

Nature of α,β -CCC agostic bonding in metallacyclobutanes

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Abstract

The α,β -CCC agostic bonding in metallacyclobutanes is examined on the basis of structural, bonding, energetics, and electron density features. The structural features such as $C_\alpha-C_\beta$, $M-C_\alpha$, and $M-C_\beta$ distances and $C_\alpha C_\beta C_\alpha$ and $MC_\alpha C_\beta$ angles of the agostic metallacyclobutanes were distinctly different from those of the corresponding non-agostic complexes. Two different orbital interactions characteristic of the agostic complex, causing the deformation of the propane-1,4-diyl unit of the metallacyclobutane were identified. The energy difference between the propane-1,4-diyl unit of metallacyclobutane in an agostic complex to that in a non-agostic complex is proposed as a good measure for the strength of α,β -CCC agostic interaction (E_{agostic}). E_{agostic} values of 37.0, 36.2, 13.7, 28.6, and 23.9 kcal/mol were obtained for the Grubb's first generation Ru, Grubb's second generation Ru, Ti, W, and Ta metallacyclobutane complexes and these values showed a linear correlation with the electron density at the ring CPs. The QTAIM features of the agostic complexes viz. the smaller ρ value at the $C_\alpha-C_\beta$ BCPs, larger ellipticity of the $C_\alpha-C_\beta$ BCPs, and diminished covalent character of $C_\alpha-C_\beta$ bonds as seen in their Laplacian of the electron density ($\nabla^2\rho$) at the BCPs, when compared with the non-agostic systems, fully supported the agostic bonding interactions. The α,β -CCC bonding is considered as the first example of a π type orbital formed between a metal atom and a carbon atom, where there is no σ bond connectivity and this type of bonding is anticipated with all transition metals provided that the metal center is highly electron deficient.

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1. Introduction

Nearly two decades ago Brookhart and Green introduced the C–H agostic bonding in organometallic chemistry [1] describing various manifestations of covalent bonding interactions between C–H σ bonds and d orbitals on transition metal centers. Hundreds of examples are known for C–H agostic bonding and it is now considered as a general phenomenon in organometallic chemistry [2–6]. This phenomenon mainly occurs when a C–H bond comes in the vicinity of an electron deficient metal center. There is growing evidence that σ bonds other than C–H can also participate in agostic bonding when they come in the vicinity of an electron deficient metal center [7–12]. The strength of such interactions will vary according to

the position of the metal in the periodic table, electron deficiency of the metal, oxidation state of the metal, type of the σ bond, the distance between the σ bond and the metal center, etc. Agostic bonding leads to the partial removal of electron density from the concerned σ bond, leading to the weakening of that bond and therefore this type of bonding is understood as an important component of many catalytic bond breaking processes [13–18].

Apart from C–H agostic bonds, a few examples of C–C agostic bonds are reported in the literature [19–24]. Recently, the analysis of the structural and bonding features of the ruthenacyclobutane intermediate located for the dissociative metathesis reaction mechanism of Grubbs 1st and 2nd generation catalyst has revealed strong interaction between the metal-centered d orbitals and the two $C_\alpha-C_\beta$ σ bonds on the propane-1,4-diyl unit [25,26]. This type of interaction is named as the α,β -CCC agostic interaction and it is considered as the main cause of the

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C–C bond activation in the olefin metathesis reaction [26]. For instance, as a result of α,β -CCC agostic interaction, the propane-1,4-diyl unit of the ruthenacyclobutane showed unusually long C–C single bond of length 1.59 Å (this value is ~ 0.07 Å longer than a typical C–C single bond) supporting the facile C–C bond fission in metathesis reactions [25,27–30]. Further, this interaction accounted for the short distance of 2.227 Å observed between Ru–C $_{\beta}$ bond. The structural feature of the ruthenacyclobutane unit suggested a non-classical nature for it as a 16 electron bisphosphine metallacyclobutane Cl $_2$ Ru(PH $_3$) $_2$ (C $_2$ H $_6$) showed normal C–C single bonds (C–C distance = 1.511 Å) and quite long Ru–C $_{\beta}$ distance (2.821 Å) [25].

Bader's quantum theory of atoms-in-molecule (QTAIM) [31,32] is a powerful method for characterizing the bonding features of a chemical system [33,34]. In this technique the topological properties of electron density at the bond critical points (BCP), ring critical points (RCP), and cage critical points (CCP) are used to obtain information on the nature of covalent/non-covalent interactions. For instance, this method is frequently used to obtain the characteristic features of covalent bonds in strained systems, metal–ligand bonding and for eliciting the hydrogen bond interactions in molecular systems [33,35–40]. Apart from the electron density (ρ) at the BCP, the QTAIM quantities such as Laplacian of electron density ($\nabla^2\rho$) at the critical points (CPs) and the ellipticity (ϵ) of the BCPs are also important quantities often used to quantify the various bonding interactions.

In the present work, we have considered metallacyclobutane complexes of Ru, Ti, Nb, W and Ta, which are encountered in metathesis reactions for a detailed computational study at density functional theory (DFT) level to understand the nature of the α,β -CCC agostic bonding. The QTAIM theory was also used to explore the bonding features of the metallacyclobutane region.

2. Computational details

All the molecular geometries were optimized at the DFT level of theory using the B3LYP hybrid functional [41,42] with the GAUSSIAN03 suite of programs [43]. For Ru, Ti, Nb, W, and Ta atoms, the basis set LanL2DZ with extra f-polarization functions was used [44–46]. The values of the f-exponents used in the calculations were Ru = 1.235, Ti = 1.506, Nb = 0.952, W = 0.823, and Ta = 0.790 [44]. For H, C, O, and N atoms the 6–31G** and for P and Cl, 6–31+G* basis sets were selected. This method abbreviated here as B3LYP/BI would give reliable geometries. Normal coordinate analysis has been performed for all stationary points to confirm that all the structures are energy minima. Using the B3LYP/BI level wavefunction, QTAIM properties or the topological features of electron density has been obtained using the AIM2000 program [47]. Mainly the bond critical points (BCP) and ring critical points (RCP) of the metallacyclobutane regions were analyzed.

3. Results and discussion

3.1. Optimized geometries of α,β -CCC agostic and non-agostic metallacyclobutanes

In Fig. 1, the optimized geometries of the complexes **Ru_1a** (a model for the Chauvin intermediate in Grubb's first generation catalyst), **Ru_1b** (a model for the Chauvin intermediate in Grubb's second generation catalyst) [48,49], **Ti_1** (a model for Grubb's titanium metathesis catalyst) [50], **Nb_1** (a model for Mashima's niobium metathesis catalyst) [51], **W_1** (a model for Schrock's tungsten metathesis catalyst) and **Ta_1** (a model for Schrock's tantalum metathesis catalyst) [52] are depicted. It may be noted that the X-ray structures of substituted systems of **Ti_1**, **Nb_1**, **W_1**, and **Ta_1** are known in the literature [50–52]. Some important geometrical parameters of all these systems are presented in Table 1. In these complexes, following general features can be observed: (i) all of them show significantly long C $_{\alpha}$ –C $_{\beta}$ single bonds in the range of 1.577–1.599 Å on the propane-1,4-diyl unit; (ii) the \angle C $_{\alpha}$ C $_{\beta}$ C $_{\alpha}$ bond angle (115.2–118.0°) is around 39 to 53% wider than the \angle MC $_{\alpha}$ C $_{\beta}$ bond angle (77.0–81.6°); (iii) the M–C $_{\beta}$ distance (M is the metal atom) is around 14–18% longer than the M–C $_{\alpha}$ bond distance; (iv) the metal is always in a high oxidation state, viz. **Ru_1a**, **Ru_1b**, and **Ti_1** in +4, **Nb_1** and **Ta_1** in +5, and **W_1** in +6; (v) none of them possess 18-electron configuration, which means that all are electron deficient systems. All these five features may be considered as unique to the metallacyclobutanes showing α,β -CCC agostic bonding or these complexes may be classified as agostic complexes [26].

The first three features describing the structure of the metallacyclobutane of an agostic complex may be compared with the structural features of a complex showing normal C–C bond lengths for the metallacyclobutane region (non-agostic metallacyclobutanes). Therefore, the complexes **Ru_2a**, **Ru_2b**, **Ti_2**, **W_2**, and **Ta_2** have been optimized to locate their minimum energy structures (Fig. 2). Among these complexes, **Ru_2a** and **Ru_2b** are models for the intermediate metallacyclobutane located for the associative mechanism of the Grubb's first and second generation olefin metathesis catalyst, respectively. **Ti_2**, **W_2** and **Ta_2** are constructed from the X-ray structures containing similar structural units [53–55]. To the best of our knowledge, the X-ray structure of a niobacyclobutane complex showing normal C–C bond length is not yet reported in the literature and therefore, a non-agostic system for niobium is not attempted in this work.

The optimized geometries of the non-agostic complexes **Ru_2a**, **Ru_2b**, **Ti_2**, **W_2** and **Ta_2** are presented in Fig. 2. Their important geometrical parameters are depicted in Table 1 along with those of the agostic complexes. As we can see from Fig. 2, the C $_{\alpha}$ –C $_{\beta}$ bond in all these complexes are significantly shorter than their corresponding agostic complexes. For instance, in the case of **Ru_2a**, **Ru_2b**, **W_2** and **Ta_2** the C $_{\alpha}$ –C $_{\beta}$ bond lengths in the range of

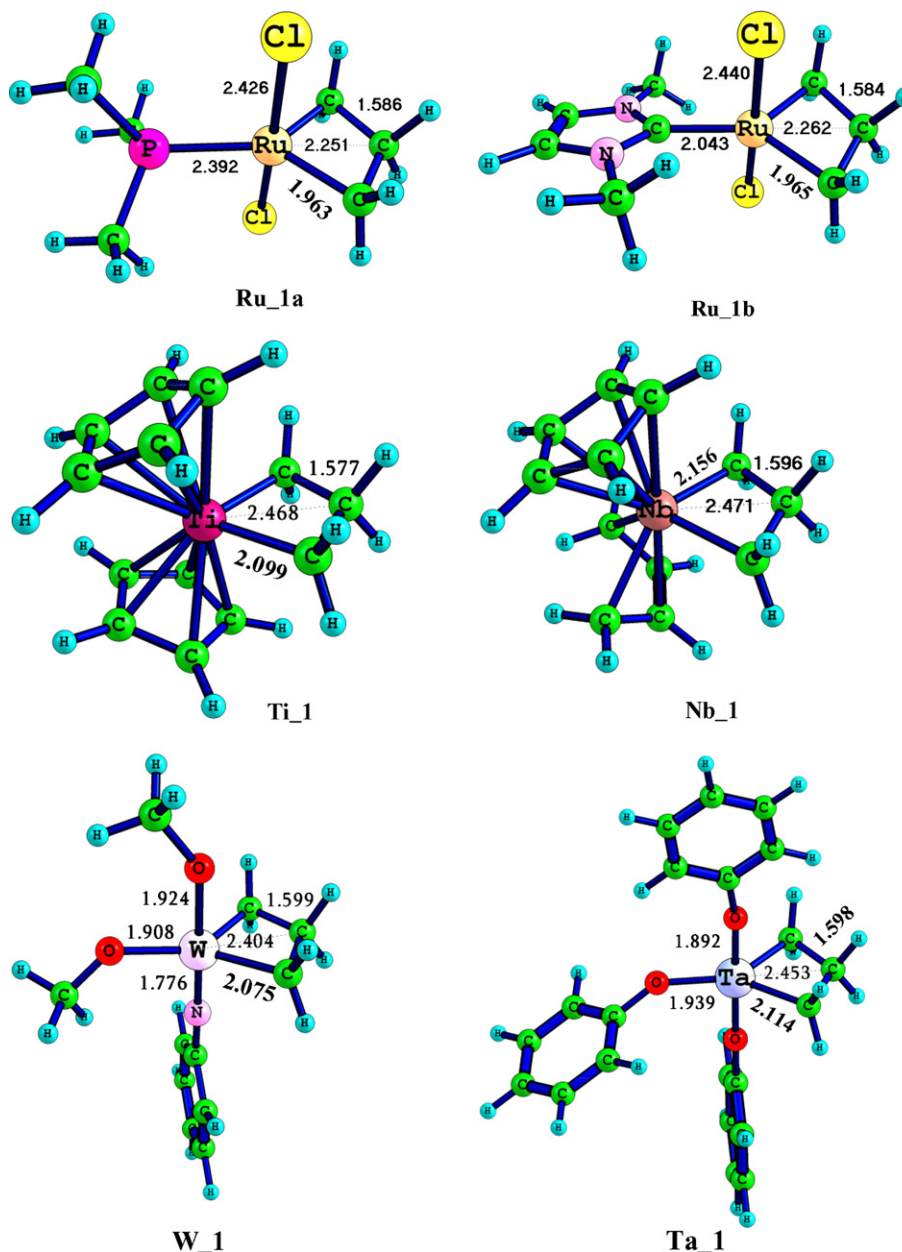


Fig. 1. Optimized geometries of agostic complexes.

Table 1
Some important geometrical parameters of agostic and non-agostic complexes

Complex	$C_\alpha-C_\beta$	$M-C_\alpha$	$M-C_\beta$	$\angle C_\alpha C_\beta C_\alpha$	$\angle MC_\alpha C_\beta$
Ru_1a	1.585	1.963	2.251	117.1	77.9
Ru_2a	1.511	2.189	2.826	96.7	97.9
Ru_1b	1.584	1.965	2.262	116.6	78.4
Ru_2b	1.515	2.181	2.836	97.7	98.6
Ti_1	1.577	2.099	2.468	115.2	83.0
Ti_2	1.549	2.152	2.556	102.6	85.7
Nb_1	1.596	2.156	2.471	118.5	80.9
W_1	1.599	2.075	2.404	116.8	80.6
W_2	1.531	2.177	2.777	96.6	95.4
Ta_1	1.598	2.114	2.453	116.7	81.6
Ta_2	1.529	2.247	2.856	97.7	96.5

All bond lengths are in Angstrom and bond angles in degrees.

1.514–1.531 Å are close to the typical C–C bond length of 1.53 Å. However, in the case of **Ti_2**, the $C_\alpha-C_\beta$ bond of length 1.549 Å is slightly higher than the typical C–C single bond length, but definitely lower than the $C_\alpha-C_\beta$ bond lengths in the corresponding agostic complex **Ti_1**. It means that $C_\alpha-C_\beta$ bonds in **Ti_2** may still possess some amount of agostic character because the electronic structure of this complex is expected to be similar to that of the agostic complex **Ti_1**, apart from the bridging CH_2 moiety between the metallacyclobutane and the cyclopentadienyl ring. It seems that the structural restriction imposed by the bridging CH_2 unit is reducing the α,β -CCC agostic interaction in **Ti_2** resulting to an increase in the C–C σ bonding effect. The M– C_β distance observed in the range of 2.556–2.856 Å in non-agostic complexes is

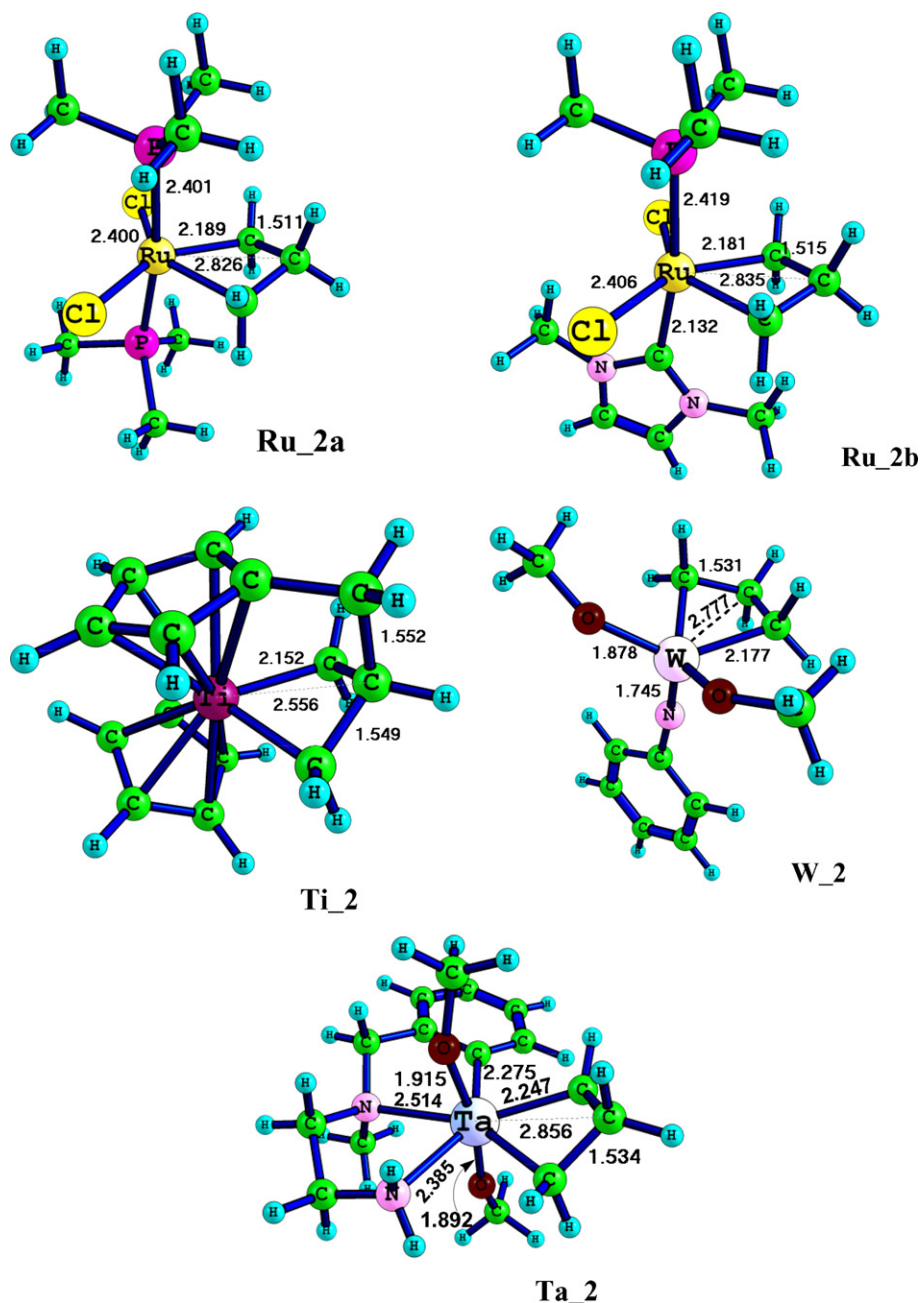


Fig. 2. Optimized geometries of non-agostic complexes.

significantly longer than the $M-C_{\beta}$ distance in the range of 2.251–2.471 Å found in the agostic complexes. Moreover, except the **Ti_2** complex, both the $\angle C_{\alpha}C_{\beta}C_{\alpha}$ and the $\angle MC_{\alpha}C_{\beta}$ bond angles are close to a value of 97° in non-agostic complex, whereas the agostic complexes showed a larger value of $\sim 117^{\circ}$ for $\angle C_{\alpha}C_{\beta}C_{\alpha}$ and a smaller value $\sim 81^{\circ}$ for $\angle MC_{\alpha}C_{\beta}$ bond angles. The structural distinction between agostic and non-agostic complexes were also obtained on the basis of the ratio of the $M-C_{\alpha}$ and $M-C_{\beta}$ bond lengths and the ratio of the $\angle C_{\alpha}C_{\beta}C_{\alpha}$ and $\angle MC_{\alpha}C_{\beta}$ bond angles. The quantities $(M-C_{\alpha})/(M-C_{\beta})$ and $(\angle C_{\alpha}C_{\beta}C_{\alpha})/(\angle MC_{\alpha}C_{\beta})$ when plotted on a graph show two distinctly different linear correlations, viz. one for ago-

stic and the other for non-agostic complexes (Fig. 3). A value of 0.1885 is obtained for the slope of the linear equation for agostic complexes while a relatively higher value of 0.3269 is obtained for the non-agostic complexes.

3.2. Bonding features of α,β -CCC agostic and non-agostic metallacyclobutanes

It may be noted that in all the agostic systems, the $M-C_{\alpha}$ bond is shorter than the $M-C_{\beta}$ bond in the non-agostic complexes. This may be considered as a consequence of the α,β -CCC agostic bonding because in such systems a characteristic bonding interaction between the empty d_z^2

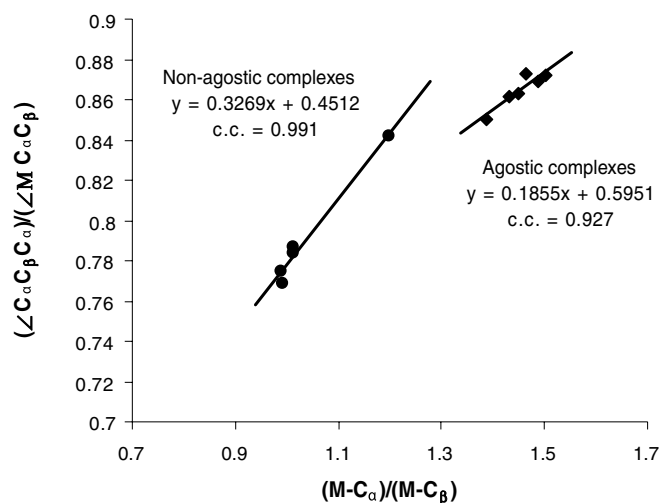


Fig. 3. Correlations between structural parameters of agostic and non-agostic complexes. The linear equations and the correlation coefficients (c.c.) are also given.

orbital on the metal and one of the occupied orbitals of the propane-1,4-diyl unit is always found. This bonding MO (MO_1) is plotted for the ruthenacyclobutane **Ru_1a** in Fig. 4 along with the constituting fragment molecular orbitals (MO_f1 and MO_f2). Similar to MO_1, MO_2 is located for the non-agostic complex **Ru_2a** which is also depicted in Fig. 4. As we can see from Fig. 4, in MO_1, all the three lobes of the d_z^2 orbital can participate in the bonding interaction while in the case of MO_2, only one lobe of the d_z^2 orbital can participate in bonding interaction and therefore the former interaction is expected to be stronger than the latter. This may be the main reason for the shortening of the M–C $_{\alpha}$ bond in agostic complexes.

Further, along the M–C $_{\beta}$ direction of MO_1, a bonding component is seen while, along the M–C $_{\beta}$ direction of MO_2, an antibonding component is found. The existence of the bonding component along the M–C $_{\beta}$ direction is one of the reasons for the shortening of M–C $_{\beta}$ distance in the agostic complex. Moreover, the bonding as presented in

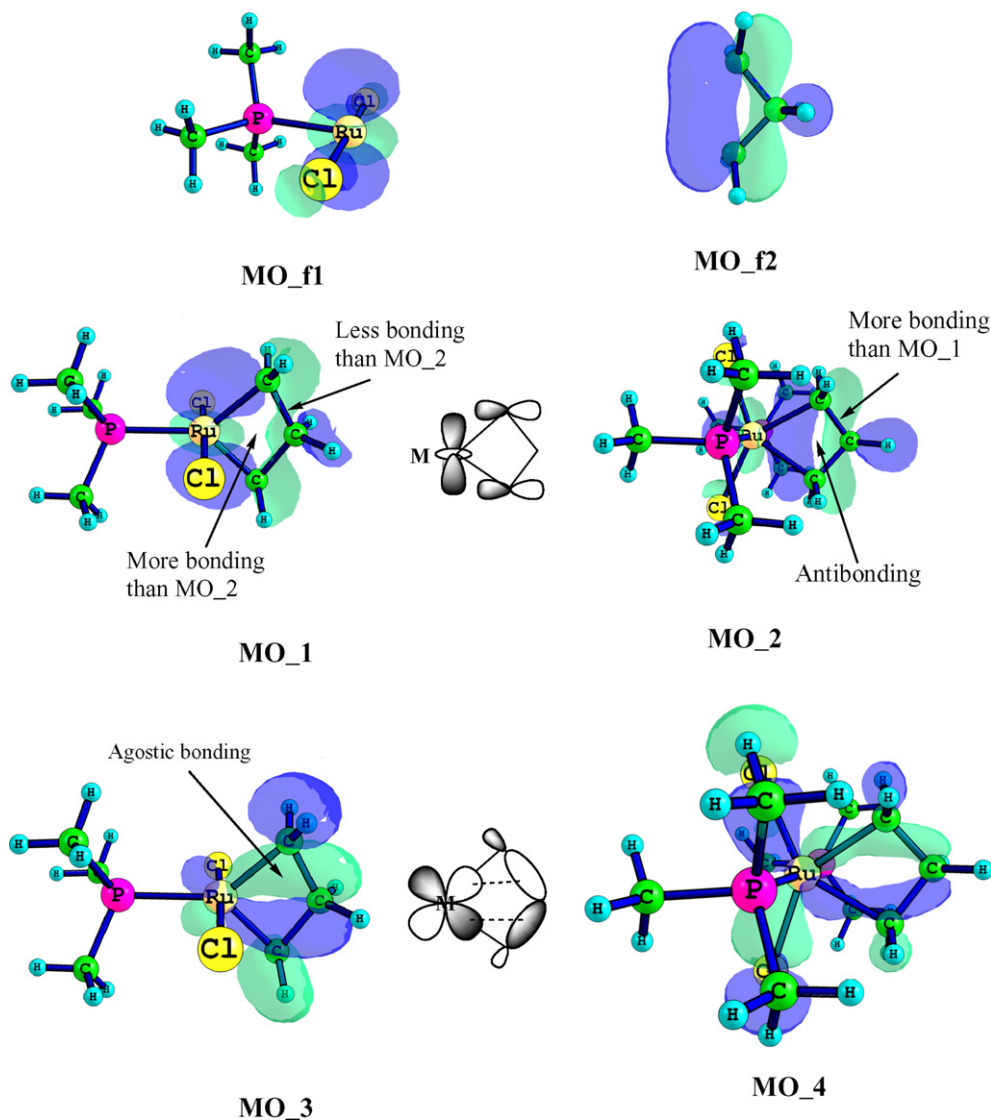


Fig. 4. Fragment molecular orbitals MO_f1 and MO_f2 and molecular orbitals showing bonding interactions in ruthenacyclobutane region of **Ru_1a** (MO_1 and MO_3) and **Ru_2a** (MO_2 and MO_4) systems.

MO_1 has a direct influence on the $C_\alpha-C_\beta$ bond as it decreases the bonding component along this σ bond as compared to the MO_1. Suresh and Koga have recently analyzed this unique bonding situation in Grubbs first generation ruthenacyclobutanes and considered it as an important element of agostic interaction [25]. Although we do not see a direct interaction of the $C_\alpha-C_\beta$ bond and the metal d orbitals in MO_1, the presence of the bonding component along the Ru– C_β direction and the weakening of the bonding effect along $C_\alpha-C_\beta$ bond direction suggests that MO_1 is indeed an important component of α,β -CCC agostic interaction.

Also depicted in Fig. 4 is MO_3 and MO_4, the bonding molecular orbitals for the ruthenacyclobutane region of the agostic complex **Ru_1a** and the non-agostic complex **Ru_2a**, respectively. MO_3 clearly shows the well defined interaction between the metal-centered d_{xy} orbital and the two $C_\alpha-C_\beta$ σ bonds. In other words, we can say that the formally sp^3 hybridized two α and one β carbon atoms of the propane-1,4-diyl unit are simultaneously interacting with metal d_{xy} orbital and therefore this type of interaction is named as the α,β -CCC agostic bonding interaction. It may be noted that such an interaction is nearly absent in MO_4 of the non-agostic complex **Ru_2a**. A detailed MO-diagram representing the metallacycle formation is already published elsewhere [26]. The orbital features presented for the agostic complex **Ru_1a** are seen in all other agostic complexes studied herein.

3.3. α,β -CCC agostic bonding strength

Although the agostic bonding is well evident in the structural and bonding features of the complexes, the quantification of the strength of this interaction is rather difficult as it involves simultaneous interaction of the metal and the three carbon atoms. However, if we assume that the structural deformation in the propane-1,4-diyl unit of an agostic complex is mainly due to α,β -CCC agostic interaction, the strength of this interaction can be quantified. However, in this approach, a regular structure of a propane-1,4-diyl unit showing normal C–C single bond length behavior is required for comparison with the deformed structure. Since in the present work, except the niobium system, we have a non-agostic complex corresponding to all the agostic complexes, the propane-1,4-diyl unit of the non-agostic complex can be considered as the regular structure. Therefore, the propane-1,4-diyl fragment from all the optimized geometries of agostic (fragment_1) and non-agostic complexes (fragment_2) were taken out and determined their energy values using a closed shell B3LYP/6-31G** level calculation. In all the cases, fragment_1 was less stable than fragment_2, meaning that the propane-1,4-diyl structure is more deformed in the agostic complex than the non-agostic complex. The difference in the energy between fragment_1 and fragment_2 is considered as a good measure of the α,β -CCC agostic interaction energy (E_{agostic}). The ruthenium-based Grubbs first (**Ru_1a**) and second (**Ru_1b**)

generation metathesis systems showed much higher E_{agostic} values of 37.0 and 36.2 kcal/mol, respectively than others. The tungsten-based Schrock metathesis system (**W_1**) also showed a high value of 28.6 kcal/mol for E_{agostic} whereas relatively lower E_{agostic} values of 23.9 and 13.7 kcal/mol were obtained for **Ta_1** and **Ti_1**, respectively. It may be noted that E_{agostic} values are significantly higher than the strength of a C–H agostic bond. For instance, very recently Grunenberg et al. [56] suggested a value ≤ 10 kcal/mol for the C–H agostic bond. The higher strength of α,β -CCC is not surprising because the simultaneous interactions of four atoms through two molecular orbitals of the type MO_1 and MO_3 given in Fig. 4 is expected to be stronger than that of a typical C–H agostic bond which involves three atoms and one molecular orbital.

3.4. Electron density critical point analysis

QTAIM theory is used to explore the bonding interactions at the metallacyclobutane region of the agostic and non-agostic complexes. In QTAIM theory, a (3, –1) CP is observed between a bonded pair of atoms [33]. This criterion is even seen in the case of hydrogen bonds and also observed in the case of C–H agostic bonds [38,57]. In the present case, only the M– C_α and $C_\alpha-C_\beta$ bonds showed the presence of (3, –1) CPs. Although the short M– C_β distance found in agostic complex as compared to the non-agostic complex suggests bonding interaction between M and the C_β atom in the former, a (3, –1) BCP in the M– C_β direction was not observed. Instead, a (3, +1) RCP is always observed in the M– C_β direction. Similar topological features of electron density were reported in the case of bridged cobalt complexes $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ systems [58–60]. In these complexes, no direct Co–Co bond in terms of a (3, –1) BCP was characterized and instead a (3, +1) RCP was located. It means that in some weak bonding situations, even constructive orbital overlap may not be sufficient to produce a (3, –1) BCP in the topology of the electron density. In the present case, the α,β -CCC agostic bonding MO (MO_3) can be considered as a π -type orbital with respect to the M– C_β direction and therefore no bonding component along the M– C_β direction is possible. Perhaps this may be the reason for the absence of a (3, –1) BCP between M and C_β . In normal bonding situation, this case will not occur because a π bond is observed between two atoms already connected with a σ bond. In other words, the α,β -CCC agostic bonding interactions of the type MO_3 may be considered as the first example of a π type orbital formed between a metal atom and a carbon atom, where there is no σ bond connectivity.

In Table 2, the electron density (ρ) at the BCP and RCP, Laplacian of the electron density at the BCP ($\nabla^2\rho$), and ellipticity (ε) of the BCPs are presented for all the agostic and non-agostic systems studied herein. Ellipticity, ε , is defined as $\varepsilon = \lambda_1/\lambda_2 - 1$, where λ_1 and λ_2 are the negative eigenvalues of the Hessian of the electron density at the BCP. The sum of the eigenvalues λ_i will give the $\nabla^2\rho$ at

Table 2
QTAIM properties of agostic and non-agostic complexes

System	Type of CP	Agostic			Non-agostic		
		ρ (e/a_0^3)	$\nabla^2\rho$ (e/a_0^5)	ε	ρ (e/a_0^3)	$\nabla^2\rho$ (e/a_0^5)	ε
Ru_1a and Ru_1b	BCP ($C_\alpha C_\beta$)	0.212	-0.097	0.105	0.256	-0.153	0.019
	BCP ($M-C_\alpha$)	0.145	0.035	0.166	0.102	0.010	0.311
	RCP ($M-C_\beta$)	0.066			0.051		
Ru_2a and Ru_2b	BCP ($C_\alpha C_\beta$)	0.212	-0.098	0.107	0.254	-0.151	0.019
	BCP ($M-C_\alpha$)	0.145	0.033	0.177	0.103	0.011	0.328
	RCP ($M-C_\beta$)	0.064			0.050		
Ti_1 and Ti_2	BCP ($C_\alpha C_\beta$)	0.218	-0.106	0.081	0.235	-0.125	0.066
	BCP ($M-C_\alpha$)	0.104	0.017	0.035	0.097	0.011	0.058
	RCP ($M-C_\beta$)	0.038			0.039		
Nb_1	BCP ($C_\alpha C_\beta$)	0.209	-0.095	0.104			
	BCP ($M-C_\alpha$)	0.108	0.034	0.001			
	RCP ($M-C_\beta$)	0.043					
W_1 and W_2	BCP ($C_\alpha C_\beta$)	0.206	-0.092	0.119	0.245	-0.139	0.028
	BCP ($M-C_\alpha$)	0.132	0.018	0.078	0.119	0.007	0.083
	RCP ($M-C_\beta$)	0.052			0.053		
Ta_1 and Ta_2	BCP ($C_\alpha C_\beta$)	0.206	-0.091	0.119	0.242	-0.136	0.039
	BCP ($M-C_\alpha$)	0.123	0.020	0.113	0.103	0.011	0.020
	RCP ($M-C_\beta$)	0.047			0.048		

the BCP. The ρ values at the $C_\alpha-C_\beta$ BCPs of the agostic complex **Ru_1a**, **Ru_1b**, **Ti_1**, **W_1**, and **Ta_1** are smaller than those of the corresponding non-agostic $C_\alpha-C_\beta$ BCPs, by 17.2, 16.5, 7.2, 15.9, and 14.9%, respectively, suggesting the weakening of the $C_\alpha-C_\beta$ bond in the former systems. This $C_\alpha-C_\beta$ bond weakening can be mainly assigned to the orbital interactions of the type MO_3 given in Fig. 4. On the other hand, ρ values at the $M-C_\alpha$ BCPs of the agostic complex **Ru_1a**, **Ru_1b**, **Ti_1**, **W_1**, and **Ta_1** are found to be higher than those of the corresponding non-agostic $M-C_\alpha$ BCPs, by 42.2, 40.8, 7.2, 10.9, and 19.4%, respectively, indicating that agostic systems possess some double bond character in their $M-C_\alpha$ bonds and this can be assigned mainly to the orbital interactions of the type MO_1 given in Fig. 4. In fact, a near perfect linear correlation is obtained between the $C_\alpha-C_\beta$ bond length values and the ρ at the BCPs of the agostic and non-agostic complexes (Fig. 5). However, such a correlation was not very clear in the case of $M-C_\alpha$ bond lengths and the corresponding ρ values (Fig. 5).

In all the cases, the ellipticity (ε) values of $C_\alpha-C_\beta$ BCPs of agostic systems are found to be larger than the corresponding values of the non-agostic systems. It means that in agostic complexes, the electron density is more distorted in the perpendicular directions away from the bond axis than the non-agostic complexes which is an expected outcome of the agostic bonding leading to the bond weakening [57,61]. On the other hand, compared to the ε values of the $M-C_\alpha$ bonds of agostic complexes, the ε values of the $M-C_\alpha$ bonds of non-agostic complexes are higher in magnitude. A negative value is always observed for the $\nabla^2\rho$ of the $C_\alpha-C_\beta$ BCPs reflecting their covalent character while it was positive for all the $M-C_\alpha$ BCPs indicating the ionic character of the bonds. The $\nabla^2\rho$ value of the agostic

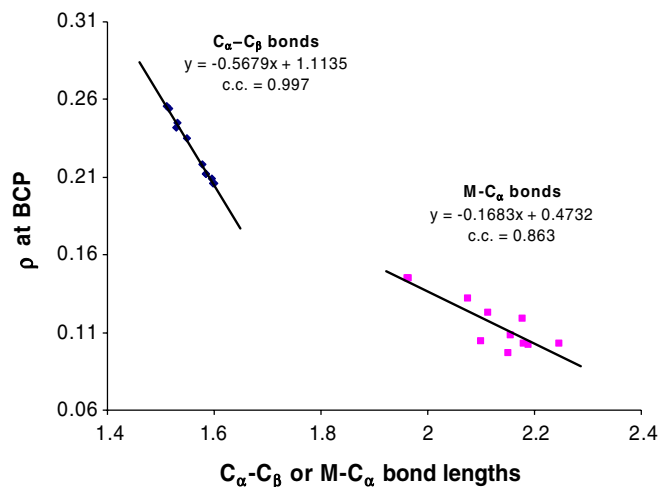


Fig. 5. Correlations between ρ values at the $C_\alpha-C_\beta$ and $M-C_\alpha$ BCPs of agostic and non-agostic complexes.

$C_\alpha-C_\beta$ BCP was less negative than the corresponding non-agostic BCPs, suggesting weakening of the covalent character of that bond. On the other hand, the non-covalent character of the $M-C_\alpha$ bond is increased in the agostic systems as the corresponding BCPs showed more positive $\nabla^2\rho$ value than those of the non-agostic complexes. The QTAIM features of the agostic complexes, viz. the smaller ρ value at the $C_\alpha-C_\beta$ BCPs, larger ε of the $C_\alpha-C_\beta$ BCPs and diminished covalent character of $C_\alpha-C_\beta$ bonds as seen in their $\nabla^2\rho$ value at the BCPs when compared with the non-agostic systems, fully support the agostic bonding interactions.

In QTAIM theory, the ring structure of a molecular system is identified by locating a (3, +1) ring critical point

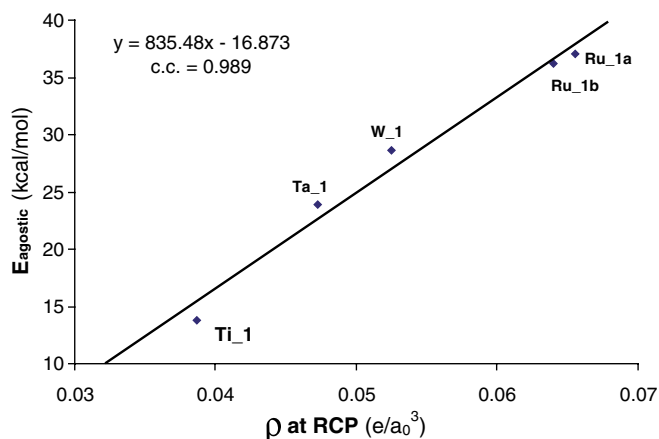


Fig. 6. Correlation between E_{agostic} and ρ values at the RCP of agostic complexes.

(RCP). In all the metallacyclobutanes studied herein, the RCP is always located between the M and the C_{β} atom. Since in α,β -CCC agostic interactions, the metal and all the three carbon atoms are involved, it is felt that ρ value at the RCP would reflect the agostic bonding strength as the combined effect of all the atoms may be reflected at a point inside the ring. It means that the ρ values at the RCP would be proportional to the E_{agostic} values. This statement is found to be true as the ρ values at the RCP showed a good linear correlation with the E_{agostic} values (Fig. 6). According to this linear correlation, the strength of α,β -CCC agostic bonding in **Nb_1** complex can be predicted using ρ value of 0.048 at RCP and the predicted value is turned out to be 23.2 kcal/mol.

4. Conclusions

The structural features of metallacyclobutane region of the agostic complexes are markedly different from those of the corresponding non-agostic complexes. The metallacyclobutane region of the agostic complex is always characterized by the presence of unusually long $C_{\alpha}-C_{\beta}$ single bonds and significantly short $M-C_{\beta}$ distance. The α,β -CCC agostic bonding is the main cause of the substantial amount of deformation found in the propane-1,4-diyl unit of the agostic complexes. This type of bonding may be considered as the first example of a π type orbital formed between a metal atom and a carbon atom, where there is no σ bond connectivity. The energy difference between the propane-1,4-diyl unit of the agostic and non-agostic complexes is proposed as a good and easy way to obtain the agostic bond strength. The QTAIM features of the agostic complexes are markedly different from the non-agostic complexes. The ρ value at the RCP of agostic complexes showed a linear correlation with the E_{agostic} values. The computed E_{agostic} values are found to be much higher than the strength of C–H agostic bonds. It may be noted that in the present work, the analysis of agostic bonding has been performed only with the B3LYP procedure and other func-

tional and pure ab initio methods were not tested, but they may give similar results.

Since α,β -CCC agostic bonding is expected in metallacyclobutanes with electron deficient metal centers, such a bonding would play an important role in C–C bond metathesis reactions as it leads to the substantial weakening of the C–C bonds and at the same time retaining the stability of the complex. It is felt that like the C–H agostic bonding, the new type α,β -CCC agostic bonding may be possible with all the transition elements provided that the metal center is highly electron deficient and therefore it could be a general phenomenon in organometallic chemistry.

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