

Structure and bonding of metallacyclocumulenes, radialenes, butadiyne complexes and their possible interconversion: a theoretical study

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Received 2 May 2001; accepted 9 July 2001

Abstract

Density functional theory is used to study the dimerization of metallacyclocumulenes (**1**, **2** and **9**) to metal substituted radialenes (**3**, **4** and **5**). These were compared to the dimerization of ethylene to cyclobutane and cumulene to radialene. The bonding of the metallacyclocumulenes were discussed in the light of the Dewar–Chatt–Duncanson model. A possible mechanism for the formation of bis(butadiyne) complex of Ni (**8**) is also presented. Correlation diagrams constructed for the conversion of the radialene type structure to that of the bis(butadiyne) complex show that it is allowed for both Ti and Ni. © 2001 Published by Elsevier Science B.V.

Keywords: Metallacyclocumulenes; Radialenes; Butadiyne complexes; Titanocene; Zirconocene

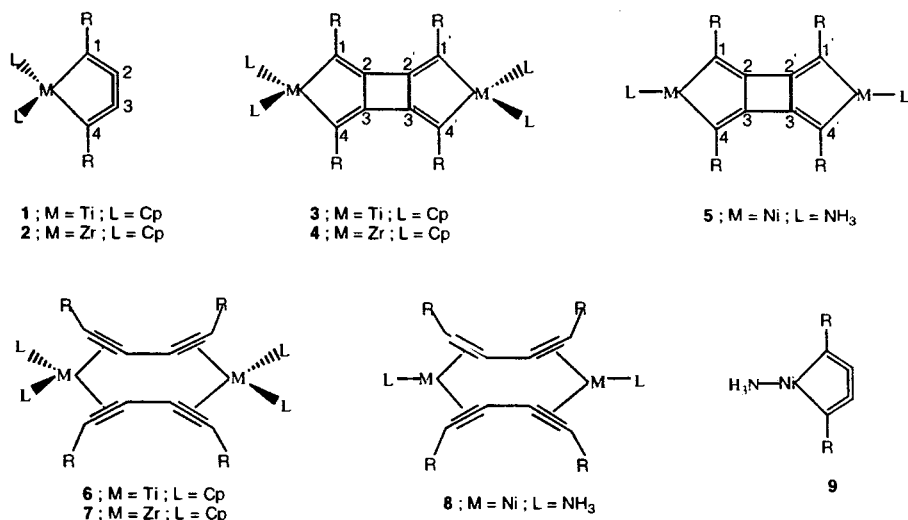
1. Introduction

The Dewar–Chatt–Duncanson (DCD) model gave an elegant and simple description of the transition metal–alkene bonding in terms of π donation and metal back-donation [1]. The properties of a complexed double bond depend on the extent of back-bonding [2]. We consider here π bond which is flanked by π bonds on either side in an orthogonal plane as in cumulenes. Metallacyclocumulenes (**1** and **2**), obtained from Cp_2Ti and Cp_2Zr fragments contain such π bonds [3,4]. These are key intermediates in several C–C single bond for-

mations as well as cleavage reactions [5]. The Ti complex also dimerizes to give a radialene derivative (**3**), arising from a 2 + 2 cycloaddition of the middle π bond [6]. However, this structural type is not known for Zr (**4**). In principle, a cycloreversion of **3** could lead to the bis(butadiyne) complex (**6**). This structural pattern is indeed known, but with the metal Ni (**8**) [7]. However, neither the metallacyclocumulene **9** nor the radialene **5** is known with Ni. We present here the nature of bonding of the middle π -bond in the cyclocumulene complexes **1**, **2**, and **9**, correlation diagrams for its dimerization to the radialenes **3** and **4**, and its isomeric butadiyne structures of Ti and Ni (**6** and **8**). The electronic structure of the titanium substituted radialene (**3**) and the ways to get similar complexes for zirconium using different substituents at the 1,4-position of the butadiyne are also probed. The electronic structure of butadiyne bridged nickel complex (**8**) and the dimerization energy for the process **1** → **3** is also briefly presented.

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2. Computational details

All structures were optimized using the hybrid exchange–correlation functional B3LYP [8]. This is based on Becke's three-parameter functional [8a] including Hartree–Fock exchange contribution with a non-local correction for the exchange potential proposed by Becke [8b] together with the non-local correction for the correlation energy provided by Lee et al. [8c]. We used LANL2DZ basis set with the effective core potentials of Hay and Wadt [9]. Studies involving Cp₂Ti, Cp₂Zr, Cl₂Ti and Cl₂Zr fragments have indicated that the energetic trends are reproduced by the dichloro derivatives [10]. However, absolute comparisons between Cp₂Ti and Cp₂Zr systems required Cp ligands. Since this is not practical with our computational facilities, we have used Cl in place of Cp. The bis(butadiyne) complex of Ni (**8**) and the hypothetical structure **9** were optimized by modeling pyridine with NH₃. We used H, OH and NH₂ as the butadiyne substituents, R¹ and R², in complexes **1**–**4**. For all other structures, H is used as the substituent. Stationary points were characterized by vibrational frequency analysis. The nature of bonding was studied through NBO analysis [11]. GAUSSIAN 94 suite of program was used for all the calculations [12]. The MOLDEEN program

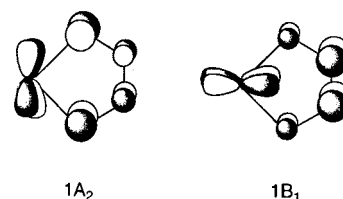


Fig. 1. MOs responsible for the bond length equalization in titanacyclocumulene (**1**).

was used for the graphical representation of the molecular orbitals (MOs) [13].

3. Results and discussion

We first discuss the structure and bonding of the cyclocumulenes followed by a description of the dimerization reactions and finally the nature of bonding in these metal substituted radialenes.

3.1. Structure and bonding of metallacyclocumulenes (M = Ti, Zr and Ni)

All three metallacyclocumulenes, **1**, **2**, and **9** are planar with the four carbon atoms and the metal atom

Table 1
Important geometric parameters of the metallacyclocumulenes at the B3LYP/LANL2DZ level of theory

M	R	L	M–C1	M–C2	C1–C2	C2–C3	C1–M–C4	M–C1–C2	C1–C2–C3
Ti	H	Cl	2.11 <i>0.737</i>	2.14 <i>0.404</i>	1.311 <i>1.979</i>	1.347 <i>1.487</i>	108.5	73.3	142.4
Zr	H	Cl	2.264 <i>0.695</i>	2.298 <i>0.343</i>	1.324 <i>1.948</i>	1.343 <i>1.574</i>	101.4	74.5	144.7
Ni	H	NH ₃	2.19 <i>0.351</i>	2.02 <i>0.183</i>	1.287 <i>2.358</i>	1.369 <i>1.378</i>	110.2	65.1	149.8

The numbers in italics indicate Wiberg Bond Index (WBI).

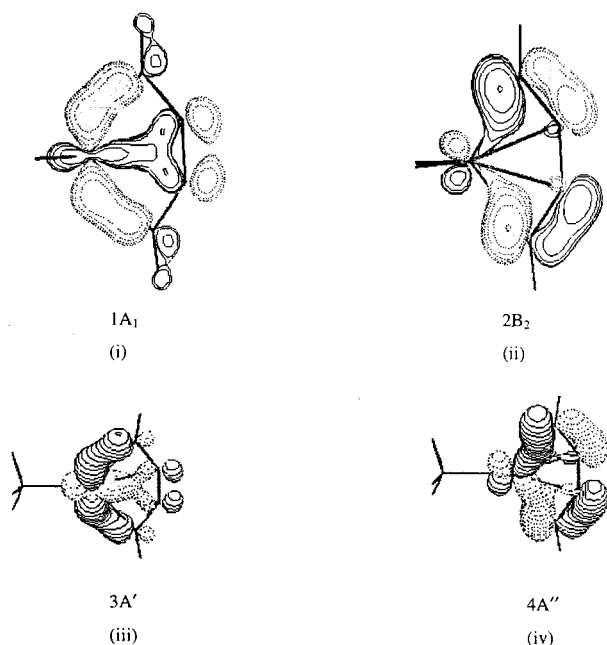


Fig. 2. Three dimensional drawings of MOs showing the 'bonding' and 'back-bonding' interaction between the metal and the middle C–C bond. (i) and (ii) show the metal–carbon bonding in the Ti complex and (iii) and (iv) represent the π bonding and back-donation in the Ni complex, respectively.

lying in the same plane. For $M = \text{Ti}$ (**1**), all three C–C bond lengths are of almost equal order ($\approx 1.3 \text{ \AA}$) and they are within the range of C–C distance expected for a $\text{sp}^2\text{--sp}$ bond (Table 1). No metal to π^* back-bonding is expected here as the formal oxidation state of metal is +4, with d^0 electron count. The C–C bond equalization here comes more from the π delocalizations, indicated by the MOs $1A_2$ and $1B_1$ (Fig. 1). The small value of the Ti–C1–C2 angle indicates considerable strain in the five-membered ring. The geometrical features of Zr complex **2** are similar to those of **1** [3]. However, our calculated bond lengths differ from that of the experimental structure [14]. While the calculated M–C distances (**1**: M–C1 = 2.11, M–C2 = 2.14 and **2**: M–C1 = 2.264, M–C2 = 2.298) are shorter than those

from the experimental geometry (**1**: M–C1 = 2.252, M–C2 = 2.209 and **2**: M–C1 = 2.357, M–C2 = 2.303), the C–C bond lengths (**1**: C1–C2 = 1.311, C2–C3 = 1.347 and **2**: C1–C2 = 1.324, C2–C3 = 1.343) are longer (**1**: C1–C2 = 1.243, C2–C3 = 1.339 and **2**: C1–C2 = 1.28, C2–C3 = 1.31). The experimental structures have Cp or Cp* as the ligand and 'Bu, Ph or SiMe₃ as substituents, whereas calculations were performed using Cl instead of Cp and H in place of 'Bu, Ph or SiMe₃. These would contribute to the differences in the geometries between the model structures calculated and the experimental values. The middle C–C bond in the hypothetical nickel complex is longer than the other two C–C bonds, thereby showing back-bonding interaction between the filled metal d-orbitals and the in-plane empty π^* orbital of the middle C–C bond. This is also reflected in the length of the Ni–C bonds. The Ni–C2 bond is shorter than the Ni–C1 bond by 0.17 Å. Thus the Ni complex, **9**, has the typical DCD bonding. The bonding of the middle C–C bond in both the Ti and Ni complexes can be described in terms of the DCD model except that there are no electrons in the metal orbitals of the Ti complex for back-bonding with the in-plane π -orbitals. Interaction diagrams constructed using the calculated geometries at the extended Huckel level exemplifies this anticipation. The $1A_1$ and $1B_2$ (Fig. 2, i and ii) of the Ti complex corresponds to the in-plane and out-of-plane combination of the σ hybrid orbitals of the end carbons of the cumulenic unit interacting with the metal orbitals. On the other hand, back-donation plays a very dominant role in the Ni complex where the metal is formally d^8 . The corresponding MOs are shown in Fig. 2 (iii and iv). With an intact middle π bond, which is in the σ plane, **1** and **2** are expected to dimerize. The variations in the dimerization energy of the π bond is discussed next.

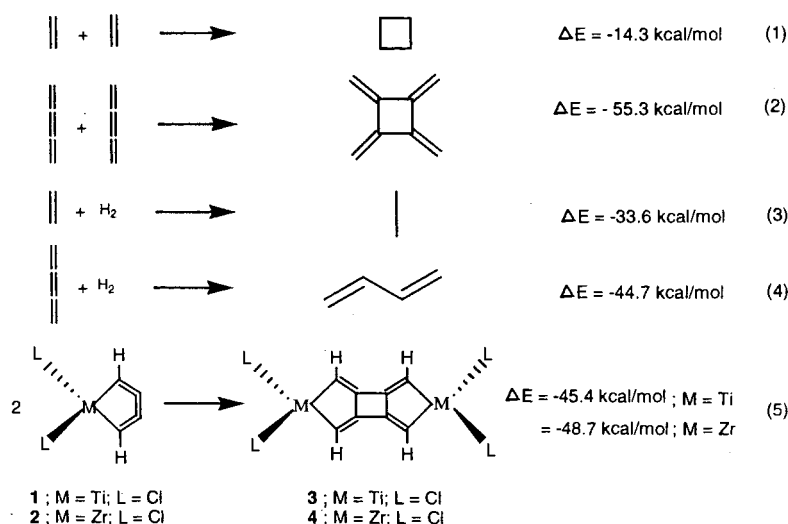
3.2. Dimerization energies for the process $\mathbf{1} \rightarrow \mathbf{3}$ and the structure and bonding of metal substituted radialenes

The first point to note here is that experimentally a Zr-based cumulene structure is not known to give a

Table 2
Dimerization energies of the metal substituted radialenes at B3LYP/LANL2DZ level of theory including ZPVE

M	L	R	Emonomer (au)	Edimer (au)	Dimerization energy (kcal mol ⁻¹)
Ti	Cl	H	-241.57810	-483.22853	-45.4
	Cl	OH	-391.98639	-784.07610	-64.8
	Cl	NH ₂	-352.27406	-704.61738	-43.5
Zr	Cl	H	-230.09988	-460.27737	-48.7
	Cl	OH	-380.50955	-761.12674	-67.5
	Cl	NH ₂	-340.79346	-681.65573	-43.2
Ni	NH ₃	H	-379.25407	-758.59569	-54.9
	C ₂ H ₄		-78.52689	-157.07658	-14.3
	C ₄ H ₄		-154.64576	-309.37967	-55.3

The energies of C₂H₄, C₄H₄ and their dimers are given for comparison.



Scheme 1.

Table 3
Important geometric parameters of the metal substituted radialenes at the B3LYP/LANL2DZ level of theory

M	L	R	M–C1	M–C1	C1–C2	C2–C3	C2–C2'	C1–M–C4	M–C1–C2	C1–C2–C3	C3–C2–C2'
Ti	Cl	H	2.219	2.015	1.353	1.578	1.494	106.0	89.7	127.3	90.0
			<i>1.195</i>	<i>0.903</i>	<i>1.704</i>	<i>0.915</i>	<i>1.012</i>				
		OH	2.221	2.02	1.364	1.542	1.473	105.3	89.6	127.1	90.0
Zr	Cl	H	2.401	2.176	1.361	1.579	1.497	99.1	90.8	129.6	90.0
			<i>1.026</i>	<i>0.792</i>	<i>1.740</i>	<i>0.942</i>	<i>1.01</i>				
		OH	2.40	2.181	1.368	1.546	1.473	99.6	89.5	130.1	90.0
Ni	NH ₃	H	2.423	2.166	1.381	1.575	1.474	103.0	87.3	130.8	89.8
			<i>0.969</i>	<i>0.765</i>	<i>1.505</i>	<i>0.956</i>	<i>1.053</i>				
		NH ₂	1.956	1.989	1.286	2.779	1.412	164.2	72.5	115.5	90.2
		<i>0.388</i>	<i>0.307</i>	<i>2.289</i>	<i>0.104</i>	<i>1.170</i>					

The numbers in italics indicate WBI.

The first and second column in the Ni complex refer to Ni–C1 and Ni–C2 bond lengths, respectively.

radialene, even though the dimerization of the Ti complex is well known. Calculations on the model complexes **1**, **2**, and their dimers **3** and **4** indicate that these are minima. The difference between the two dimerization energies is small; it is not possible to assign any specific explanation for the experimental observation. Calculations using the cyclopentadienyl ligands could change this small energy difference. Estimation of the barrier heights for dimerization is required to explain the difference in behavior of Ti and Zr complexes. The dimerization energies of different combinations of metal and substituent is shown in Table 2. To provide a comparison with the parent hydrocarbon systems, we calculated the dimerization energies of ethylene and cumulene at the same level of theory (Scheme 1). The dimerization energy of cumulene is more than that of ethylene. The *sp* hybridized middle C=C π bond of

cumulene releases more energy upon dimerization. The unavoidable closed shell repulsions between the π bond and the pseudo CH₂ π orbital on either side may be destabilizing this π bond. This is also evident from a comparison of the hydrogenation of ethylene to ethane and cumulene to 1,3-butadiene (Eqs. (3) and (4)). The hydrogenation energy of cumulene is more exothermic than that of ethylene by $-11.0 \text{ kcal mol}^{-1}$. Further, the radialene is stabilized by the cyclic delocalization of π -electrons of the four exocyclic C=C bonds around the ring, which is absent in the parent cyclobutane. On the other hand, the dimerization energies of **1** and **2**, where the metal is formally d⁰, are less than that of cumulene (Eq. (5)). This reduction in the dimerization energy comes from the delocalization of perpendicular π orbitals of the carbon atoms to the vacant d levels of Ti and Zr. It is also possible that the destabilization of the

middle C–C π bond mentioned above is not as high in **1** and **2** as in the parent cumulene because of the nonlinearity of the carbon string in **1** and **2**.

The dimerization energies are dependent on the butadiyne substituents. These increase in the order $\text{NH}_2 < \text{H} < \text{OH}$. A contributor to the enhanced dimerization energy of the OH substituted complex is the $\text{O–H}\cdots\text{O}$ -bonding. On the other hand, hydrogen bonding is not very significant in NH_2 substituted complexes. The calculated geometrical parameters of the metal substituted radialenes are comparable to those found experimentally (Table 3). In the H and OH substituted complexes of Ti and Zr, the metal and all the four carbon atoms of the metallacycle are in the same plane. However, in the NH_2 substituted complexes, the metal atom is forced out of the plane of the metallacycle (Fig. 3). With $\text{M} = \text{Zr}$ and $\text{R} = \text{NH}_2$, the central cyclobutane ring deviates from planarity by about 5° .

The M–C bond is more polarized toward the carbon atom as expected, more so when the metal is Zr. A cycloreversion can in principle lead to a bis(butadiyne) complex **6**, but this is not observed with **3**. Structure **9** or any other cumulene complex of Ni is not known experimentally. The radialene structure of Ni (**5**) on optimization collapses to the bis(butadiyne) complex **8**. Such a complex has been synthesized by starting with a

monomeric Ni complex, $(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})\text{Ni}(\eta^1, \eta^2\text{-C}_7\text{H}_{12})$ [7]. The model nickel complex, **8** with $\text{R} = \text{H}$ and $\text{L} = \text{NH}_3$ calculated at the same level of theory is a planar molecule with both the Ni atoms bridged by two butadiyne units (Table 3). The nickel atoms are in zero oxidation state. The environment around both the nickel atom is trigonal planar with each Ni(0) atom coordinated to one NH_3 ligand and one each of the $\text{C}\equiv\text{C}$ bonds of two different butadiyne units. The calculated Ni–C bond lengths are comparable to the experimental values [7] and indicate considerable delocalization of electrons between the metal atom and the butadiyne unit. The middle C–C bond in **8** is 1.412 Å long, as expected for a sp-sp bond.

Our inability to get optimized geometries corresponding to **5** and **6** prompted us to analyze the conservation of orbital symmetry during the transformation of **1** \rightarrow **3** (Fig. 4), **3** \rightarrow **6** (Fig. 5) and **5** \rightarrow **8** (Fig. 6). These are all found to be symmetry allowed processes. The specifics of individual reactions need to be studied for further quantitative details. It is interesting to note that complexation with metal changed the symmetry disallowed dimerization of cumulene to an allowed one.

The difficulty in getting a radialene type structure for Ni may arise from the non availability of the in plane π orbitals of the middle C–C bond of the parent cyclocu-

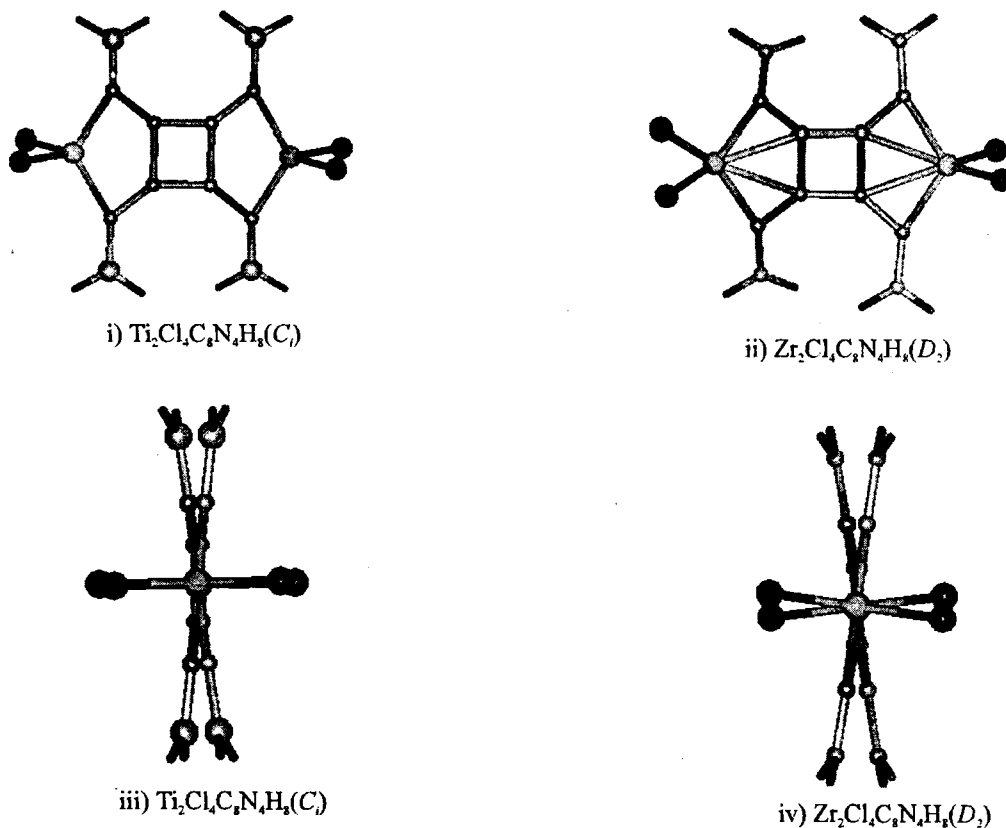


Fig. 3. The changes in the skeleton of Ti and Zr complexes brought in by the substituent NH_2 . Structures (iii) and (iv) are perpendicular views of (i) and (ii) respectively.

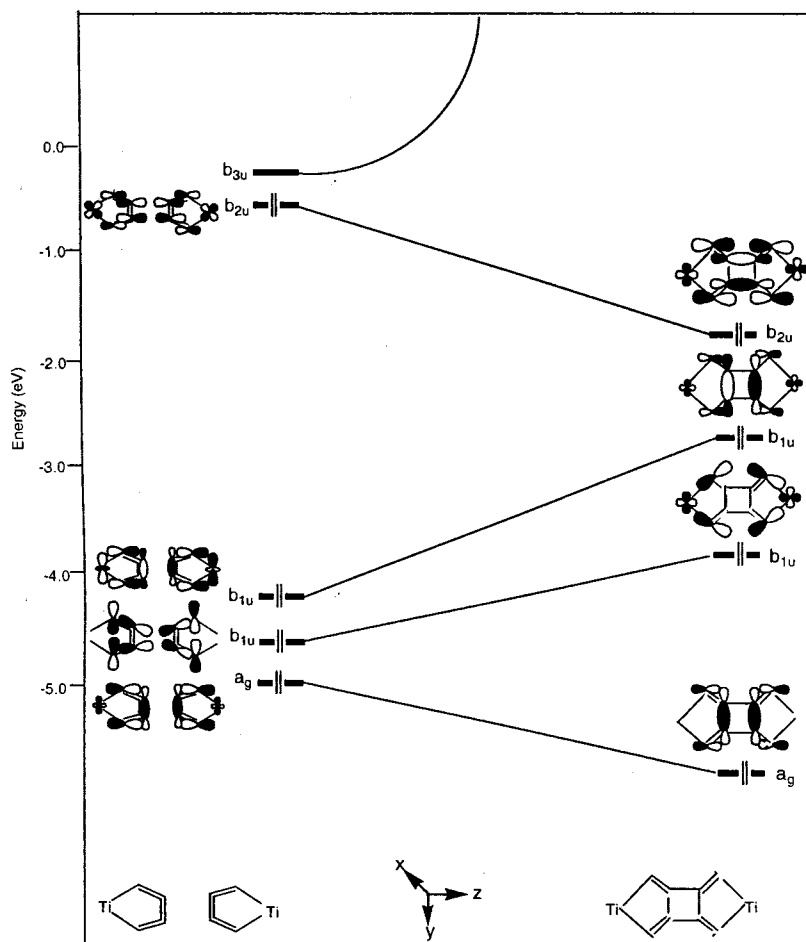


Fig. 4. Correlation diagram for the dimerization of Ti substituted cumulene. The hydrogen atoms and the ligands (Cl) are omitted for clarity.

mulene which is already involved in bonding and back-bonding interaction with the metal d orbitals. But, in the Ti complex, where there is no back-bonding, these orbitals are readily available for interaction with another cyclocumulene unit. In view of these calculations, it is clear that the formation of the diyne structure **8** does not involve the cyclocumulene **9**. We suggest the following notional mechanistic steps for the formation of **8** (Scheme 2) reported by one of us earlier [17]. The first step involves the coordination of a butadiyne molecule to the Ni atom forming the monoligand Ni(0) olefin–alkyne complex [15]. This is followed by coordination of one more molecule of butadiyne to the metal atom and subsequent removal of the diene moiety. There is precedence for such type of mechanism in the literature [16,17]. In the third step, one more molecule of the initial monoligand Ni(0) diene complex attacks one of the two butadiyne units available for coordination. The formation of such dinuclear complexes by coordination of two Ni(0) complex fragments at one 1,3-diyne is well known [17]. In the last step, the diene unit is removed from the coordination sphere of the Ni atom and the bis(butadiyne) complex of Ni is formed [7].

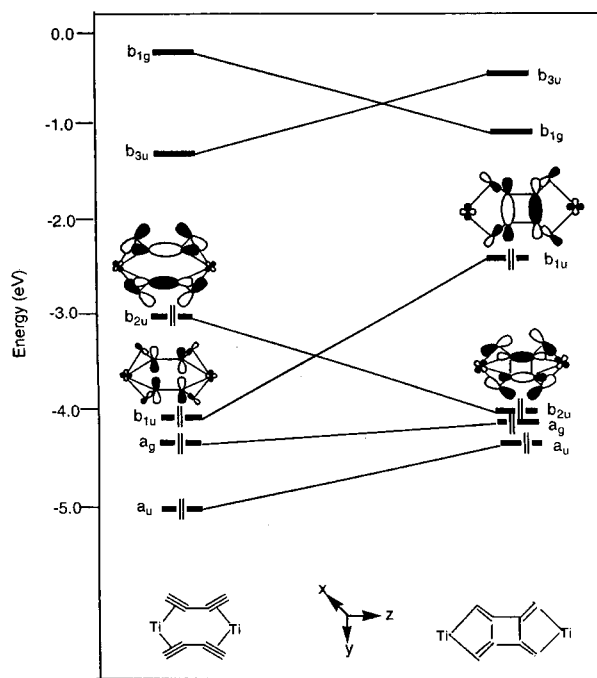


Fig. 5. Correlation diagram for the process 3→6. The hydrogen atoms and the ligands (Cl) are omitted for clarity.

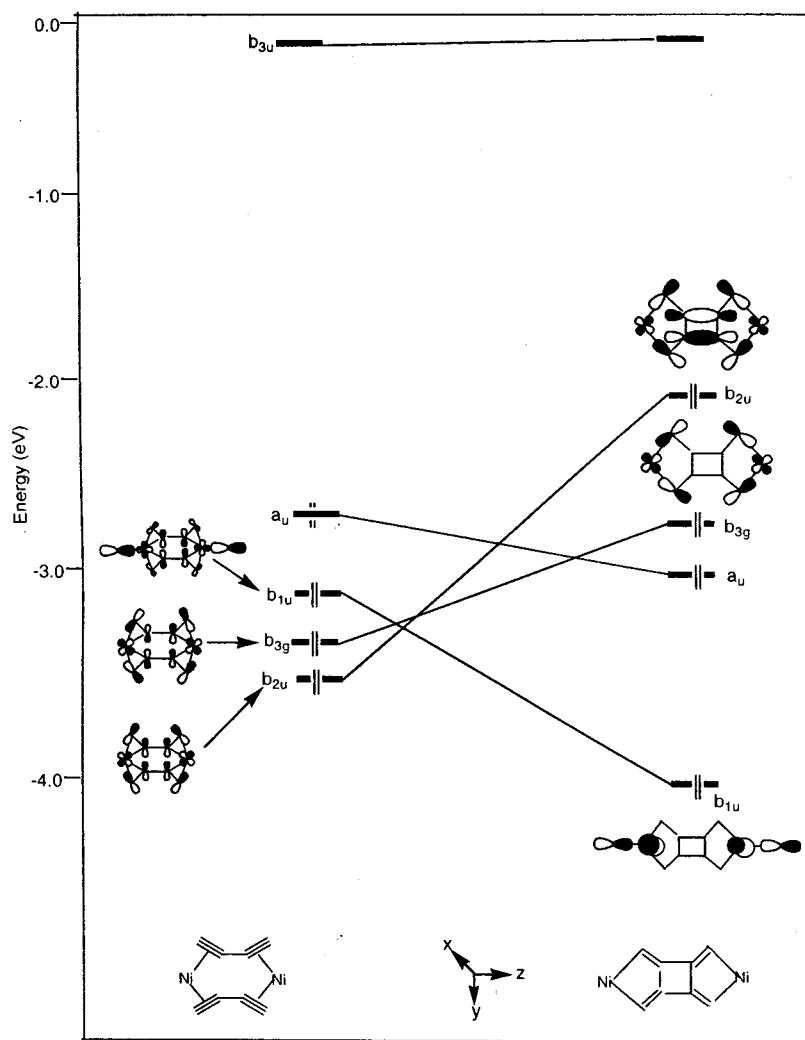
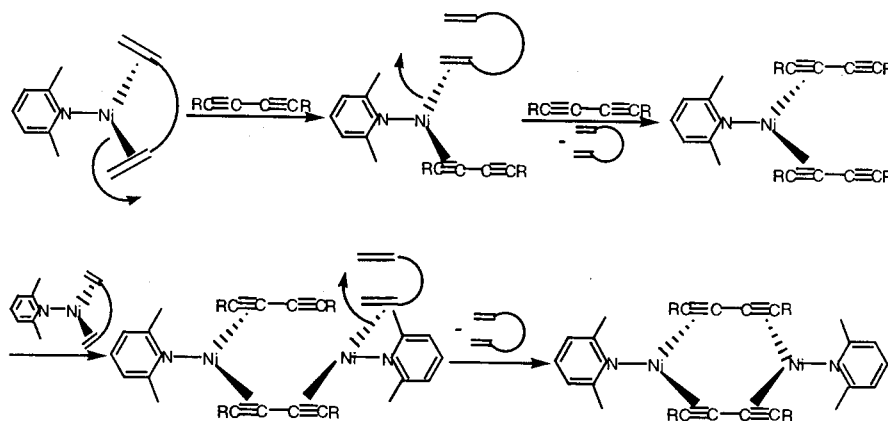


Fig. 6. Correlation diagram for the process 5→8. The hydrogen atoms and the ligands (pyridine) are omitted for clarity.



Scheme 2.

4. Conclusions

The middle double bond in the metallacyclocumulenes involving Ti and Zr (**1** and **2**) is intact; there is no back-bonding observed here. Consequently, the Ti complex is found to dimerize to **3**. Such a process is not observed for Zr. Quantitative studies of the reaction barrier are needed to establish the details. With a d^0 electron count, the back-bonding part of the DCD model is not applicable here. Though the corresponding Ni complex, **9**, is shown to be a minimum, its radialene dimer, **5**, is not even a stationary point. A bis(butadiyne) complex, **8**, is obtained instead. Corresponding complexes of Ti and Zr (**6** and **7**), on optimization, collapse to the radialenes **3** and **4**. Correlation diagrams constructed for the dimerization of **1** and **2** as well as for conversion of the radialene type structure to that of the bis(butadiyne) complex show that these are symmetry allowed. The effect of substituents on the dimerization of metallacyclocumulenes is also studied and it shows similar energetics for Ti and Zr.

Acknowledgements

This work was supported by the Council of Scientific and Industrial Research (CSIR), New Delhi, India. A.K.P. thanks CSIR for a Junior Research Fellowship.

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