

# Unexpected mechanism for formal [2 + 2] cycloadditions of metallacyclocumulenes

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The formation of radialene complex **6M** proceeds through a three-membered metallacycpropene complex **7M**, contrary to the prevailing notion of simple dimerization of metallacyclocumulene **1M**. The **1M–7M** equilibrium, which is predominantly governed by the size-dependent ligand binding of the metal atoms, plays a decisive role in the chemistry of  $\text{Cp}_2\text{M}$ –ligand complexes. This size dependency is further fine-tuned by the substituents on the substrates and helps in exploiting these classes of metallacycles to generate new chemistry.

**Keywords:** Cumulene, metallacycles, radialene complex, transition metals.

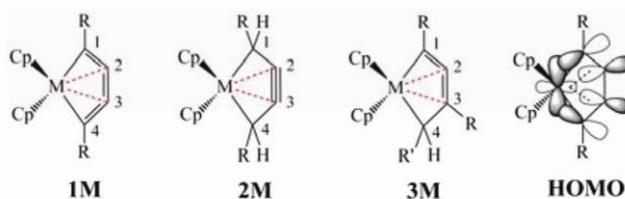
## Introduction

STABILIZATION of high-energy organic species and altering normal reactivity norms of organic fragments by transition metals have been a triumphing feat of organometallic chemistry<sup>1</sup>. In this context, group 4 metals have unlocked a fascinating chemistry by stabilizing strained unsaturated  $\text{C}_4$  organic fragments in the form of metallacyclocumulene (**1M**)<sup>2–5</sup>, metallacyclopentyne (**2M**)<sup>4,6</sup> and metallacycloallene (**3M**, Scheme 1)<sup>7,8</sup>. Early on, we had been involved in deciphering the ‘unusual stability’, i.e. limited chemical reactivity of these metallacycles theoretically<sup>3,9</sup>. We formulated the unique M–C (internal) interaction to account for the unusual stability of these metallacycles (HOMO, Scheme 1)<sup>8,9</sup>. This kind of bonding is intriguing from a fundamental perspective and has great relevance in synthesizing unusual structures<sup>10</sup> with interesting properties and in catalysis<sup>11–15</sup>.

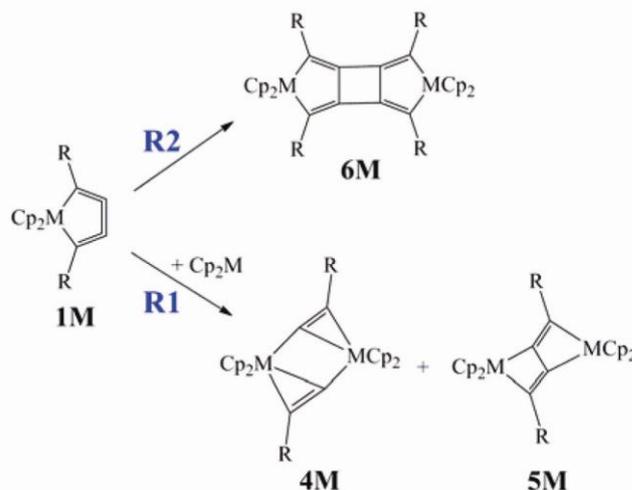
Interestingly, the metallacyclocumulene **1Ti**, which was formed from the reaction of  $\text{Cp}_2\text{M}$  with butadiyne ( $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$ )<sup>16</sup>, produces a radialene complex **6Ti**, the dimerized product of the metallacyclocumulene (Scheme 2)<sup>17</sup>. But for Zr, such complex **6Zr** was not observed, which was quite surprising. Instead, only the C–C cleavage product **4Zr** was obtained (Table 1)<sup>18</sup>. Earlier, Buchwald and co-workers<sup>11</sup> were also unsuccessful in synthesizing such a complex **6Zr** with  $\text{SiMe}_3$  substituents.

Generally, the metallacyclocumulene **1M** reacts with  $\text{Cp}_2\text{M}$  to produce the C–C cleavage product **4M** or the C–C coupled product **5M**, depending on the metal and the

substituents (Table 1 and Scheme 2)<sup>19</sup>. Our group established the mechanism and unravelled the reason for the different product formation by Ti (**5Ti**) and Zr metals (**4Zr**), which was found to be a consequence of thermodynamic energy differences of complexes **4M** and **5M**, attributed to the variation in the diffuse nature of the



**Scheme 1.** Schematic representations of five-membered metallacyclocumulenes (**1M**), metallacyclopentyne (**2M**), metallacycloallenes (**3M**) and HOMO of **1M**; M = Ti, Zr.



**Scheme 2.** Various reaction products of the metallacyclocumulene **1M** (see Table 1).

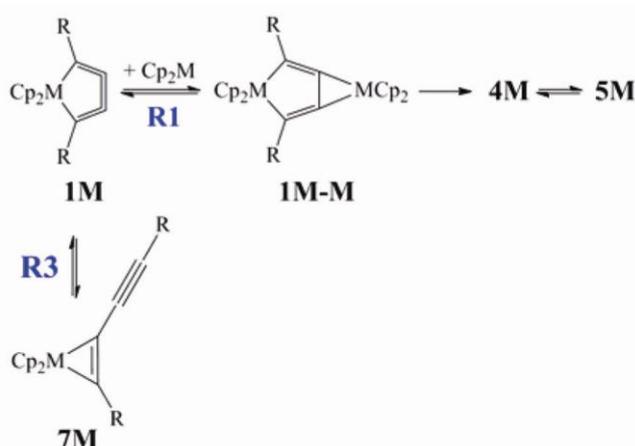
**Table 1.** Experimentally reported structures of various homobimetallic titanium and zirconium complexes (Scheme 2) (M = Ti, Zr of the  $\text{L}_2\text{M}$  moiety, L = Cp). Cp =  $\text{C}_5\text{H}_5$ ,  $\text{Cp}^* = \text{C}_5\text{H}_4\text{CH}_3$ . The notation **1M\_R** represents complex **1M** with R substituents on C1 and C4

L	Cp	Cp	Cp	Cp	$\text{Cp}^*$
R	Ph	<i>t</i> Bu	$\text{SiMe}_3$	Me	Ph
	<b>5Ti</b>	<b>5Ti</b>	<b>4Ti</b>	<b>5Ti</b>	<b>4Zr</b>
	<b>6Ti</b>		<b>4Zr</b>		

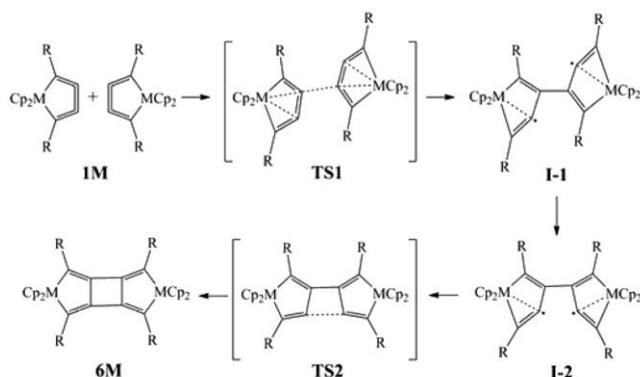
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orbitals of the two metals (see [Supporting Information online](#), Scheme S1 and Figure S1)<sup>3,9</sup>. The complexation of  $\text{Cp}_2\text{M}$  to **1M** being highly favoured and the low barrier associated with the subsequent steps make **R1** pathway the most dominant reaction of the metallacyclocumulene (Schemes 2 and 3).

The pathway for generation of **6Ti** as well as the reason for lack of formation of **6Zr** is not known<sup>20</sup>. Is it a case of dimerization of metallacyclocumulene **1M** as perceived by the experimentalists? Are there other pathways? We explore these questions and their interesting ramifications here. These metallacycles are emerging as important intermediates for various other chemical transformations<sup>13</sup> and an upsurge is observed in the chemistry of these metallacycles because of its interesting applications, e.g. stabilization of molecular  $\text{MgH}_2$  by zirconacycloallene<sup>14</sup> and various new reactivity<sup>15</sup>. Unlike alkynes, metallacyclopentyne **2M** does not undergo [2 + 2] cycloaddition reaction with alkenes<sup>6</sup> and also could not be trimerized by  $\text{Ni}^0$  catalyst<sup>21</sup>. In spite of its growing



**Scheme 3.** Relevant part of the coupling and decoupling reaction pathway (**R1**), which is already fully studied (Scheme S1 and Figure S1) and the equilibrium between  $\eta^1$ -complex **1M** and  $\eta^2$ -complex **7M**.



**Scheme 4.** Dimerization route (**R2**) of the metallacyclocumulene **1M** to form the radialene complex **6M**.

importance, the factors that control the reactions of these metallacycles still remain unclear. The formation of the radialene **6Ti** is taken for granted as a [2 + 2] cycloaddition reaction of the two metallacyclocumulenes (Scheme 4). Our experience in the contrasting behaviour of Ti and Zr suggests that this need not be true<sup>9</sup>. We demonstrate here that the formation of radialene **6Ti** follows a rather unusual reaction pathway involving a three-membered ring. Our results have general implications of immediate interest to the workers in this area.

## Results and discussion

We begin our analysis by considering the possibility of dimerization of metallacyclocumulene **1M** directly to form the radialene complex **6M**. Complex **6M** is calculated to be thermodynamically feasible in comparison to **1M** by 18.9 and 18.6 kcal mol<sup>-1</sup> (dimerization energy; basis set superposition error (bsse) corrected) for Ti and Zr metals respectively. Therefore, the answer must lie with kinetic rather than thermodynamic factors. We then checked the possibility of direct dimerization of the metallacyclocumulene **1M** (**R2**, Scheme 4). This is not a single-step [2 + 2] cycloaddition reaction<sup>22</sup>. The stepwise process (Scheme 4) involves two intermediates. The barrier for the first step in the dimerization of **1M** is 17.0 kcal mol<sup>-1</sup> for Ti, while it is 20.8 kcal mol<sup>-1</sup> for Zr (Scheme 4; see [Supporting Information online](#), Figure S3). Taking note of the point that the first step involves rupture of the M–C2/C3 bonds in **1M**, the difference in barrier can be appropriately assigned to the significant M–C (internal) interactions (HOMO, Scheme 1). The reaction barrier for the dimerization of Ti and Zr metallacyclocumulenes is close to each other and hence from this potential energy profile we cannot conclude why **6Zr** is not observed. We therefore turned to other pathways for the formation of radialene **6M**.

The  $\eta^4$ -metallacyclocumulene **1M** exists in equilibrium with its isomeric three-membered  $\eta^2$ -metallacyclopentene **7M** (Scheme 3)<sup>5,23</sup>. The barrier for isomerization of **1M**–**7M** via **TS3** is 10.8 kcal mol<sup>-1</sup> for Ti and 22.8 kcal mol<sup>-1</sup> for Zr (Table 2). HOMO of **TS3** shows

**Table 2.** Calculated barrier heights and differences in free energy,  $\Delta G$  (kcal mol<sup>-1</sup>) for **1M**–**7M** transformation at the B3LYP/def2-SVP level of theory

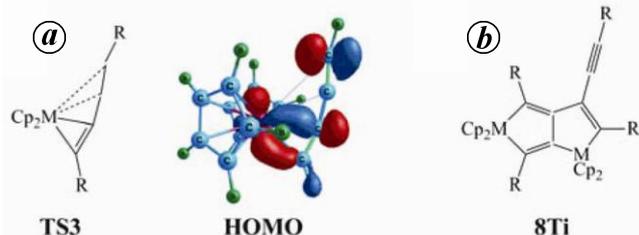
R	Ti		Zr	
	Barrier	$\Delta G$	Barrier	$\Delta G$
H	10.8	–0.1	22.8	11.4
Me	9.9	–2.1	21.6	8.4
<i>t</i> Bu	7.5	–5.0	20.1	8.3
Ph	9.4	–0.5	21.3	10.8
SiMe <sub>3</sub>	5.9	–5.0	16.8	5.7

the interaction between the metal and the ring C atoms (Scheme 5 a). This barrier difference is a fascinating reflection of the ability of the two metals to interact with the carbon atoms of the  $C_4$   $\pi$ -ligand. The Ti with its more contracted orbitals is more effective in interacting with a  $C_2$  ligand in **7Ti**, while the bonding of Zr is better with the  $C_4$  ligand in **1Zr**. The free energy difference of the two complexes **1M** and **7M** for the two metals shows this trend for all the substituents (Table 2). The larger  $Cp_2^*Zr$  on reaction with  $Me_3SiC\equiv C-C\equiv CSiMe_3$  forms the  $\eta^4$ -complex,  $Cp_2^*Zr(\eta^4-1,2,3,4-Me_3SiC_4SiMe_3)$ , while smaller  $Cp_2^*Ti$  generates the three-membered  $\eta^2$ -complex,  $Cp_2^*Ti(\eta^2-1,2-Me_3SiC_2C\equiv CSiMe_3)$ <sup>24</sup>. Generally Zr needs an additional ligand to form a  $\eta^2$ -complex<sup>25</sup>.

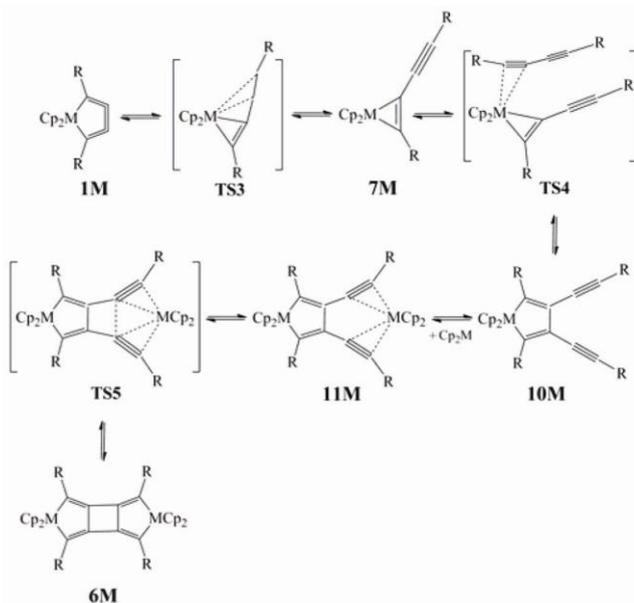
Indeed, isolation of the titanacyclopentadiene–titanacyclopentene complex **8Ti** supports the existence of **7Ti** during the formation of complex **6M** (Scheme 5 b)<sup>17</sup>. The metallacyclopentene **7M** can then easily form the bis(alkynyl)metallacyclopentadiene **10M** through reductive coupling of 1,3-butadiynes ( $RC\equiv C-C\equiv CR$ , **9**) with

low barrier height (Scheme 6 and Figure 1)<sup>26</sup>. Such bis(alkynyl)metallacyclopentadienes are well documented<sup>27,28</sup>. Reaction of **10M** with  $Cp_2M$  being significantly exothermic can facilitate the formation of this bis(alkynyl)metallacyclopentadiene predominantly and then drive the overall reaction to produce **6M**. This kind of reaction path was suggested for the reaction of  $Me_3SiC\equiv C-CH_2-C\equiv CSiMe_3$  with zirconocene<sup>29</sup>. The bis-alkyne complex **11Ti**, which is 8.3 kcal mol<sup>-1</sup> higher than **6Ti**, easily converts to the radialene complex with almost no barrier. So, this appears to be the most feasible pathway for the formation of **6Ti** involving **1M–7M** transformation as the decisive step, compared to the dimerization route **R2**. Attempts to locate a bis-alkyne complex **11Zr** always converge to the radialene **6Zr**. Such Zr complex is only obtained as a minimum with  $SiH_3$  substituents. It may be mentioned that a bis-alkyne complex of zirconocene was earlier isolated with the  $SiMe_3$  substituents<sup>12</sup>. It is possible that with *t*Bu or similar groups, a cycloadduct product may be obtained.

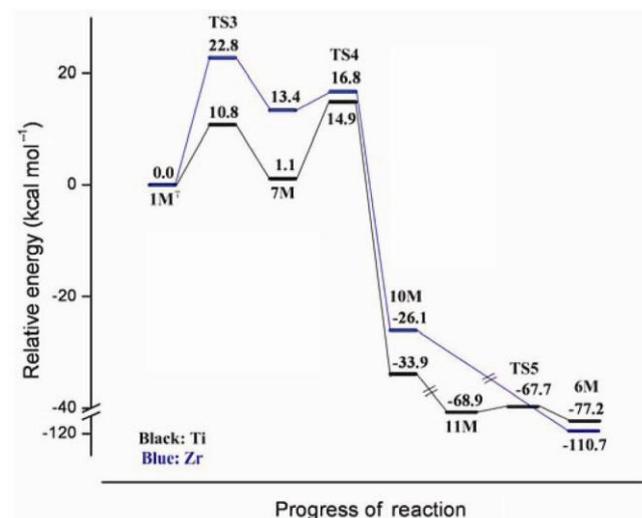
In essence, Ti can form **6Ti** through facile formation of **7Ti**, while Zr has high kinetic barrier for the formation of **7Zr** from **1Zr** and reacts predominantly through **1Zr** (**R1** pathway). Thus, it nicely explains the inability of Zr to form **6Zr** as well as accounting for the formation of cleavage product **4Zr** from **1Zr** at the same time. So, consideration of the two competing reactions, **R1** and **R3** only solves the puzzle why no **6Zr** is formed. Considering the not-so-high barrier height, the **1Zr–7Zr** transformation and eventual formation of **6Zr** should be possible at higher temperature. Encouragingly, the formation of the corresponding **6Hf** complex<sup>30</sup> (a close analogue of **6Zr** because of the similarity in size of the two metals) at



**Scheme 5.** Schematic representations of (a) transition state for **1M–7M** conversion and HOMO of the TS3 (R = H) and (b) titanacyclopentadiene-titanacyclopentene complex **8Ti** (R = Ph, Me).



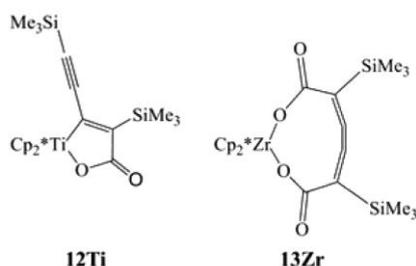
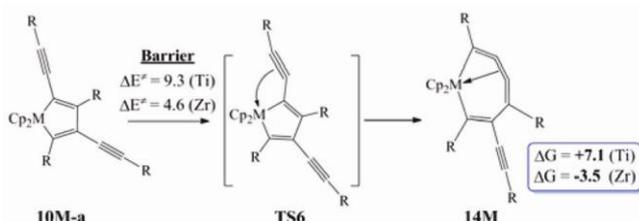
**Scheme 6.** Plausible mechanistic path for the formation of radialene complex **6M**. The **1M–7M** equilibrium is the decisive step in this reaction pathway.



**Figure 1.** Potential energy profile of the pathway at the B3LYP/def2-SVP level of theory for the formation of radialene complex **6M** as depicted in Scheme 6 (for R = H). Relative energies (ZPE, zero-point energy corrected) are plotted with respect to **1M**. †Energies of butadiyne,  $RC\equiv C-C\equiv CR$  and the isolated  $Cp_2M$  are added to make the potential energy profile uniform.

**Table 3.** Calculated bond lengths (Å) and bond angles (°) of complex **1M** at the B3LYP/def2-SVP level of theory. Experimental values of the complex **1M\_tBu** are given in parenthesis

	M–C1	M–C2	C1–C2	C2–C3	C1–C2–C3	M–C1–C2
<b>1Ti_H</b>	2.236	2.227	1.288	1.333	146.2	72.8
<b>1Ti_Me</b>	2.244	2.211	1.288	1.335	147.0	71.8
<b>1Ti_tBu</b>	2.269	2.210	1.290	1.333	148.3	70.8
	(2.252)	(2.210)	(1.277)	(1.338)	(147.6)	(70.3)
<b>1Ti_Ph</b>	2.249	2.217	1.299	1.323	147.1	71.8
<b>1Ti_SiMe<sub>3</sub></b>	2.314	2.207	1.286	1.334	150.5	69.0
<b>1Zr_H</b>	2.334	2.333	1.302	1.329	147.3	73.8
<b>1Zr_Me</b>	2.338	2.320	1.303	1.332	147.8	73.0
<b>1Zr_tBu</b>	2.350	2.318	1.305	1.330	148.5	72.4
	(2.357)	(2.303)	(1.280)	(1.310)	(150.0)	(71.7)
<b>1Zr_Ph</b>	2.344	2.327	1.314	1.321	147.9	73.0
<b>1Zr_SiMe<sub>3</sub></b>	2.402	2.314	1.301	1.330	151.0	70.3

**Scheme 7.** Schematic representations of a single CO<sub>2</sub>-inserted titanocene complex, **12Ti** and a double CO<sub>2</sub>-inserted zirconocene complex, **13Zr** (Cp\* = C<sub>6</sub>Me<sub>5</sub>).**Scheme 8.** Conversion of **10M-a** to seven-membered metallacyclocumulene **14M** (R = H, energy values in kcal mol<sup>-1</sup>). The formation of **14Ti** is thermodynamically less favourable.

higher temperature supports this proposition and also validates the above pathway. Formation of the zirconacyclopentadiene **7Zr** should be possible at higher temperatures to generate the desired products as well<sup>31</sup>.

The preference of Zr for **1M** is evident from the structural features as well. The wider C1–C2–C3 and M–C1–C2 angles of 147.3° and 73.8° in **1Zr** compared to that of 146.2° and 72.8° in **1Ti** is a direct reflection of the bigger size of the Zr atom, which helps reduce the strain in the molecule (Table 3). The comparatively closer Zr–C1 and Zr–C2 distances (2.334 and 2.333 Å) show the uniform interaction between the Zr atom and the four-ring C atoms across the ZrC<sub>4</sub> plane in **1Zr** than that in **1Ti**. The observation that Zr prefers **1Zr** while Ti tends to choose **7Ti**, is widely supported by several product formations like **8Ti** (Scheme 5b), **12Ti** and **13Zr** (Scheme 7)<sup>19</sup>. In fact, there are other instances where the larger atomic radius

of Zr leads to distinctive chemical behaviour from that of Ti<sup>32</sup>.

We have already noticed that the more diffuse nature of orbitals of Zr leads to significant interaction between this metal and the four-ring C atoms in **1Zr**, which causes high energy barrier for the conversion of **1Zr** to **7Zr**. Is there any way to tune this barrier for the Zr metallacyclocumulene circumventing the inherent reason?

Interestingly, for the SiMe<sub>3</sub> and CN substituent, the barrier is relatively lower (16.8 and 17.5 kcal mol<sup>-1</sup> respectively) compared to other substituents (Table 2). The lowering of the barrier by these substituents can be attributed to the withdrawal of electron density from the butadiyne by the groups<sup>2</sup>, which minimizes the Zr and C<sub>4</sub> ligand interaction in **1Zr** reflected in comparatively longer terminal Zr–C1/C4 (2.402 Å for R = SiMe<sub>3</sub>) bond distances. Hence, substituents like SiMe<sub>3</sub> and CN can facilitate the **1Zr**–**7Zr** conversion to form the corresponding bis(alkynyl)metallacyclopentadiene. For SiMe<sub>3</sub> substituents, the unsymmetrical isomer **10Zr-a** (Scheme 8) forms instead of the symmetrical **10Zr** since this would have resulted in a highly sterically congested **6Zr** (of high energy) around the radialene unit with bulkier SiMe<sub>3</sub> substituents<sup>33</sup>. The two isomers differ by 7.0 kcal mol<sup>-1</sup>, with the unsymmetrical isomer being lower in energy than the symmetrical one.

The complex **10Zr-a** further transforms to the seven-membered metallacyclocumulene **14Zr** with a small barrier of 4.6 kcal mol<sup>-1</sup> (Scheme 8). This is what Buchwald and co-workers<sup>11</sup> obtained when they attempted to synthesize **6Zr**. Thus, our theoretical study also explains the unexpected formation of the seven-membered cumulene complex **14Zr**. Interestingly, the CN substituent can force the formation of **10Zr** and this may lead to the formation of complex **6Zr**. We would like this to be tried experimentally. It may be noted that for Ti, only the unsymmetrical bis(alkynyl)metallacyclopentadiene **10Ti-a** is isolated with SiMe<sub>3</sub> substituents<sup>24</sup>; no seven-membered complex is obtained. This is in accordance with the calculations which show that the formation of **14Ti** is thermodynamically less favourable (Scheme 8). Similar results are

obtained with SiH<sub>3</sub> substituents. Again size-effect prevails here. It also reveals how the reactivity of these metallacycles can be further fine-tuned by changing the substituents.

## Conclusion

In conclusion, we have shown that the formation of radialene complex **6M** proceeds through a three-membered metallacyclopentene complex **7M**, contrary to the prevailing notion of simple dimerization of the metallacyclocumulene **1M**. The **1M–7M** equilibrium, which is predominantly governed by the size of the metal atoms, plays a decisive role in the chemistry of Cp<sub>2</sub>M–ligand complexes. Thus, it is shown how the size of a metal affects its ability to control the reactivity of metallacyclocumulene **1M** through unique M–C interactions to form a radialene complex. Furthermore, the reactivity of the metallacyclocumulene can be fine-tuned by using substituents like SiMe<sub>3</sub> and CN groups. The control of reactivity of these exotic molecules to generate new chemistry through metal size and electronic fine-tuning of ligands must be true in general for this class of metallacycles with unique M–C interactions (e.g. **2M** and **3M**). Similar study of other metallacycles of this class is underway to get more insight into the nature of the reactivity of these unique organometallic complexes.

## Computational details

We have studied complex **1M** and other complexes at the B3LYP (refs 34 and 35)/def2-SVP (ref. 36) level of theory using Gaussian 09 program package<sup>37</sup>. Larger complexes are reliably modelled with H substituents to reduce the computational cost and the discussion is with this substituent unless otherwise stated. However we have studied the **1M–7M** equilibrium, which primarily decides the reactivity of the metallacyclocumulene **1M**, using exact substituents. The stability of all the reactants, products, transition states and intermediates was checked and the most stable wavefunction used for the optimization. The open-shell singlet states (OSSS) of **I-1**, **I-2** and **TS2** (Scheme 4) were treated using the unrestricted broken-spin-symmetry approach (UBS-B3LYP)<sup>38</sup>. Intermediates **I-1** and **I-2** was calculated to have similar energy for both OSSS and triplet states. Transition state **TS2** had OSSS as the more stable state. All the complexes were characterized as a minimum or a transition state based on the vibrational frequency calculations. IRC calculations were done to make sure of the connectivity of reactants and products with the transition states. See [Supporting information](#), online for more details.

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