

Topological Analysis of The Electron Density of Triruthenium Clusters $[(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_2(\mu^3\text{-}\eta^2\text{-N=CPhH})(\mu\text{-C=N-tBu})]$ and $[\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu^3\text{-NCH}_2\text{Ph})]$

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Abstract: Based on the QTAIM methodology, the bonding interactions of Ru...Ru, Ru-Cp, Ru-H, and Ru-L (L is $\mu^3\text{-N=CPh}$, and $\mu\text{-C=N-tBu}$) in the triruthenium complexes; $[(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_2(\mu^3\text{-}\eta^2\text{-N=CPhH})(\mu\text{-C=N-tBu})]$ (1) and $[\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu^3\text{-NCH}_2\text{Ph})]$ (2) have been analyzed. The description of topological properties (both local and integral) for these complexes was successfully done. We found that there is no direct Ru...Ru bonding for all these complexes. Also, the multicenter interaction (5c-6e) is proposed for (Ru1-H1-Ru2-H2-Ru3) involving in core of cluster 1, while for (Ru1-H1-Ru2-H2-Ru3-H3) in cluster 2, an interaction is (6c-9e) delocalized over six membered $\text{Ru}_3(\mu\text{-H})_3$ ring. Finally, the different bridging ligands between complex 1 and 2 creates some changes in the computed properties related to them.

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I. Introduction

The amines are of great significance basic backbone having many implementations to pharmaceuticals, agrochemicals, chemical industry, biotechnology and materials science [1, 2]. Recently, huge number of works have been produced involving the catalysis of nitriles compounds to prepare amines [3-5]. Because their applications, especially in activity, selectivity and pharmaceutical applications, ruthenium complexes have used for this purpose and attracted an attention in comparison to other transition metals [6, 7]. In recent years, Bader's quantum theory applied to atoms in molecules [8] has been produced as an increasingly popular tool used in study the bonding for molecules in order to finding

various interactions in the certain molecular system. in systems of weakly bound such as those with metal-olefin complexes, hydrogen bonds and p-p interactions. Herein, we tested these clusters by Quantum Theory of Atoms in Molecules (QTAIM) [9,10] involving local and integral topological properties to find information about the bonds between atoms [11]. Additionally, the method is very useful in avoiding the difficult way of an appropriate pro-molecule [12-14]. Furthermore, atoms in molecules theory has been used in clarification of the interactions nature Some literature on interactions of metal-metal is at now depending on the concept of QTAIM [15,16]. Many confirmations indicate dependency of classification only on Laplacian sign, may be

particularly inefficient for higher atoms as example; transition metals. So, there are features must be considered as topological indicators to obtain sufficient interpretation for this interactions [17, 18].

The clusters; $[(Cp^*Ru)_3(\mu-H)_2(\mu^3-\eta^2-N=CPhH)(\mu-C=N-tBu)]$ (1) [6] and $[\{Cp^*Ru(\mu-H)\}_3(\mu^3-NCH_2Ph)]$ (2), (Figure 1), ($Cp^* = \eta^5-C_5Me_5$) [6] have no QTAIM studies discussing their topological features yet.

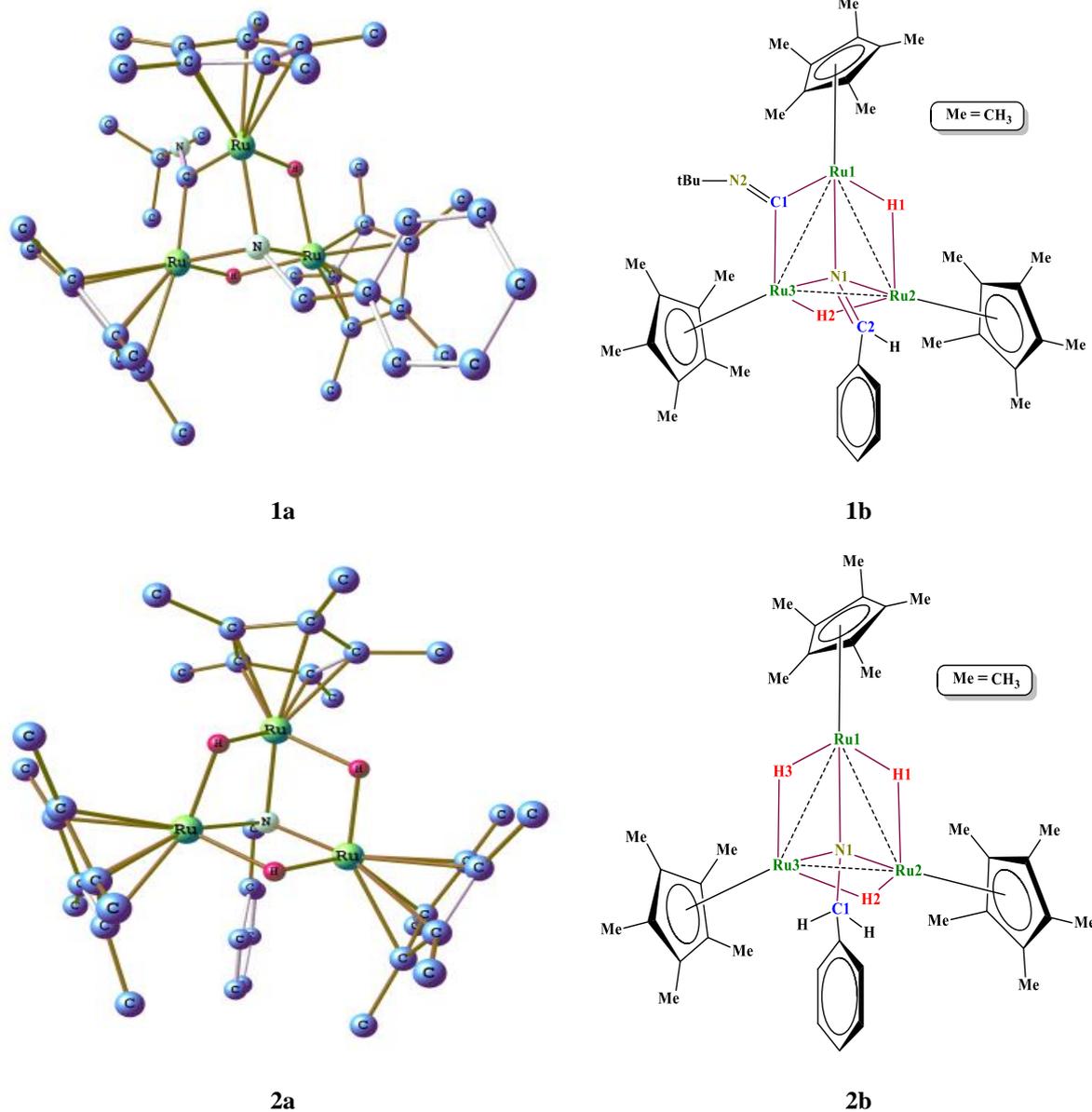


Fig 1: (a): geometry optimization structure, (b): Schematic structure of clusters; $[(Cp^*Ru)_3(\mu-H)_2(\mu^3-\eta^2-N=CPhH)(\mu-C=N-tBu)]$ (1) and $[\{Cp^*Ru(\mu-H)\}_3(\mu^3-NCH_2Ph)]$ (2)

We can see that these complexes give a significant comparison between topological parameters. Also, the interactions of Ru...Ru, H-bridged versus L-bridged (L = μ^3 -NCH₂Ph, μ^3 - η^2 -N=CPhH, and μ -C=N-tBu). Finally, ligand-unsupported Ru...Ru paths, in addition to Ru-hydride compared Ru- μ^3 - η^2 -N=CPhH interaction. We can get many important features of different *interactions* by this comparison *such as Ru...Ru*, hydride versus μ^3 - η^2 -N=CPhH-bridging ligands rather than Ru-Cp*.

I. COMPUTATIONAL METHODS

Using the Density functional theory (DFT) approach, our calculations have been carried out with GAUSSIAN09 [19] software depending the structures of X-ray diffraction measurement as a starting point of 1 and 2 triruthenium systems for geometry optimization. The resultant data were obtained applying PBE1PBE [11] as a function and basis function 6-31G (d, p) [16] with atoms H, C, N and O. Additionally, basis set LANL2DZ [15] has been used to find data of ruthenium, while

PBE1PBE/6-31G(d,p)/WTBS [14] was used to further topological calculations. Interestingly, the many-electron system structures are completely tested using QTAIM topological analysis including both local and integral properties performed with the AIM2000 programs.

II. RESULTS

The electron density $\rho(b)$, local kinetic energy density $G(b)$, Laplacian $\nabla^2\rho(b)$, local potential energy density $V(b)$, local energy density $H(b)$, and ellipticity $\varepsilon(b)$ at critical points in addition to the delocalization indices are the most common properties can be obtained by QTAIM [20,21]. The kinetic energy densities at the bcp's $G(\mathbf{r})$ were evaluated using the Abramov's approximation:

$$G(\mathbf{r}) = \left(\frac{3}{10}\right) (3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3} + (1/6)\nabla^2\rho(\mathbf{r})$$

It is an appropriate equation to calculate $G(\mathbf{r})$ [26, 27] for interactions with closed shell, in case $\nabla^2\rho(\mathbf{r}) > 0$.

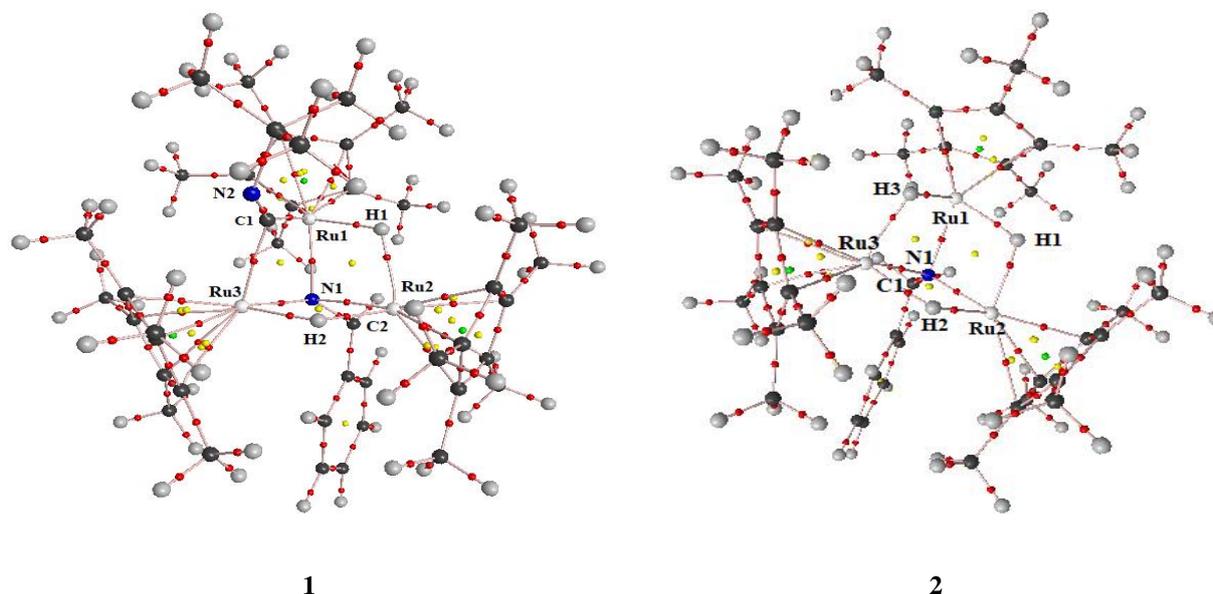


Fig 2: Molecular structure of 1 and 2 clusters, bond paths (gray lines) bp's and the bond (small red circles) bcp's and ring (yellow circles) rcp's critical points

Critical Points

As clearly seen in Figure 2, A set of critical points and bond paths were completely found by application of AIM device. While, the bond paths are important indicators of their associated bcp's

connecting the atomic pairs, so from these images of 1 and 2 clusters, the bcp's and bonding lines have been clearly found in addition to rcp's. For every Ru-C and C-C (in C₅Me₅) bonds there are bp's connect them intersecting the corresponding

bcp's in both molecules with one rcp related to each cyclopentadienyl ring 5(C-C).

In this sense, it was clearly found three Ru-C bond critical points and three Cp ring critical points in each compound. Also, three Ru-N1 bp's with associated bcp's were observed in 1 and 2 clusters. Consequently, because the existing of bridging ligands, three rcp's were emerged in each complex.

Additionally, for complex 1 four Ru-H bp's with corresponding bcp's rather than two Ru-C bcp's were shown. In contrast, six bcp's and bp's were obviously found in complex 2. Furthermore, there are also other bp's of benzene ring C-C with related bcp's and rcp's. Finally, the Ru...Ru interactions have no bcps and bps.

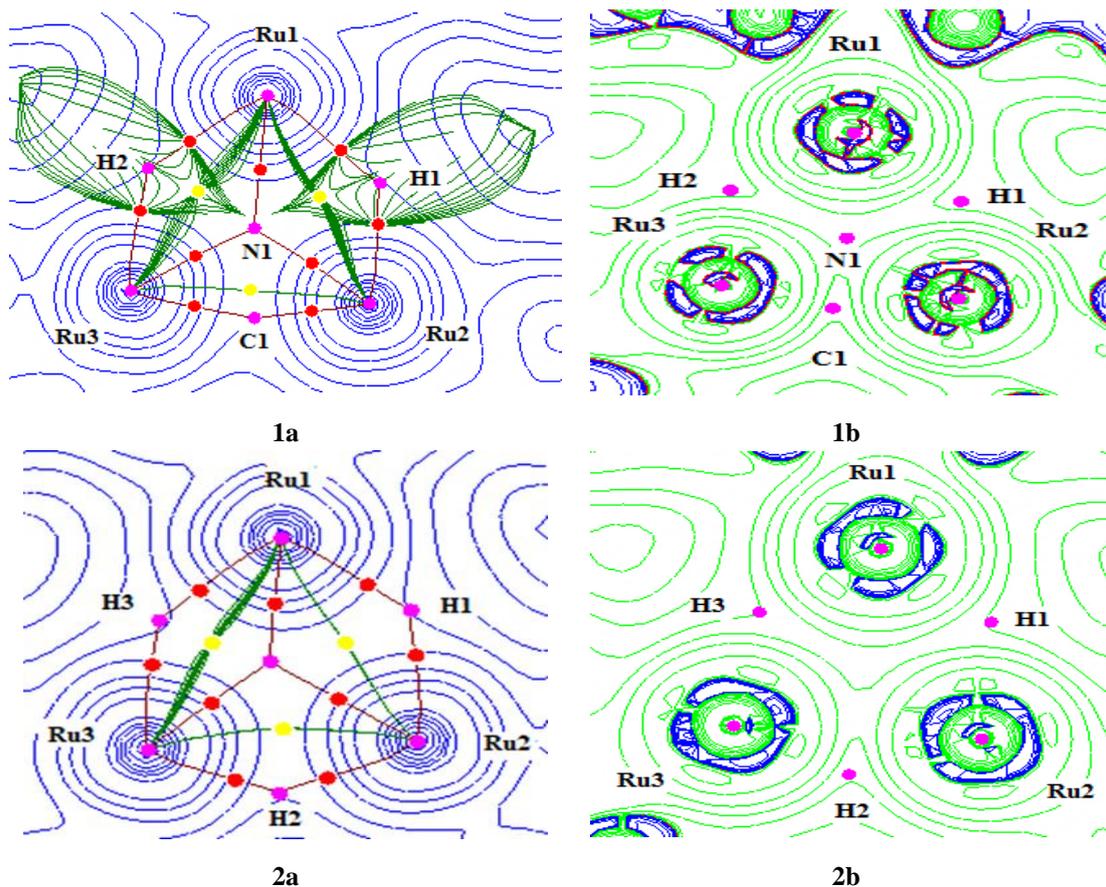


Fig 3: (a) and (b): Gradient trajectories and Laplacian maps of the electron density respectively of 1 and 2 clusters core

Ru-Ru and Ru-Ligand Interactions

A gradient trajectory and Laplacian maps for 1 and 2 clusters core of the total electron density consisted of ruthenium atoms for this mentioned two compounds are shown in Fig 3. It is obvious by studies that, when the values of ρ_{BCP} are large, $\nabla^2\rho_{BCP} < 0$ and $H_{BCP} < 0$, the result is covalent bond which is shared interaction, on the other hand, when ρ_{BCP} values are small, and values of $\nabla^2\rho_{BCP}$

> 0 and $H_{BCP} > 0$ the calculation is described for ionic interactions i.e. closed-shell interactions [23]. Also, instead of $\nabla^2\rho_{BCP}$, the H_{BCP} is very useful parameter for indicating the best bonding[24]. Herein, we examine the bonding in 1 and 2 using various QTAIM indicators. All these local topological characteristics of the systems are given in Table 1.

Table 1. Some topological parameters at critical points for 1 and 2 clusters

Bond ^a	$\rho_b(e\text{\AA}^{-3})^b$	$\nabla^2\rho_b(e\text{\AA}^{-5})^c$	$G_b(\text{he}^{-1})^d$	$V(\text{he}^{-1})^e$	$H_b(\text{he}^{-1})^f$	ϵ_b^g
Cluster 1						
Ru1-H1	0.088	0.169	0.102	-0.215	-0.112	0.037
Ru2-H1	0.078	0.153	0.085	-0.180	-0.094	0.048
Ru2-H2	0.071	0.158	0.076	-0.163	-0.086	0.022
Ru3-H2	0.095	0.169	0.112	-0.234	-0.122	0.052
Ru1-N1	0.120	0.528	0.202	-0.436	-0.235	0.205
Ru2-N1	0.111	0.328	0.152	-0.325	-0.172	0.02
Ru3-N1	0.124	0.470	0.195	-0.419	-0.224	0.142
Ru1-C1	0.104	0.188	0.121	-0.254	-0.133	0.058
Ru3-C1	0.120	0.278	0.160	-0.337	-0.177	0.143
Ru1-Cp*	0.077	0.249	0.099	-0.213	-0.114	4.812
Ru2-Cp*	0.084	0.249	0.106	-0.228	-0.122	1.789
Ru3-Cp*	0.074	0.244	0.094	-0.203	-0.109	5.952
N1-C2	0.322	-0.739	0.748	-1.451	-0.702	0.245
Cluster 2						
Ru1-H1	0.086	0.138	0.094	-0.196	-0.102	0.063
Ru2-H1	0.089	0.140	0.097	-0.203	-0.106	0.009
Ru2-H2	0.096	0.156	0.111	-0.232	-0.121	0.065
Ru3-H2	0.087	0.154	0.097	-0.204	-0.107	0.122
Ru1-H3	0.102	0.172	0.124	-0.259	-0.135	0.118
Ru3-H3	0.085	0.278	0.099	-0.216	-0.117	0.233
Ru1-N1	0.123	0.445	0.191	-0.410	-0.219	0.244
Ru2-N1	0.147	0.538	0.248	-0.530	-0.282	0.163
Ru3-N1	0.095	0.366	0.138	-0.300	-0.161	0.166
Ru1-Cp*	0.085	0.246	0.108	-0.231	-0.123	1.455
Ru2-Cp*	0.084	0.254	0.108	-0.232	-0.124	1.222
Ru3-Cp*	0.086	0.209	0.089	-0.191	-0.102	1.645
N1-C1	0.272	-0.718	0.409	-0.774	-0.364	0.027

An Interaction of Ru...Ru

Each Ru atom is connecting to three bridging ligands; the bridging ligands are spanned to Ru...Ru interactions of 1 and 2 clusters. Therefore, as a result, all Ru...Ru in these complexes have two bridging ligands, so this may be the most effective reason explains lacking critical points between Ru...Ru bond paths in the cores. This result is in agreement with an important fact of many studies [11, 25] "when the M-M bonds are bridged with ligands, in this case a bcp and a bps are usually absent in the M-M path". But the bond paths in metal-metal exist clearly when it is unsupported with bridging ligands. This result was reported and confirmed in many studies [18, 26] "only for the unsupported interactions of Co-Co in [Co₄(CO)₁₁(PPh₃)], the bond paths is existing". Some studies about triclinic [27] and orthorhombic [28] improvement of the μ -(5-oxofuran-2(5H)-ylidene) supported system [Co₂(CO)₆(μ -CO)(μ -

C₄O₂H₂)] have exhibited the bps for supported Co atoms, nevertheless that result was lately not clear [29]. In our study on triruthenium complexes, there are no direct bcps have indicated in Ru-Ru paths in both 1 and 2 systems because the Ru atoms do not have enough atomic orbitals to form.

Ru-Cp* Interaction

From Table 1, it can be observed that the values of electron density of Ru1-Cp*, Ru2-Cp* and Ru3-Cp* are respectively about [0.078, 0.084 and 0.074 e \AA^{-3}] and Laplacian are [0.249, 0.249 and 0.244 e \AA^{-5}] for cluster 1, also, the values corresponding to Ru-Cp* in cluster 2 is [0.084, 0.086 and 0.085 e \AA^{-3}], and Laplacian is [0.254, 0.209 and 0.246 e \AA^{-5}]. So, the observation is the high electron density and Laplacian values of Ru2-Cp* than Ru1-Cp* and Ru3-Cp* for cluster 1. This can be attributed to the most obvious difference between them which is clearly indicated by the Figure 3, that Ru2 is

bonded to the two bridged hydrides, while each of the Ru1 and Ru3 are bonded to μ -C1=N2-tBu and only one hydride bridged ligand.

The presence of μ -C1=N2-tBu ligand may rationalize the non-negligible difference [26,30] of values as previously referred. In contrast, the cluster 2 has no differences in values of (ρ_b) and ($\nabla^2\rho_b$) because the symmetry and, in which, each ruthenium atom has the same bonding in cluster. Additionally, the parameter which give information on stability of the corresponding chemical bond is the ellipticity [31]. This feature has proposed the highest values for the Ru-Cp* coordination bonds compared with other bonds in compounds 1 and 2 (Table 1). For instance, in complex 1, Ru3-Cp* and Ru1-Cp* have higher ellipticity values (5.952 and 4.812 respectively) than for Ru2-Cp* (1.789) affected by presence of μ -C1=N2-tBu ligand bridged to Ru1 and Ru3. Oppositely, as expected in complex 2, the ellipticity values for Ru1-Cp*, Ru2-Cp* and Ru3-Cp* have no significant differences because all Ru...Ru are bridged with hydride ligands.

Also, the electronic energy density index can be more appropriate than Laplacian in explain the interaction of molecular systems [25], so the negative values ranging (-0.109) - (-0.122) he^{-1} , (-0.102) - (-0.124) he^{-1} for 1 and 2 compounds respectively indicating the covalent character for Ru-Cp* bonds.

Ru-H Bridging Ligand Interactions

As shown in Fig 3 presented by the gradient trajectory map for Ru1-Ru2-Ru3 plane of the total electron density, we can see many different types of bridging ligands spanned the metal-metal (M-M) in M-L-M (M: transition metal, L: Ligand) form of bridged bonds. Both clusters have hydride bridging ligands. Then, by data of Table 1 which propose us deep explanation of some important interactions in molecular systems, it can be found a comparison between strength of the Ru-H bonds from these interactions and of covalent related to one order bonds in non-mineral atoms [32,33]. Accordingly, it is important to observe that the (ρ_b) of Ru-H bonds have variety values ranging from (0.071 - 0.095) $e\text{\AA}^{-3}$ and (0.085 - 0.102) $e\text{\AA}^{-3}$, and ($\nabla^2\rho_b$) have (0.153 - 0.169) $e\text{\AA}^{-5}$ and (0.138 - 0.278) $e\text{\AA}^{-5}$ for 1 and 2 compounds respectively. At Ru-H-Ru

planes of these compounds, the Laplacian maps were given through Fig 3, in which, a Valence shell charge concentration (VSCC) of bridging μ -H atoms is appearing a polarization toward the midpoint of the Ru...Ru edges.

In this context, as previously mentioned, the values of H_{BCP} index which is an insightful tool to explain this interactions (Ru-H), were (-0.086) - (-0.122) he^{-1} and (-0.102) - (-0.135) he^{-1} for 1 and 5 clusters respectively. These values of (ρ_b), ($\nabla^2\rho_b$) and (H_{BCP}) are comparable with these of bridged M-H for many clusters studied such bridged Fe-H in $[(\mu\text{-H})_2\text{Fe}_3(\mu\text{-Q})(\text{CO})_9]$ [36] has ($\rho_b = 0.075 e\text{\AA}^{-3}$), ($\nabla^2\rho_b = 0.162 e\text{\AA}^{-5}$) and ($H_{BCP} = -0.083 he^{-1}$), Ru-H ($\rho_b = 0.822, 0.766$ and $0.564 e\text{\AA}^{-3}$), ($\nabla^2\rho_b = 1.92, 0.045$ and $4.556 e\text{\AA}^{-5}$) and ($H_{BCP} = -0.735, -0.222$ and $-0.314 he^{-1}$) in $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-}\kappa\text{3C2,NHCpyCH2ImMe})(\text{CO})_8]$ [37], $[\text{Ru}_3(\mu\text{-H})(\mu\text{-}\kappa\text{2-Haminox-N,N})(\text{CO})_9]$ [11] and $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-MeImCH})(\text{CO})_9]$ [26] respectively, and Os-H ($\rho_b = 0.553 e\text{\AA}^{-3}$), ($\nabla^2\rho_b = 4.352 e\text{\AA}^{-5}$) and ($H_{BCP} = -0.398 he^{-1}$) in $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ [15]. Finally, in contrast with above studies, the ellipticity values corresponding to described bond $\epsilon(\text{Ru-H})$ of our compounds were relatively small in contrast with those of other bonds [0.022 - 0.052] and [0.009 - 0.233] in 1 and 2 respectively. Consequently, we can importantly emphasize that the values of these parameters describing topological properties in compound 2 are particularly the highest of that for compound 1, taking into account the symmetry of this cluster. Thus, the Ru-H and Ru-Cp* bonds in cluster 2 is considerably more covalent character according to (ρ_b), ($\nabla^2\rho_b$) and (H_{BCP}) values.

Ru-L Bridging Ligands

Other bridging ligands than hydride ligand referred to them by (L) such; $\mu^3\text{-N=CHPh}$ and $\mu\text{-C=N-tBu}$ (in 1) and $\mu^3\text{-NCH2Ph}$ (in 2) are also significantly influencing on the interactions of these systems rather than hydride bridged ligands. However, all these ligands have π -bonding thus they differ from hydride in an influence. In the Ru-L fragment, we can appreciate the bonding nature of complexes 1 and 2 as shown graphical draw of Laplacian property related to total electron density in Ru-L-Ru planes of these systems (Fig 3). In this sense, concerning the bonds of Ru atoms with the bridging

μ^3 -N-CHPh and μ^3 -N=CH₂Ph it is interesting comparison between Ru-(μ^3 -N-CH₂Ph) and Ru-(μ^3 -N=CHPh) bonds with Ru-(μ -H) bonds which are previously analyzed. For complex 1, all properties listed in Table 1 of Ru-(μ^3 -N=CPh) are relatively higher than those for Ru-(μ -H) and Ru-(μ -C=N-tBu). While in complex 2 there are only Ru-(μ -H) rather than Ru-(μ^3 -N-CH₂Ph), it is the same result as complex 1 especially in Ru₂-(μ^3 -N-CH₂Ph)-Ru₃ interaction.

By summarizing these above mentioned features, which are also clear in Fig 3, thus, the Ru-L-Ru planes is clearly depicting the Laplacian. Regardless, VSCC's of each atom N1 and C1 are distorted towards Ru₂ and Ru₃ atoms in both 1 and 2. According to the analysis results of parameters for μ^3 -N=CHPh ligand bonds confirmed the existence of some double-bond character in the interaction of C atom with the adjacent N atoms. In this sense, the μ^3 -N-CH₂Ph can act as pure σ -donors [38] and as π -acceptor or π -donor species, basing on availability of electrons on metal complex [36-40].

Hence, by looking to Laplacian maps and other properties of electron density values, Ru₃(L) can be analyzed depending on polarization of VSCC of these bridging ligands toward the midpoint of the Ru...Ru edges. Interestingly, these polarizations are small, so it can give slightly higher positive values in the Ru- μ NC bcp's (an average 0.451 eÅ⁻⁵) for system 1 than those of μ^3 -NCH₂Ph in system 2 (0.447 eÅ⁻⁵).

The Integral Topological Properties

In addition to the local topological parameters, herein another criterion which is the useful topological tool to describe an important interaction such Ru...Ru and Ru-ligands. This index is electron density delocalization between two bonded or non-bonded atoms referred as $\delta(a, b)$, that estimates the density integration over an interatomic shell and calculate the number of electrons delocalized through this pair of atoms [41,42], Table 2 shows all computed delocalization indexes.

Table 2. Delocalization Indexes between several atomic pairs $\delta(a,b)$ in compounds 1 and 2 clusters

atoms (a, b)	$\delta(a, b)$	atoms (a, b)	$\delta(a, b)$
Cluster 1			
Ru ₂ ...Ru ₁	0.230	Ru ₁ -N ₁	0.781
Ru ₂ ...Ru ₃	0.250	Ru ₂ -N ₁	0.646
Ru ₁ ...Ru ₃	0.376	Ru ₃ -N ₁	0.783
Ru ₂ -H ₁	0.460	Ru ₁ -C _{av. of Cp}	0.423
Ru ₁ -H ₁	0.528	Ru ₂ -C _{av. of Cp}	0.472
Ru ₂ -H ₂	0.416	Ru ₃ -C _{av. of Cp}	0.394
Ru ₃ -H ₂	0.579	N ₁ -C ₂	1.127
Ru ₁ -C ₁	0.721	C ₁ -N ₂	1.558
Ru ₃ -C ₁	0.905		
Cluster 2			
Ru ₂ ...Ru ₃	0.383	Ru ₃ -H ₃	0.587
Ru ₂ ...Ru ₁	0.355	Ru ₂ -N ₁	0.979
Ru ₃ ...Ru ₁	0.551	Ru ₃ -N ₁	0.646
Ru ₁ -H ₁	0.511	Ru ₁ -N ₁	0.817
Ru ₂ -H ₁	0.517	Ru ₁ -C _{av. of Cp}	0.432
Ru ₁ -H ₂	0.497	Ru ₂ -C _{av. of Cp}	0.434
Ru ₂ -H ₂	0.551	Ru ₃ -C _{av. of Cp}	0.465
Ru ₁ -H ₃	0.467	N ₁ -C ₁	0.915

Delocalization of Ru...Ru Interaction

From Table 2, we can observe that, delocalized index has very small values for this type of interaction (metal-metal) and slightly different from complex 1 to complex 2. Thus in complex 1, 0.230, 0.250 and 0.376 values were found for Ru1...Ru2, Ru2...Ru3, and Ru1...Ru3 respectively. The higher value is seen for Ru1...Ru3 which differs by the μ -C=N-tBu than hydride bridging ligand for others (Ru2...Ru1, Ru3), where μ -isocyanido (CN-tBu) ligand bridges the Ru1 and Ru3 atoms.

All these investigations refer to lack direct bonding between Ru-Ru atoms in 1 and 2 clusters, and there is no any valence shell charge concentration polarization in direct Ru-Ru path to each other rationalizing absence such these bonds at all. In this sense, these nonbonding interactions appear small delocalization magnitudes (0.2380-0.5510). So, it can be compared with other corresponding cases shown in previous studies such H-bridged M...M nonbonding interaction which is 0.246 for Ru...Ru in $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-3-MeImCH})(\text{CO})_9]$ [25], Os...Os interaction has 0.177 in $[\text{Os}_3(\mu\text{-H})(\mu\text{-Cl})(\text{CO})_{10}]$ [15], also 0.208 for Fe...Fe interaction of $[\text{Fe}_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}]$ [43]. Additionally, it is observed by delocalization data that $\delta(\text{Ru}, \text{Ru})$ of supported M...M interaction to these clusters appear smaller than that for unsupported M...M interaction [44].

Delocalization of Ru-Cp* Bonding

Interestingly too, the delocalization indexes of Ru-Cp* of these two studied clusters have been pointed out. The values of these interaction are significantly similar for each Ru-Cp* in one compound and that for other systems (close to 0.429 at all). So, we can see the direct path of Cp* to Ru coordinated with π -electrons of five carbon atoms. Among them, one can see that the highest magnitude of this interaction in each complex is ordered as follow; Ru2-Cp* (0.472) in complex 1 > Ru3-Cp* (0.465) in complex 2.

Delocalization of Ru-Bridging Ligands

Ru- μ H is an important bridged ligand coordinated to Ru atom in both 1 and 2 systems, so, one should be shedding more light on this interaction and know how can polarized to Ru-Ru path. An agreement has been satisfied in delocalization index values

obtained for this interaction in these compounds (0.496, 0.522 for complex 1 and 2 respectively as average) with corresponding in literatures such $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-3-MeImCH})(\text{CO})_9]$ cluster in which the Ru- μ H interaction was recorded 0.474 delocalization [25]. Additionally, this result is in line with some others [45].

In complex 1, Ru- μ H interaction appears as higher value for Ru2 and Ru3 than that for Ru1, this can be attributed to presence another bridging ligand shared with Ru2 and Ru3 rather than hydride bridging ligand which found only one for them but two for Ru1, so, we can conclude that the bridged hydride ligand effect to reduce delocalization between Ru...Ru more than bridging μ -CN-tBu ligand do. Thus, the expected interaction is of 5c-6e type for Ru1-H1-Ru2-H2-Ru3 interaction in cluster 1. The large repulsion of direct Ru...Ru in addition to small bonding, the hydrides act as a glue connecting this parts [46]. But in complex 2, 6c-9e for Ru1-H1-Ru2-H2-Ru3-H3 delocalized over six membered $\text{Ru}_3(\mu\text{-H})_3$ ring. So, for complex 2 there is reasonable interpretation in contrast with complex 1, because all Ru atoms were supported by hydride ligands.

III. CONCLUSION

In this work, our aim is to introduce new topological analysis for both previous complexes. The interatomic interactions of 1 and 2 triruthenium clusters have been studied by characterization the topological electron density parameters (local and integral) calculations according to AIM data. From resultant data, a comparison between complexes 1 and 2 can be done taking into account the most important interactions such; Ru...Ru interactions, different bridged ligands for instance hydride bridging versus others bridging ligands such (N=CHPh, N-CH₂Ph, C=N-tBu). Both clusters were similar in lacking the direct bond in three Ru...Ru interactions due to the effect of many supporting ligands bridged to them. 3c-2e interaction type was found to appear between three Ru atoms plan for these systems. But the multicenter interaction (5c-6e) is proposed for (Ru1-H1-Ru2-H2-Ru3) involving in core of cluster 1, while for (Ru1-H1-Ru2-H2-Ru3-H3) in cluster 2, an interaction is (6c-9e) delocalized over six membered $\text{Ru}_3(\mu\text{-H})_3$ ring. In this sense, the local

topological parameters for Ru...Ru interactions in complex 1 were considerably differ from those for complex 2 according to bridging ligands.

It was important to shed light on the efficiency of bridging ligands in the electron density delocalization of supported Ru atoms. Referencing to electron density of resultant data, can attract an attention to fact that the lower electron density involved in the supported Ru metals of clusters 1 and 2 has been compensated through the higher electron density participated by atoms of ligands in Ru-L (L: N=CHPh, N-CH₂Ph, C=N-tBu) bonds. Herein, it was also demonstrated that the bridging ligands availability affect considerably the concentration of electron density and then the topological properties of Ru...Ru interactions. Finally, in order to explain which topological indexes are intrinsically shared with the foundation of metal-metal bonds of variety formal bond order, there is needing to additional studies dealing with unsupported metal-metal bonded systems.

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