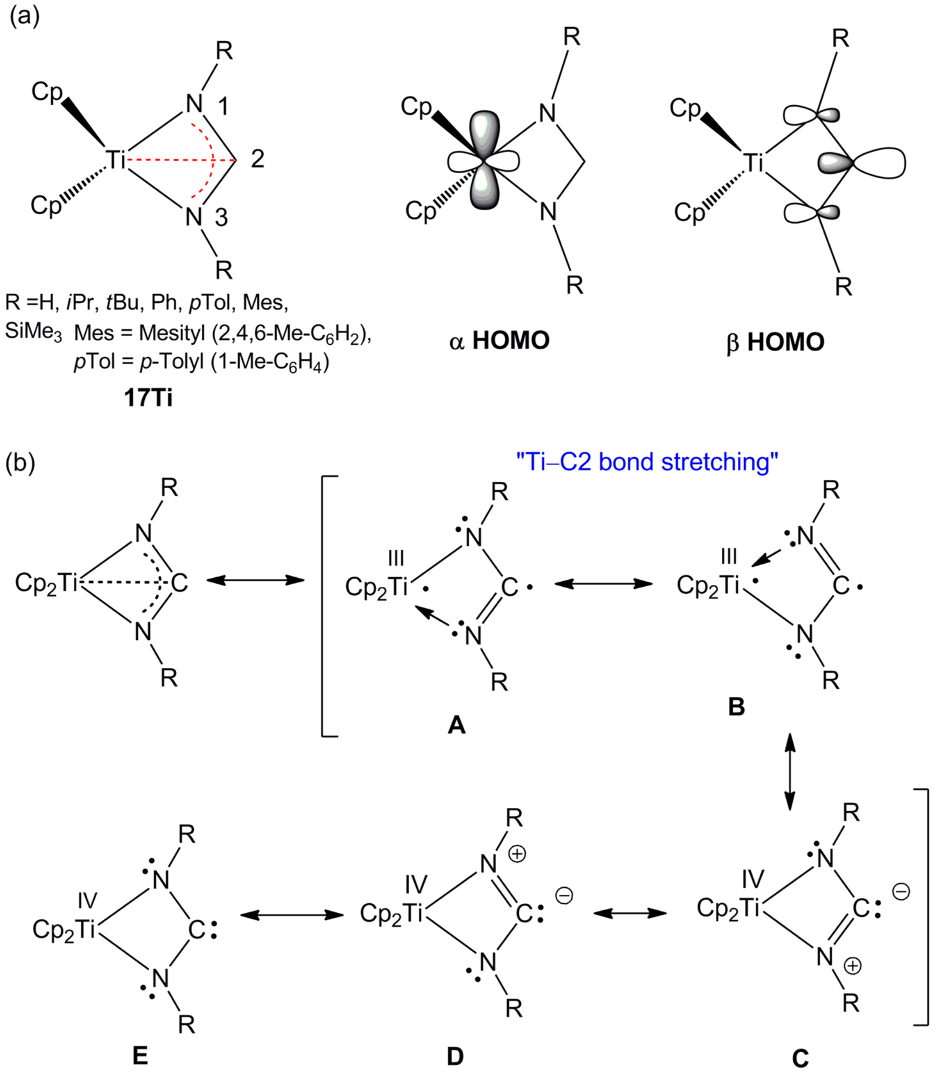
A correlation diagram (Figure 3) is drawn between the planar and tilted structure of **9Ti** (R = Ph), which reveals that the planar **9Ti**′ has a very small HOMO−LUMO energy gap. As a consequence, it undergoes a structural distortion, which allows mixing of these MOs to stabilize the tilted complex **9Ti** to a greater extent. This is nothing but a pseudo-Jahn−Teller distortion. We observed that the LUMO has a strong M−C2 bonding character (Figure 3). Addition of two electrons therefore stabilizes the planar structure, **9Ti**′. Indeed, dianionic **9Ti**″ having two extra electrons than **9Ti** adopts a planar structure. We can provide two electrons to **9Ti** (a) by using suitable substituents that are capable of donating two electrons to **9Ti** (R = NH_2, NMe_2, piperidino, NHC, CO), (b) by

Scheme 13. Schematic Representations of (a) Known Metallacycles Containing Heteroatoms and (b) a Heterometallacycloallene 17Ti



17Ti

Scheme 14. Schematic Representations of (a) a four-membered Heterometallacycloallene, 17Ti, with various Substituents (R) and Its *α* and *β* HOMO and (b) Plausible Resonance Structures for 17Ti That Include the Ti–C2 Bond Stretching

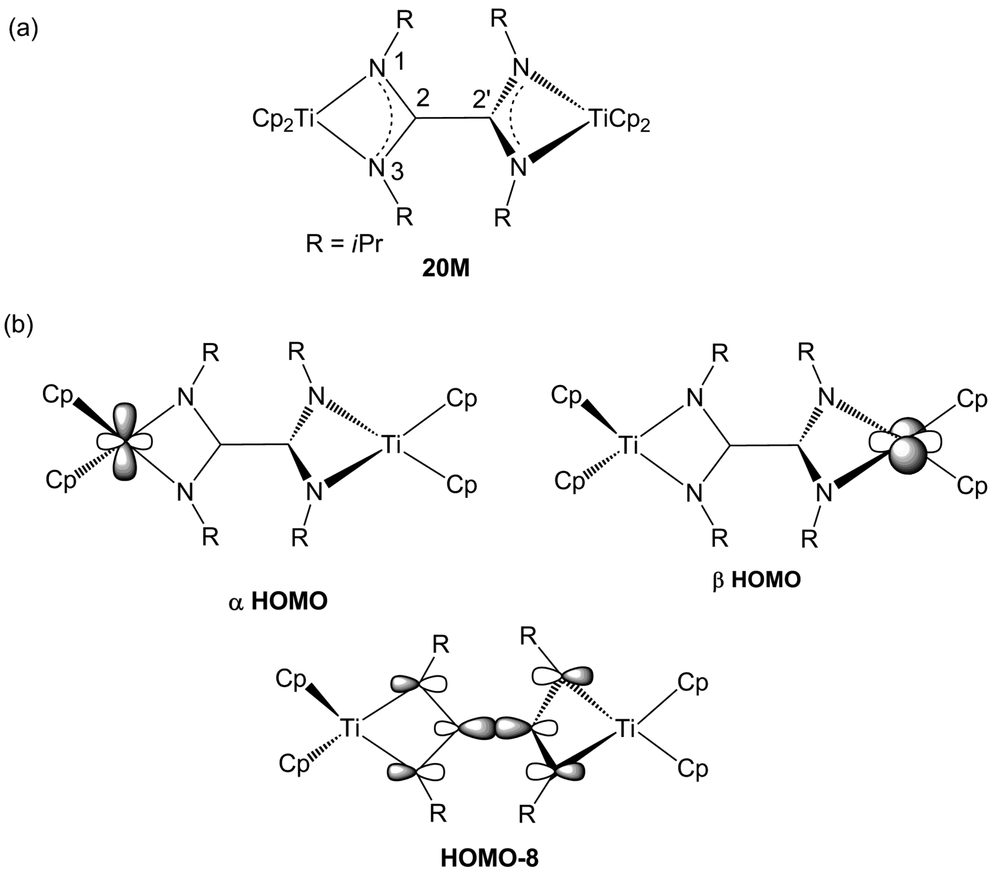


incorporating two nitrogen atoms in the ring to form a heterometallacycloallene (**17Ti**), and (c) by using group 6 metals (**18M**) (Scheme 10).

The isodesmic equation, which is devised to ascertain the thermodynamic feasibility of synthesizing **9Ti** for R = H, CH$_3$, or Ph with respect to the model known complex **16Mo**′ (obtained by replacing the −OCH(CF$_3$)$_2$ and pyridine by −OH and −NH$_3$, respectively, in **16Mo** with R = H) reveals the reactions to be endergonic (Scheme 11). Indeed, this is in agreement with the unsuccessfully attempted synthesis by one of us of **9Ti**, employing lithiated allenes (LiRC═C═CRLi; R = Ph) and metallocene dichlorides [Cp′$_2$MCl$_2$] (Cp′ = C$_5$H$_5$ or C$_5$Me$_5$; M = Ti, Zr, or Hf).[28]

Interestingly, the optimized structures of **9Ti** (R = NH$_2$, NMe$_2$, piperidino, NHC, and CO) indicate that these substituents provide additional electrons to the complex and

Scheme 15. (a) Dimetallacycle 20M and (b) Its *α* and *β* HOMO Showing Biradical Nature of the Complex and HOMO − 8 of Complex 20M



make the MC_3 unit planar, in comparison to **9Ti** (R = H, Ph, CH_3) (Scheme 12). The HOMO (Scheme 12) along with a HOMO − 2 orbital (Scheme 9) explains the short Ti−C bond lengths in the planar complexes, which range between 2.072 and 2.081 Å (Table S4, Supporting Information). Specifically, the significant Ti−C2 interaction in **9Ti** (R = piperidino) is reflected in the filled MO (HOMO, Scheme 12). This is crucial for the stability of the unusual four-membered ring and is supported by NBO analysis with an occupancy of 80.9% with 0.297 Ti(d)+0.703 C2(p) composition (Table S5, Supporting Information).

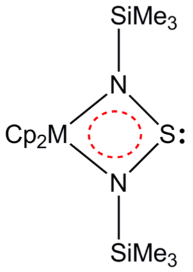
The *π*-donating effect of the piperidino group into the p orbitals at C1 and C3 in **9Ti**, which causes polarization of the *π* bonds toward the central carbon atom, is responsible for the longer average allene C−C bond length (1.378 Å) in **9Ti** than the standard allene C−C bond length of 1.307 Å.[31] The HOMO, which involves significant interaction between the Ti atom and the central carbon atom C2 and the nonbonding HOMO − 1, have larger contributions from the central carbon atom C2 (Scheme 12). The Ti···C2 interaction is unprecedented and may render complexes with interesting chemical properties.

Encouragingly, the isodesmic equation shows **9Ti** with R = NH_2, NMe_2, piperidino, NHC, and CO to be significantly exothermic (Scheme 11). The increased stability of these complexes is attributed to the existence of the in-plane HOMO (Scheme 12), which results in planar structures with the novel Ti···C2 bonding interaction. **9Ti** attains the familiar 18-electron configuration with the formation of the Ti−C2 bond in the planar complexes, justifying further its stability. In contrast, the tilted complex **9Ti**, a 16-electron complex, does not have this interaction. Recent characterization of a four-membered carbocyclic allene[32] molecule with cyclic amine substituents provides strong motivation for the experimental realization of these complexes.

■ HETEROMETALLACYCLOALLENES

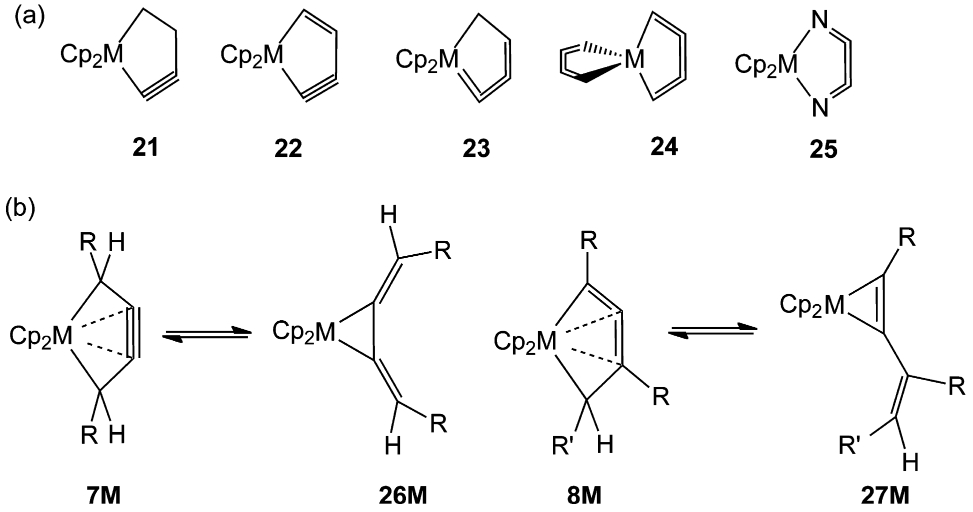
Strained metallacycles are also isolated with heteroatoms in the ring. This is exemplified by the formation of five-membered 1-zircona-2,5-disilacyclopent-3-yne, heterometallacycloallenes (Scheme 13a).[33]

Scheme 16. Schematic Representations of a Heterometallacycle



We have just seen from the theoretical analysis of **9Ti** that the four-membered heterometallacycloallene **17Ti** can be a candidate for synthetic exploration (Scheme 10 and Scheme 13b). In this part, we present a detailed theoretical analysis of the electronic structure and bonding of heterometallacycles

Scheme 17. (a) Schematic Representations of Some Interesting Metallacycles and (b) η^4−η^2 Equilibrium for Metallacyclopentyne (7M) and Metallacycloallene (8M)



17Ti with substituents of varying electronic and steric influences (Scheme 14a). A detailed study of **17Ti** unravels the peculiar electronic nature of this strained four-membered heterometallacycle.[34] We investigated **17Ti** using a density functional theory approach (DFT-broken-spin-symmetry). Complexes **17Ti** have open-shell singlet state (OSSS) character (at the B3LYP/def2-SVP level) as revealed by stability checking the wave function of the complexes. The delicate Ti−C2 interaction in **17Ti** provides support for it (Scheme 14b). Unrestricted broken-spin-symmetry approach (UBS-B3LYP) is employed to obtain the stable wave functions for these complexes. Optimized **17Ti** takes up a planar geometry (Ti−N1−C2−N3 ≈ −0.8° for R = *i*Pr, Table S6, Supporting Information).

Interestingly, electron-donating substituents reduce the natural orbital occupation number (NOON)[35] values of Ti−C2 in **17Ti** LUMO from 34.9% to 13.6% for H and *t*Bu, (Table S7, Supporting Information). This is in tune with the short Ti−C2 distance (from 2.384 to 2.274 Å for H and *t*Bu, Table S7, Supporting Information). Furthermore, the Ti−C2 distance of 2.316 Å in **17Ti** (R = *i*Pr) is only marginally longer than the calculated Ti−C σ bond distance of 2.160 Å in Cp_2TiMe_2. These observations point to the description of Ti···C2 as a "stretched" chemical bond.

Both the electronic and steric effects of the Mes groups are needed to explain the higher NOON value of **17Ti** (R = Mes). Mes is more electron donating than a *p*-Tol group, but it is bulkier. The higher steric requirement of the Mes group hinders stronger complexation of the respective carbodiimide to the Cp_2Ti moiety. This results in comparatively longer Ti−N (2.189 Å) and Ti−C2 (2.462 Å) bond lengths. So, electronic as well as steric effects contribute to the effective complexation of the carbodiimide with Cp_2Ti to result in the four-membered **17Ti**.

The calculated NOON values correctly describe the bonding in **17Ti** because the complex does not represent a perfect biradical (for which NOON should be close to 100%)[35a] but is an appropriate "biradicaloid" species on account of the Ti···C2 interaction. Among the five resonating structures, **A** and **B** are the major descriptors of the molecule (Scheme 14b). This draws support from spin density calculations as well as from the isolated complexes (**20M**), which contain a Ti(III) center.[34] Several unusual metallacycles including dimetallacyle **20M** (Scheme 15a) resulted when the metallocene−alkyne complexes reacted with a variety of carbodiimides.[34]

The "stretched" Ti−C2 bond (2.316 Å) of the monometallic complex **17Ti** (R = *i*Pr) disappears in dimetallacycle **20M** (Ti··· C2 = 2.632 Å), which corroborates the above interpretation. The occupation of the metal d orbitals in **20M** with electrons of opposite spin (α and β HOMO, Scheme 15b) renders the complex an almost perfect biradical (NOON is 98%). The allene orbitals of the two RNCNR moieties in **20M** interact strongly to form a C−C single bond (C2−C2′ = 1.542 Å) corresponding to HOMO − 8 (Scheme 15b). Substituents (R) with proper balance of electronic and steric influences are required to assist in the formation of the crucial Ti−C2 bond so that a derivative of **17Ti** can be isolated.

Formation of various metallacycles from the reaction of titanocene with carbodiimide prompted us to investigate substitution reactions with other heteroallenes such as sulfurdiimide. We have investigated also the structure and bonding of the four-membered heterometallacycle (Scheme 16), which is best described as a complex with cyclic delocalization of electrons in it.[36]

■ SUMMARY AND OUTLOOK

Our theoretical study has shown that the unusual stability of the unsaturated five-membered metallacycles stems from the unique (M−C_β) interaction of the internal carbon atoms with the metal atom. The investigation of the reactivity of metallacyclocumulenes reveals that the formation of the radialene complex **6M** proceeds through a three-membered metallacyclopropene complex **12M**, contrary to the prevailing notion of a simple dimerization of **5M**. The equilibrium between the three- and five-membered ring (**5M**−**12M**) is predominantly governed by the extent of diffuse nature of metal orbitals and is fine-tuned by the substituents. This equilibrium plays a crucial role in the chemistry of Cp_2M−ligand complexes. On the basis of this understanding, we have predicted and unraveled the stabilization factors of a challenging four-membered metallacycloallene complex **9M**, which is found to contain a unique crucial M−C2 bond in the MC_3 ring. Electron donating substituents, such as NMe_2, piperidino, and NHCs, are calculated to stabilize the complex significantly. The MO and NBO analyses support the existence of the crucial M−C2 bond in the MC_3 ring, which enhances the stability of the complexes. We predicted an unusual bonding situation in the four-membered heterometallacycle **17Ti** and realized it experimentally. This heterometallacycle features biradicaloid character resulting from a stretched M−C2 bond, which gets manifested in its reactivity. This observation of the substituent-dependent biradicaloid character lends itself to obvious extension.

Several implications of interest have emerged from these studies. Incorporation of nonlinear cumulenic double bond (C═C═C═C) or alkyne (C−C≡C−C) or allenic (C═C═C−C) moieties into the metallacyclic rings leads to unusual systems, which not only are structurally interesting but also show reactivity very different from their carbocyclic analogues. It would be worthwhile to investigate some interesting metallacycles as shown in Scheme 17a, which may reveal new bonding features with unusual reactivity.

The metallacyclopentyne **7M** does not undergo [2 + 2] cycloaddition reaction with alkenes.[14] **7M** also does not trimerize by Ni^0 catalyst.[37] Interestingly, the metallacycloallene is found to stabilize the MgH_2 indicating the many possibilities that exist for these complexes.[38] The equilibrium that exists between **5M** and **12M** (η^4-complex and η^2-complex) prompts us to suggest similar possibilities for metallacyclopentyne **7M** and metallacycloallene **8M**[39] (Scheme 17b). We feel that consideration of the η^4−η^2 equilibrium along with judicious selection of substituents will lead to a rich chemistry in this area. An in-depth study is required to understand the reactivity of these and related metallacycles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Important structural parameters and NBO analysis of some complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jemmis@ipc.iisc.ernet.in.

Notes

The authors declare no competing financial interest.

Biographies

Subhendu Roy received his B.Sc. in Chemistry from Visva-Bharati University, West Bengal, in 2006. In the same year, he joined the Integrated Ph.D. program in Chemical Sciences at the Indian Institute of Science, Bangalore. In 2009, he completed his M.S. from the same Institute and pursued his Ph.D. under the supervision of Prof. Eluvathingal D. Jemmis. He received his Ph.D. from Indian Institute of Science, Bangalore, in 2013. His research interests include computational studies of the structure, bonding, and reactivity of small and large molecules and catalysis in various conditions.

Uwe Rosenthal was born in 1950, studied chemistry (1968−1972), received his Ph.D. under E. Kurras (1976), and finished his habilitation (1991) at the University of Rostock. After a stay at Nesmeyanov Institute of Organo element Compounds in Moscow with M. E. Vol'pin and V. B. Shur (1988), he was a scientific guest at Max Planck Institute of Kohlenforschung in Mülheim/Ruhr with G. Wilke and K. Pörschke (1990−1991). He headed the Max Planck Research group "Complex Catalysis" (1992−1996) and became Professor of Inorganic Chemistry at the University of Rostock (1993). Today he is Deputy Director of the Leibniz Institute for Catalysis (LIKAT) in Rostock with scientific interests in organometallic chemistry and coordination chemical catalysis. He published around 300 papers and patents on this subject.

Eluvathingal D. Jemmis studied chemistry at St. Thomas College, Trichur, University College, Thiruvananthapuram, the Indian Institute of Technology, Kanpur (M.Sc.), Princeton University (Ph.D.), and Cornell University before joining University of Hyderabad in 1980 as a lecturer. Jemmis was a Visiting Fellow at the Research School of Chemistry, Australian National University, Canberra (1991). In 2005, Jemmis accepted an invitation from IISc Bangalore and joined its Inorganic and Physical Chemistry Department. Jemmis was deputed for five years (June 2008 to June 2013) to start the IISER Thiruvananthapuram. His research interests (http://ipc.iisc.ernet.in/~jemmis/) are in applied theoretical chemistry, with an emphasis to find common threads between problems in different areas. The extension of Wade's $n + 1$ skeletal electron pair rules for polyhedral boranes by Jemmis' group (mno rule) to include condensed polyhedral boranes, metallocenes, metallaboranes, and elemental boron has become a part of textbooks of inorganic chemistry. Jemmis received several awards and honors including the SS Bhatnagar Prize of CSIR in 1994.

■ ACKNOWLEDGMENTS

We thank the SERC, IISc, and the CMSD, University of Hyderabad, for providing the computational facility to carry out our research work and the DST, New Delhi, India, for financial support through J. C. Bose Fellowship. Financial assistance by the DFG (RO 1269/8-1) is gratefully acknowledged. We thank Dr. Dandamudi Usharani for her assistance during the revision of the manuscript.

■ DEDICATION

This Account is dedicated to Professor CNR Rao on his 80th Birthday.

■ REFERENCES

(1) (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 3rd ed.; University Science Books: Mill Valley, CA, 2009. (b) Beweries, T.; Rosenthal, U. Breaking the Rules. *Nat. Chem.* **2013**, *5*, 649−650.

(2) Grubbs, R. H. Olefin-Metathesis Catalysts for the Preparation of Molecules and Materials(Nobel Lecture). *Angew. Chem., Int. Ed.* **2006**, *45*, 3760−3765.

(3) Chauvin, Y. Olefin Metathesis: The Early Days (Nobel Lecture). *Angew. Chem., Int. Ed.* **2006**, *45*, 3740−3747.

(4) Schrock, R. R. Multiple Metal−Carbon Bonds for Catalytic Metathesis Reactions (Nobel Lecture). *Angew. Chem., Int. Ed.* **2006**, *45*, 3748−3759.

(5) Jemmis, E. D.; Phukan, A. K.; Jiao, H.; Rosenthal, U. Structure and Neutral Homoaromaticity of Metallacyclopentene, -pentadiene, -pentyne, and -pentatriene: A Density Functional Study. *Organometallics* **2003**, *22*, 4958−4965.

(6) Rosenthal, U.; Burlakov, V. V.; Bach, M. A.; Beweries, T. Five-membered Metallacycles of Titanium and Zirconium − Attractive Compounds for Organometallic Chemistry and Catalysis. *Chem. Soc. Rev.* **2007**, *36*, 719−728.

(7) (a) Negishi, E.-I.; Takahashi, T. Patterns of Stoichiometric and Catalytic Reactions of Organozirconium and Related Complexes of Synthetic Interest. *Acc. Chem. Res.* **1994**, *27*, 124−130. (b) Broene, R.; Buchwald, S. Zirconocene Complexes of Unsaturated Organic Molecules: New Vehicles for Organic Synthesis. *Science* **1993**, *261*, 1696−1701.

(8) Lauher, J. W.; Hoffmann, R. Structure and Chemistry of Bis(Cyclopentadienyl)ML_n Complexes. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742.

(9) Pavankumar, P. N. V.; Jemmis, E. D. Structure and Bonding in $L_2M(\mu\text{-CCR})ML_2$and $L_2M(\mu\text{-RC}_4R)ML_2$ (L_2M = Cp_2Zr, Cp_2Ti, R_2A1, $R(NR_3)Be$, (tmpda)Li, H_2B, and H_2C^+): A Molecular Orbital Study. *J. Am. Chem. Soc.* **1988**, *110*, 125−131.

(10) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. Synthesis and Structure of the Smallest Cyclic Cumulene; Reaction of 1,3-Diynes with Zirconocene Complexes. *Angew. Chem., Int. Ed.* **1994**, *33*, 1605−1607.

(11) Pellny, P.-M.; Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg; Kempe, A. R.; Francke, V.; Rosenthal, U. Dimerization of Titanacyclocumulenes to Titanium Substituted Radialenes: Synthesis, Stability and Reactions of Five-membered Titanacyclocumulenes with a Coupling of two 1,4-diphenyl-1,3-butadiyne between two Titanocene molecules to Radialene-like fused Titanacyclopentadiene Compounds. *J. Organomet. Chem.* **1999**, *578*, 125−132.

(12) Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. Unusual Bridging of the Metal Centers in Dimeric Bis(η-methylcyclopentadienyl)-phenylethynyl zirconium. *Angew. Chem., Int. Ed.* **1986**, *25*, 463−465.

(13) Hsu, D. P.; Davis, W. M.; Buchwald, S. L. Synthesis and Structure of a Seven-Membered Cyclic Cumulene. *J. Am. Chem. Soc.* **1993**, *115*, 10394−10395.

(14) Suzuki, N.; Nishiura, M.; Wakatsuki, Y. Isolation and Structural Characterization of 1-Zirconacyclopent-3-yne, Five-Membered Cyclic Alkynes. *Science* **2002**, *295*, 660−663.

(15) Ugolotti, J.; Dierker, G.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. Five-Membered Metallacyclic Allenoids: Synthesis and Structure of Remarkably Stable Strongly Distorted Cyclic Allene Derivatives. *Angew. Chem., Int. Ed.* **2008**, *47*, 2622−2625.

(16) Pellny, P. M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. Reactivity of Permethylzirconocene and Permethyltitanocene toward Disubstituted 1,3-Butadiynes: η^4 vs η^2-Complexation or C−C Coupling with the Permethyltitanocene. *J. Am. Chem. Soc.* **1999**, *121*, 8313−8323.

(17) Roy, S.; Jemmis, E. D.; Ruhmann, M.; Schulz, A.; Kaleta, K.; Beweries, T.; Rosenthal, U. Theoretical Studies on the Structure and Bonding of Metallacyclocumulenes, -cyclopentynes, and -cycloallenes. *Organometallics* **2011**, *30*, 2670−2679.

(18) Lam, K. C.; Lin, Z. $Cp_2ZrCH(SiMe_3)CCCH(SiMe_3)$: A Five-Membered 1-Zirconacyclopent-3-yne? *Organometallics* **2003**, *22*, 3466−3470.

(19) (a) Zhu, C.; Luo, M.; Zhu, Q.; Zhu, J.; Schleyer, P. v. R.; Wu, J. I-C.; Lu, X.; Xia, H. Planar Möbius Aromatic Pentalenes Incorporating 16 and 18 Valence Electron Osmiums. *Nat. Commun.* **2014**, DOI: 10.1038/ncomms4265. (b) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.

(20) Jemmis, E. D.; Giju, K. T. Novel Mechanism for Interesting C−C Coupling and Cleavage Reactions and Control of Thermodynamic Stability Involving $[L_2M(\mu\text{-CCR})_2ML_2]$ and $[L_2M(\mu\text{-RCC-CCR})ML_2]$ Complexes (M = Ti, Zr; L = η^5-C_5H_5, Cl, H; R = H, F, CN): A Theoretical Study. *J. Am. Chem. Soc.* **1998**, *120*, 6952−6964.

(21) Roy, S.; Jemmis, E. D. Unexpected Mechanism for Formal [2 + 2] Cycloadditions of Metallacyclocumulenes. *Curr. Sci.* **2014**, *106*, 1249−1254.

(22) Bruckner, R. *Advanced Organic Chemistry*, 1st ed.; Academic Press: San Diego, CA, 2001.

(23) Jemmis, E. D.; Phukan, A. K.; Giju, K. T. 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. *Organometallics* **2002**, *21*, 2254−2261.

(24) Du, B.; Farona, M. F.; McConnville, D. B.; Youngs, W. J. Synthesis and Structure of a Tricyclic Bis(zirconacyclopentadiene) Compound. *Tetrahedron* **1995**, *51*, 4359−4370.

(25) 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. Synthesis and Isolation of Di-*n*-butylhafnocene and Its Application as a Versatile Starting Material for the Synthesis of New Hafnacycles. *Organometallics* **2009**, *28*, 2864−2870.

(26) Suzuki, N.; Hashizume, D. Five-Membered Metallacycloalkynes Formed from Group 4 Metals and [n]Cumulene (3,5) Ligands. *Coord. Chem. Rev.* **2010**, *254*, 1307−1326.

(27) Bach, M. A.; Parameswaran, P.; Jemmis, E. D.; Rosenthal, U. Bimetallic Complexes of Metallacyclopentynes: *cis* versus *trans* and Planarity versus Nonplanarity. *Organometallics* **2007**, *26*, 2149−2156.

(28) Roy, S.; Jemmis, E. D.; Schulz, A.; Beweries, T.; Rosenthal, U. Theoretical Evidence of the Stabilization of an Unusual Four-Membered Metallacycloallene by a Transition-Metal Fragment. *Angew. Chem., Int. Ed.* **2012**, *51*, 5347−5350.

(29) (a) Suresh, C. H.; Frenking, G. Direct 1−3 Metal-Carbon Bonding and Planar Tetracoordinated Carbon in Group 6 Metallacyclobutadienes. *Organometallics* **2010**, *29*, 4766−4769. (b) Suresh, C. H.; Frenking, G. 1,3-Metal-Carbon Bonding and Alkyne Metathesis: DFT Investigations on Model Complexes of Group 4, 5, and 6 Transition Metals. *Organometallics* **2012**, *31*, 7171−7180.

(30) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. Preparation of Trialkoxymolybdenum(VI) Alkylidyne Complexes, Their Reactions with Acetylenes, and the X-ray Structure of $Mo[C_3(CMe_3)_2][\ OCH(CF_3)_2]_2C(C_5H_5N)_2$. *J. Am. Chem. Soc.* **1985**, *107*, 5987−5998.

(31) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. Tables of Bond Lengths determined by X-Ray and Neutron Diffraction. Part I. Bond Lengths in Organic Compounds. *J. Chem. Soc., Perkin. Trans. 2* **1987**, *0*, S1−S19.

(32) Melaimi, M.; Parameswaran, P.; Donnadieu, B.; Frenking, G.; Bertrand, G. Synthesis and Ligand Properties of a Persistent All-Carbon Four-Membered-Ring Allene. *Angew. Chem., Int. Ed.* **2009**, *48*, 4792−4795.

(33) (a) Beweries, T.; Haehnel, M.; Rosenthal, U. Recent Advances in the Chemistry of Heterometallacycles of group 4 metallocenes. *Catal. Sci. Technol.* **2013**, *3*, 18−28. (b) Kaleta, K.; Ruhmann, M.; Theilmann, O.; Beweries, T.; Roy, S.; Arndt, P.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. Reactions of Group 4 Metallocene Alkyne Complexes with Carbodiimides: Experimental and Theoretical Studies of the Structureand Bonding of Five-Membered Hetero-Metallacycloallenes. *J. Am. Chem. Soc.* **2011**, *133*, 5463−5473.

(34) Haehnel, M.; Ruhmann, M.; Theilmann, O.; Roy, S.; Beweries, T.; Arndt, P.; Spannenberg, A.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. Reactions of TitanoceneBis(trimethylsilyl)acetylene Complexes with Carbodiimides: An Experimental and Theoretical Study of Complexation versus C−N Bond Activation. *J. Am. Chem. Soc.* **2012**, *134*, 15979−15991.

(35) (a) Breher, F. Stretching bonds in Main Group Element Compounds—Borderline between Biradicals and Closed-shell species. *Coord. Chem. Rev.* **2007**, *251*, 1007−1043. (b) Jung, Y.; Head-Gordon, M. How Diradicaloid Is a Stable Diradical? *Chem.Phys.Chem.* **2003**, *4*, 522−525.

(36) Kaleta, K.; Ruhmann, M.; Theilmann, O.; Roy, S.; Beweries, T.; Arndt, P.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. Experimental and Theoretical Studies of Unusual Four-Membered Metallacycles from Reactions of Group 4 MetalloceneBis(trimethylsilyl)-acetylene Complexes with the Sulfurdiimide Me3SiN=S=NSiMe3. *Eur. J. Inorg. Chem.* **2012**, 611−617.

(37) Rosenthal, U. Stable Cyclopentynes—Made by Metals!? *Angew. Chem., Int. Ed.* **2004**, *43*, 3882−3887.

(38) Bender, G.; Wiegand, T.; Eckert, H.; Fröhlich, R.; Daniliuc, C. G.; Mück-Lichtenfeld, C.; Ndambuki, S.; Ziegler, T.; Kehr, G.; Erker, G. Binding of Molecular Magnesium Hydrides to a Zirconocene−Enyne Template. *Angew. Chem., Int. Ed.* **2012**, *51*, 8846−8849.

(39) Podiyanachari, S. K.; Bender, G.; Daniliuc, C. G.; Kehr, G.; Erker, G. Catalytic Formation of Five-Membered Zirconacycloalle-

noids and Their Reaction with Carbon Dioxide. *Organometallics* **2014**, *33*, 3481−3488.