Theoretical topological analysis of the electron density in Picolyl N-Heterocyclic Carbene Triruthenium carbonyl cluster: $[Ru_3(\mu\text{-}H)_2(\mu^3\text{-}\kappa^3C_2,NHCpyCH_2ImMe)(CO)_8]$ (ImMe=3-methylimidazol-2- ylidene)

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الخلاصة

دراسة وتعيين عدد من الخصائص التبولوجية للكثافة الالكترونية لقوى التآصر في مركب متعدد الروثينيوم-$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^3C_2,NHCpyCH_2ImMe)(CO)_8]$ (3-methylimidazol-2- ylidene) باستخدام النظرية الكمية للذرات في الجزيئات QTAIM. تمت في هذه الدراسة مقارنة الخصائص التبولوجية لمختلف الاواصر بين الذرات. طبقا للنتائج المستحصلة تم تشخيص وجود اصرة وحيدة فقط بين الذرتين Ru(3)- Ru(1). كما وجد ان الترابط الالكتروني داخل قلب المعقد Ru_3H_2 هو من نوع خمسة ذرات وستة الكترونات (5c-6e). كما تربط الذرات الثلاث الجسرية N-C-C بين >رات الروثينيوم Ru(3)- Ru(1) وهي ليست كافية كالذرات المنفردة مثل الهدريدات في زيادة عدم تمركز الكثافات الالكترونية بين ذرات العناصر الانتقالية. كما وجد ان الخصائص التبولوجية المحسوبة لأواصر الثلاث Ru-C بين ذرات العناصر الانتقالية والليكاند NHC متشابه والتآصر من نوع σ. ان تحليل الخصائص التبولوجية لأواصر الليكاندات Picolyl، NHC اثبت وجود تمركز للكثافات الالكترونية للحلقة السداسية لليكاند Picolyl وإعادة لعدم تمركز الكترونات π للحلقة الخماسية لليكاند NHC مع بعض خصائص آصرة مزدوجة تربط بين ذرة كاربون C وذرتي النتروجين N المرتبطتين معهما.

Abstract

A number of topological parameters of the electron density of bonding interactions in the Picolyl N-Heterocyclic Carbene Triruthenium carbonyl cluster $[Ru_3(\mu\text{-}H)_2(\mu^3\text{-}\kappa^3C_2,NHCpyCH_2ImMe)(CO)_8]$ has been calculated and interpreted under the perception of the Quantum theory atoms in molecules (QTAIM). These results have allowed a comparison between topological properties of different atom-atom interactions. The QTAIM theory recognizes the existence of a bond path in only one of the Ru(1)-Ru(3) edges. Consequently, an interaction of 5c-6e type is proposed to exist in the Ru_3H_2 core. The three atoms N-C-C bridge that spans the Ru(1)-Ru(3) edge is not as efficient as bridges comprising one atom, such as hydride in order to delocalize the electronic density of the bridged metal atoms. All topological parameters calculated for the three existing Ru-C bonds between the metal atoms and the NHC ligand are similar, and they confirm that these interactions are pure σ bond. The analysis of the topological parameters of the Picolyl and NHC ligands bonds confirms the existence of π-electron delocalization within the six-membered ring for Picolyl ligand and hindered π-electron delocalization within the five-membered ring of NHC ligand with some double-bond character in the interaction of the carbine C atom with the adjacent N atoms.

Key words: *Picolyl N-Heterocyclic Carbene Triruthenium carbonyl cluster, QTAIM theory, Ru, Picolyl*

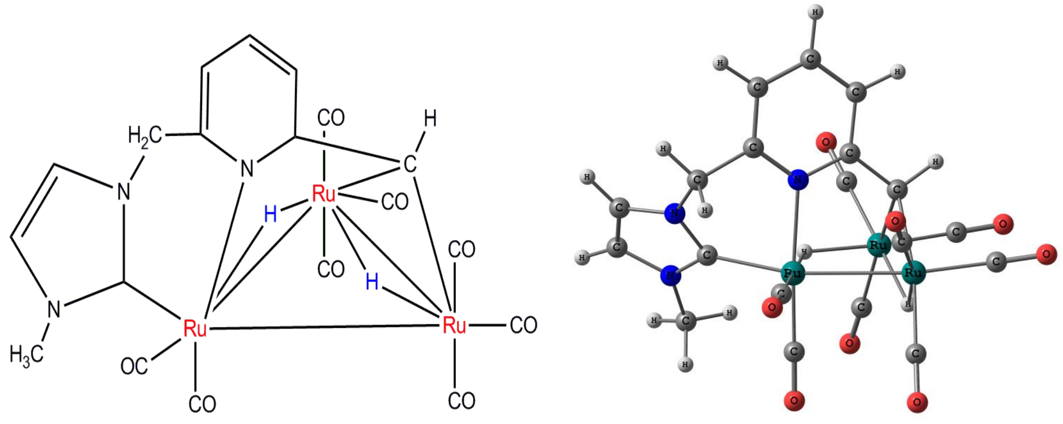
Introduction

In the last few years, the topological analysis of the electron density, within the framework of the quantum theory of atoms in molecules, developed by Bader and his co-workers [1], has become a powerful tool for exploring various interactions in a molecular system. Within this framework, the link between bonding modes and topological properties of the electron density and its Laplacian has been fully achieved for light atom molecules [2]. However, such links cannot be straightforwardly extended to organometallic compounds because bonds to a transition metal display a different and much narrower spectrum of topological indexes [3]. In addition, the nature of the bonding interactions between transition-metal atoms are not completely understood yet and much argue is still occurring on its actual presence, role and mechanism. Unfortunately, few studies have been published to date on the topology of the electron density in cluster compounds with three or more metal–metal interactions between transition-metal atoms. Therefore, more QTAIM studies on this class of complexes are desirable in order to shed additional light on the relationship between metal-metal bonds and the topology of their associated electron density.

In recent years, the interest of the chemical community in the NHC-derived chemistry of transition-metal cluster and their catalytic properties has led many researchers to include polydentate NHCs ligands in their investigations [4]. Recently, the number of papers published dealing with bi-, tri-, or polydentate ligands containing at least one NHC moiety [5].

A few of AIM theoretical analysis of bonding NHC-metal complexes have been published to date, couple on Cr-NHC [6] and one on trinuclear Ru-NHC[7] compounds, which shown that π-electron delocalisation within the five-membered ring is not completely but slightly hindered instead.

This paper reports the results of a QTAIM topological analysis of the electron density in the Picolyl N-Heterocyclic Carbene Triruthenium cluster $[Ru_3(\mu\text{-}H)_2(\mu^3\text{-}\kappa^3C_2,NHCpyCH_2ImMe)(CO)_8]$ (3-methylimidazol-2- ylidene)[8], **Figure 1**, to obtain a deeper insight into the nature of the chemical bonding.



(a) (b)

Fig. 1: (a) Schematic Structure and (b) Geometry Optimization Structure Of $[Ru_3(\mu\text{-}H)_2(\mu^3\text{-}\kappa^3C_2,NHCpyCH_2ImMe)(CO)_8]$

However, this cluster has been chosen since, firstly, no previous QTAIM studies on Picolyl N-Heterocyclic Carbene Triruthenium cluster has been hitherto reported. Secondly, this particular cluster contains two hydride bridged Ru-Ru edges and a face-capping ligands with two types of Ru-C bonds (**Figure 1**), this allowing interesting comparisons between the topological properties of related but different atom–atom interactions, within the same molecule, and $Ru\text{-}C_{NHC}$ versus other Ru-C interactions.

Computational Details

The X-ray diffraction structures of compounds 1–2 were used as starting points for geometry optimization, which were performed with the GAUSSIAN09[9] package at the DFT level of theory, using PBE1PBE[10] functional. The all electron 6-31G(d,p)[11] basis set were employed for H, C, N and O atoms. The SDD[12] effective core potential (ECP) basis set was used for Ru atoms. An extra set of f-polarisation functions was added to the Ru (αf = 1.235)[13]. The AIM results described in this work corresponding to calculations performed with the PBE1PBE/WTBS[14]/6-31G(d, P) model. These calculations were carried out with the AIM2000 program [15].

Results and Discussions

Topological Properties of the Electron Density: The main feature of atoms in molecules (AIM) theory of Bader [1], with the AIM2000 program package, is that the topology of electron density contains information about the bonding situation. Specifically, the topology of the electron density ρ(r) at the critical points, i.e. the points in space at which the gradient of the density vanishes ($\nabla\rho$ (r) = 0), carries important information about the covalency and multiplicity of the bond. A critical point that is characterised by two negative curvatures (maximum) and one positive curvature (minimum), labelled as (3, -1), is referred to as a bond critical point (BCP) and is considered to be indicative of the presence of chemical bond. A ring critical point (RCP), in contrast, has one negative curvature and two positive curvatures, and is labelled as (3, +1). Some structures necessarily contain other critical point of the density: the (3, +3) is produced inside cages (cage critical point, CCP). A chemical bond between two atoms is characterised by a line of maximum electron density (the bond path, bp) which links the two atomic nuclei and intersects an interatomic surface at the bond critical point. Based on these definitions, a chemical structure is simply the topological graph produced by the bond paths and the maxima of the electron density. The image shown in (**Figure 2**) was obtained by applying the QTAIM approach to dihydride ruthenium cluster.

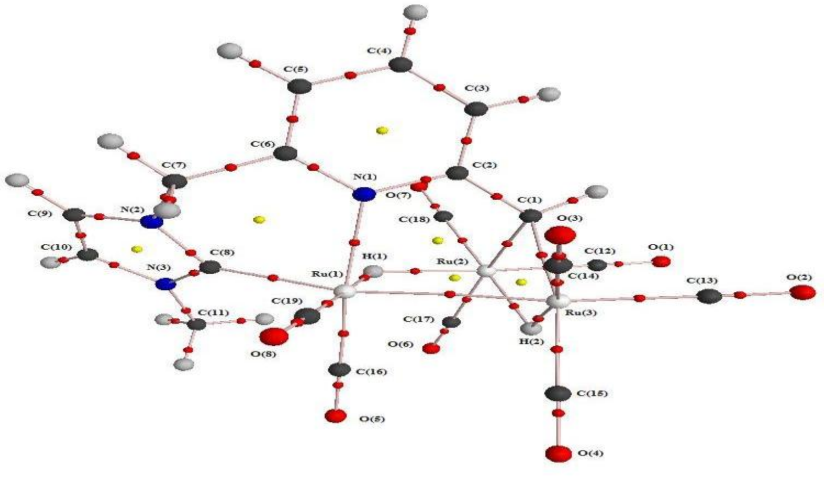


Fig. 2: Molecular Structure Of Dihydride Ruthenium Cluster, Showing The Bond Paths (Gray Lines) And The Bond (Small Red Circles) And Ring (Yellow Circles) Critical Points.

From the molecular graph, one can easily observe bond and ring critical points, together with the bond paths that connect the bonded atoms through their corresponding bond critical points. The bcp's and bp's for the Ru-C, Ru-H, C-O, C-N, C-C, and C-H bonds were clearly found. Interestingly, only bcp and bp associated to Ru(1) and Ru(3) bonds was found science no bcp's or bp's were observed between Ru(1) and Ru(2) or between Ru(2) and Ru(3). Six rcp's were clearly observed, corresponding to the C(8)-N(2)-C(9)-C(10)-N(3), Ru(1)-N(1)-C(2)-C(1)-Ru(3), Ru(1)-H(1)-Ru(2)-H(2)-Ru(3), Ru(2)-C(1)-Ru(3)-H(2), N(1)-C(2)-C(3)-C(4)-C(5)-C(6) and Ru(1)-N(1)-C(6)-C(7)-N(2)-C(8) rings.

A gradient trajectory map of the total electron density in the Ru(1)-Ru(2)-Ru(3) plane with the atomic basins are depicted in (**Figure 3**). It shows that the bp and bcp between Ru(1) and Ru(3) together with the atomic basins for these and other atoms located in the same plane. The bp's and bcp's found between the hydride ligand H(1) and Ru(1) and Ru(2) metal atoms located in these plane can also be observed. The atomic basins, bcp's and bp's of two CO ligands, located in the same plane, are also visible in the plot. A projection for the position of the H(2) hydride ligand on this plane is also shown.

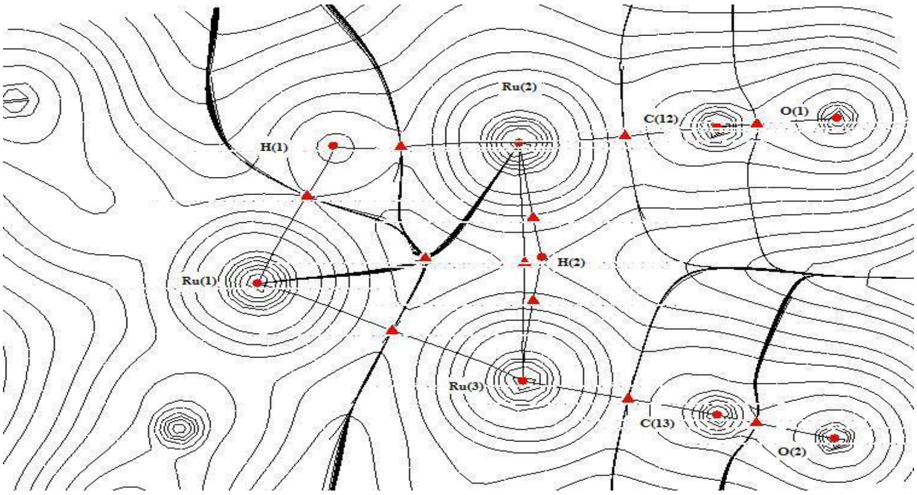


Fig. 3: Gradient Trajectories Mapped On A Total Electron Density Plot In The Ru(1)-Ru(2)-Ru(3) Plane, Showing The Atomic Basins, bp's and bcp's.

A gradient trajectory map of the total electron density in the plane spanned by the Picolyl ligand, showing the bp's, bcp's and rcp associated with this ligand, is depicted in (**Figure 4**). The bcp's and bp's, found between Ru(1) and the Picolyl ligand N(1) atom, located in this plane can also be observed. The C(1) and C(7) are also located on the picolyl ligand plane, and it is bonded to C(2) and C(6) respectively in Picolyl group.

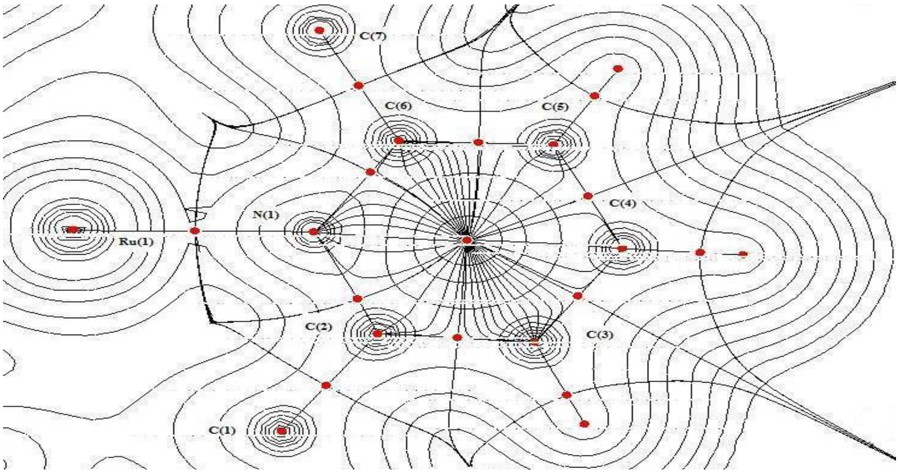


Fig. 4: Gradient trajectories mapped on a total electron density plot in the Picolyl ligand plane, showing the atom basins, bp's and bcp's.

(**Figure 5**) displays a gradient trajectory map of the total electron density in the plane spanned by the CH_2ImMe ligand showing the bp's, bcp's and rcp associated with this ligand. Both bcp's and bp's are found between Ru(1) with the NHC ligand C(3) atom. In this figure, the C(7) and C(11) are also located on the NHC ligand plane, and it is bonded to N(2) and N(3) respectively in NHC group.

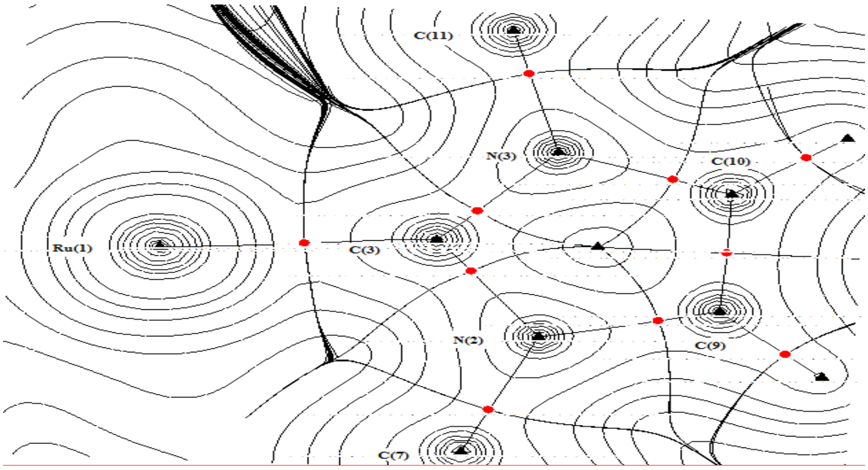


Fig. 5: Gradient Trajectories Mapped On A Total Electron Density Plot In The NHC Ligand Plane, Showing The Atom Basins, bp's and bcp's.

Atoms in Molecules Analysis: In Bader's topological QTAIM analysis, the nature of bonding in molecules is analyzed in terms of the properties of electron density and its derivatives. Among these derivatives, the Laplacian of the electron density $\nabla^2\rho(r)$ is a very useful source of information, which links between two important quantities, the kinetic energy density ***G(r)*** (everywhere positive) and the potential energy density ***V(r)*** (everywhere negative), in a local virial theorem:-

$$\frac{1}{4}\nabla^2\rho(r) = 2G(r) + V(r)$$

The sign of $\nabla^2\rho(r)$ at a BCP is determined by which energy is in excess over the viral average of 2:1 of kinetics to potential energy. In covalent interactions, electronic charge at the BCP is compressed over its average distribution. The potential energy density is dominant, and $\nabla^2\rho(r)$ is negative value at the BCP. On the other hand, in electrostatic interactions the charge density is expanded relative to its average distribution. Therefore, $\nabla^2\rho(r)$ is positive value at the BCP, and the kinetic energy density is dominant. Apart from this, the electronic energy density, $H(r)$, as :-

$$H(r) = G(r) + V(r)$$

This equation can be used to compare the kinetic and potential energy densities on an equal footing. For all interactions with significant sharing of electrons, $H(r)$ is negative at the bcp, and its absolute value reflects covalent character of the interaction. On the other hand, the ellipticity $\varepsilon(r)$ at bcp is a measure of π-character of the bonding: values close to zero indicate a cylindrically symmetric bond, while deviations away from zero indicate increasing π-character. For reference, the ellipticity ε values for ethane and ethene are 0.0 and ~ 0.3, respectively [2, 16-20].

Table 1: Selected Topological Parameters For Dihydride Triruthenium Cluster.

Bond	ρ_b(eÅ^{-3})^a	$\nabla^2\rho_b$(eÅ^{-5})^b	H_b(he^{-1})^c	G_b(he^{-1})^d	ε_b^e
Ru(1)-Ru(3)	0.437	0.668	-0.248	0.080	0.025
Ru-H*	0.822	1.925	-0.735	0.254	0.056
Ru-CO*	1.510	5.360	-2.005	0.662	0.035
Ru(1)-N(1)	0.789	4.000	-1.070	0.070	0.075
Ru(1)-C(8)	1.140	3.320	-1.236	0.404	0.058
Ru(2)-C(1)	1.009	1.800	-0.790	0.362	0.035
Ru(3)-C(1)	1.035	2.068	-0.880	0.370	0.058
C-O*	4.532	11.540	-10.326	7.438	0.001
C(6)-C(7)	2.610	-6.440	-0.570	2.190	0.048
C(7)-N(2)	2.630	-7.360	-1.670	3.520	0.047
Picolyl-ligand					
C(2)-C(3)	3.060	-8.320	-0.928	3.010	0.186
C(3)-C(4)	3.190	-8.920	-1.060	3.290	0.216
C(4)-C(5)	3.100	-8.520	-0.970	3.110	0.183
C(5)-C(6)	3.160	-8.760	-1.060	3.260	0.254
C(2)-N(1)	3.220	-7.760	-3.300	5.250	0.040
C(6)-N(1)	3.340	-8.240	-3.440	5.510	0.135
NHC-ligand					
C(8)-N(2)	3.170	5.420	-3.840	5.200	0.052
C(9)-N(2)	3.010	-6.320	-3.170	4.750	0.168
C(8)-N(3)	3.170	5.740	-3.750	5.190	0.065
C(10)-N(3)	3.020	-6.716	-3.090	4.770	0.169
C(9)-C(10)	3.350	-9.600	-1.250	3.660	0.407

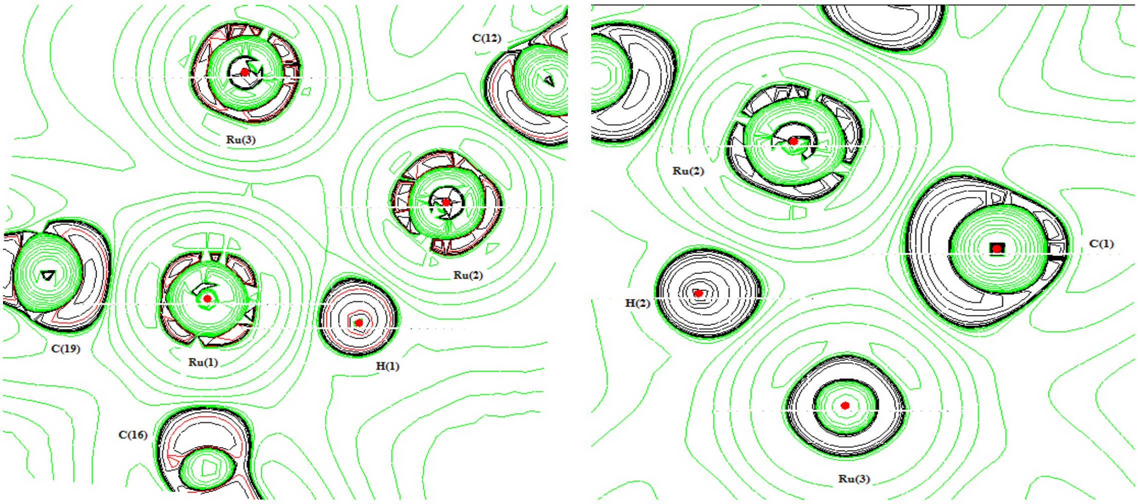
(a) Electron density , (b) Laplacian of the electron density , (c) Total energy density ratio, (d) Kinetic energy density ratio and (e) Ellipticity at the bcp. * Average values

Ru_3H_2 Interactions: In the framework of QTAIM we calculated some topological properties for selected bonds of dihydride triruthenium cluster molecule (**Table 1**). Here, the Ru(1)-Ru(3) interaction is a typical open-shell metal-metal interaction, intermediate between pure covalent and pure ionic bonds between non metal atoms, with the value of the electron density (0.437 e Å^{-3} at the bcp), the positive but small value of the Laplacian (0.668 eÅ^{-5}), the small negative value of H_b (-0.248 he^{-1}) and the positive but less than unity value of G_b (0.08 he^{-1}). These values are comparable to those previously found for ruthenium compounds, from both experimental and theoretical electron densities, such as the Ru-Ru bonds in [Ru_2-(formamidinate)$_4$] [21], [$Ru_3(CO)_{12}$][22] and [$Ru_3(\mu\text{-}H)_2(\mu3\text{-}MeImCH)(CO)_9$][23]. For instance, in the latter compound, the electron density $\boldsymbol{\rho_b}$, laplacian $\nabla^2\rho_b$, kinetic energy $\boldsymbol{G_b}$ and ellipticity $\boldsymbol{\varepsilon_b}$ values for unabridged Ru-Ru bond are 0.292 eÅ^{-3}, 0.803 eÅ^{-5}, -0.463 he^{-1} and 0.036 respectively. It is interesting to note that there is no bcp's or direct bp's were found between the hydride-bridged Ru(1) and Ru(2) or Ru(2) and Ru(3) interactions. Unusually, the Ru(1)-Ru(3) edge of cluster, although it is not bridged by a hydride ligand, is bridged by the

Picolyl ligand, but the N(1)-C(2)-C(1) bridge does not seem to favour the electronic communication between Ru(1) and Ru(3) atoms (**Figure 2**).

An average value of 0.822 $eÅ^{-3}$ and 1.925 $eÅ^{-5}$ for the electron density and Laplacian for the Ru-H bonds indicates that the strength of these bonds is comparable to that of pure covalent single bonds between nonmetal atoms [12]. Additionally, the ellipticity ε(Ru-H) for ruthenium cluster (0.056) is close to ε(Ru-H) for $[Ru3(\mu\text{-}H)_2(\mu3\text{-}MeImCH)(CO)_9]$ (0.086)[23]. No bending was found in the bond paths of Ru(1)-Ru(3) or Ru-H interactions. These facts, added to the very low ellipticities of these bonds, which are related to the bond symmetry, allow us to conclude that Ru(1)-Ru(3) and Ru-H interactions in ruthenium cluster are nearly straight bond paths.

The Ru-Ru and Ru-H interactions in the Ru_3H_2 part of the cluster may be also be analyzed by looking at the Laplacian of the electron density in the Ru(1)-Ru(3)-Ru(2)-H(1) (Figure 5-a) and Ru(2)-C(1)-Ru(3)-H(2) (**Figure 5-b**) planes of the molecule. Valence shell charge concentration (VSCC) of both bridging hydrogen H(1) and H(2) atoms are polarized toward the midpoint of the Ru(1)-Ru(2) and Ru(2)-Ru(3) edges, respectively. These polarizations are small, giving slightly more positive values for the Laplacian in the four Ru-H bcp's (1.925 $eÅ^{-5}$) than those expected in the absence of such polarization.



(a) **(b)**

Fig. 1: Laplacian Of The Electron Density In The (a) Ru(1)-Ru(3)-Ru(2)-H(1) and (b) Ru(2)-C(1)-Ru(3)-H(2) Plane Of Ruthenium Cluster.

These graphs also show that the VSCCs for both bridging C(1) and carbonyl C atoms distorted towards their bonded Ru atoms. The former has a similar situation to that previously observed for the C atoms coordinated to NHC ligand bridging two Ru atoms[9]. Then, by summarizing all these features, the multicenter (5c-6e) interaction is likely to be present in the Ru_3H_2 part of this cluster.

Ru-CO Interactions: For the Ru-CO interactions of ruthenium cluster, the mean values given in table 1 for the $\rho_{(b)}$ value close to 1.51 $Åe^{-3}$, higher than those of metal-metal bonds but lower than those of pure covalent single bonds between nonmetal atoms, a large positive value (5.3 $Åe^{-5}$) of $\nabla^2\rho_{(b)}$, a value of around 0.662 he^{-1} for G_b, and a small negative value for $H_{(b)}$ (-2.0 he^{-1}), are similar to those found in the literature for other metal-CO bonds [13-16]. In addition, a formal bond order of ruthenium cluster may be inferred from the ellipticity value, ε(Ru-C) (0.035), also shown in **Table 1**. Detecting the π-backdonation from the metal to the CO ligand is difficult because the cylindrical symmetry of the density along the M-CO bond path hides any trace of preferential accumulation planes.

Ru-Picolyl ligand interaction: Regarding the bonds between Ru atoms and the N-Picolyl ligand, Ru(1)-N(1), it is quite interest to compare with Ru(1)-C(8). The former have smaller value of electron density, high values of the Laplacian and slightly greater ellipticity as depicted in (**Table 1**). These results indicate that the Ru(1)-N(1) has slightly greater π-character than the Ru(1)-C(8) bond. The highest value of electron density, the most negative value for the Laplacian and ellipticity for C-C and C-N bonds in Picolyl ligand are consistent with a formal double bond with a certain degree of delocalization. In (**Figure 6**), it is clearly that the VSCCs of N(1) is distorted towered the Ru(1) atom to which it is attached.

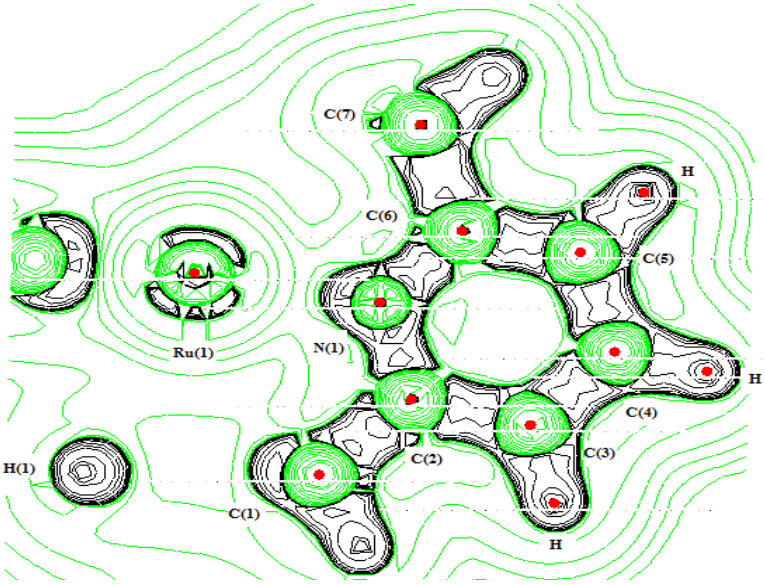


Fig. 6: Laplacian Of The Electron Density In The Picolyl Ligand Plane

Ru- NHC Ligand Interactions: The values of the topological indexes for the Ru(1) atom and the carbine C(8) atom of the face capping of NHC ligand, included in (**Table 1**), are similar to these found for almost equivalent Ru(2)-C(1) and Ru(3)-C(1) bonds, which involve the sp^3-hybridized C(1) atom. These values are also comparable to those obtained from theoretical calculation for the Ru-$C_{carbene}$ bonds of the complexes $[Ru_3(\mu\text{-}H)_2(\mu^3\text{-}MeImCH)(CO)_9]$[23] and from both experimental and theoretical electron densities for the Cr-$C_{carbene}$ bonds of the complexes $[Cr\{C\text{-}(NH_2)CH_3\}(CO)_5]$[15], $[Cr(Me_2Im)(CO)_5]$[17] and the Co-$C_{carbene}$ bond of $[Co_2(\mu\text{-}\eta^1\text{-}C_4O_2H_2)(\mu\text{-}CO)(CO)_6]$[16]. For instance, the ellipticity at the bcp of the Ru-$C_{carbene}$ bond of $[Ru_3(\mu\text{-}H)_2(\mu^3\text{-}MeImCH)(CO)_9]$ and Cr-Ccarbene bond of $[Cr(Me_2Im)(CO)_5]$, which has the same NHC ligand as ruthenium cluster, was found to be between 0.04-0.08 (calculated) and 0.08 (experimental), very close to the value found for ruthenium cluster (0.058), whereas the Laplacian (between 6.0-7.1 and 6.7 e Å^{-5} for the Cr complex vs 3.3 e Å^{-5} for ruthenium cluster) and $\rho_{(b)}$ (0.52-0.75 vs 1.14 Å e^{-3}) are not so close for both systems. These values suggest that the strength of these bonds is comparable to those of pure covalent single bonds between non metal atoms [12]. As expected the (**Figures 5-b and 7**) show that the VSCCs of C(8) and C(3) atoms are distorted toward the ruthenium atoms to which they are attached. Regarding the topological properties of the bonding between the atoms of the NHC ligand are presented in **Table 1** and may be graphically visualized in (**Figures 4 and 7**). The gradient trajectory map shows the bcp's and bp's found between the atoms of the NHC ligand as well as their atomic basins. As expected for polar bonds, with the only exception of the C(9)-C(10) bond, the positions of the bcp's are not symmetrical but shifted toward the less electronegative atom.

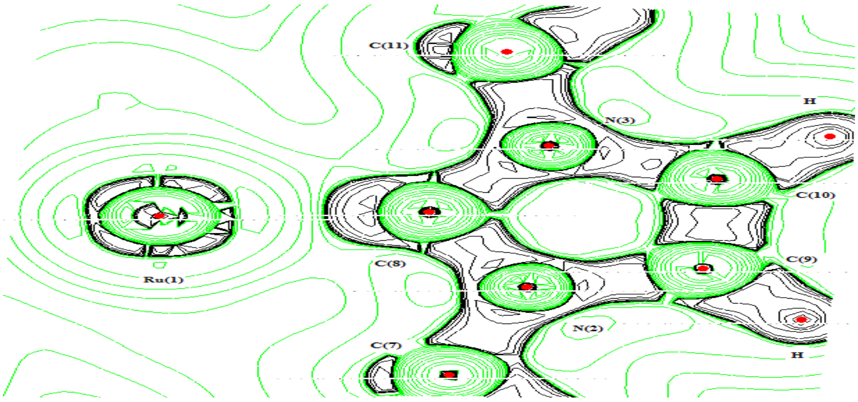


Fig. 7: Laplacian Of The Electron Density In The NHC Ligand Plane

The topological parameters values of the NHC ligand bonds are typical for covalent bonds between non-metal atoms with some degree of delocalization.[16] In this context, we considered it quite interesting to compare the topological parameters of N(2)-C(8) and N(3)-C(8) bonds with those of the N(2)-C(9) and N(3)-C(10) bonds. The former have high values of the electron density at the bcp, moderate values of the laplacian and smaller value of ellipticity. These results indicate that the N(2)-C(9) and N(3)-C(10) bonds have a slightly greater character of double bonds than the N(2)-C(8) and N(3)-C(8) bonds. These facts support the proposal that the unsaturation of the carbene C(8) atom of an NHC ligand is alleviated by π-donation of electron density from the filled p-π orbitals of the N(2) and N(3) atoms to the empty p-π orbital of the C(8) carbene atom [21]. The highest electron density value for the NHC ligand of ruthenium cluster belongs to the C(9)-C(10) bond, which also possesses the highest value of ellipticity and the most negative value for the Laplacian at bond critical points, values that are consistent with the presence of double bond character with a certain degree of delocalization within the NHC five-membered ring. On the contrary, the topological properties of the N(2)-C(7) bond are prototypical for a formal single covalent bond.

Conclusions

A number of topological parameters of the electron density for the Picolyl-NHC Triruthenium cluster $[Ru_3(\mu\text{-}H)_2(\mu^3\text{-}\kappa^3C_2,NHCpyCH_2ImMe)(CO)_8]$ have been calculated under the prospective of the QTAIM approach. Although these results recognizes the existence of a bond path in only one of the Ru-Ru edges of ruthenium cluster i.e., that unbridged by the hydride ligands, Ru(1)-Ru(3), the topological properties of the two hydride-bridged Ru-Ru edges suggest a delocalized kind of interaction in the central part of the molecule. Thus, a mlticenter (5c-6e) interaction involving the Ru_3H_2 core of the molecule here proposed.

The topological parameters calculated for the three existing Ru-C bonds between ruthenium atoms with Picolyl and NHC ligands are similar, and they confirm that these interactions are pure σ-bonds. The analysis of the topological parameters of the Picolyl ligand bonds confirms the existence of π-electron delocalization within the six-membered ring. Also, the calculated topological parameters for NHC bonds indicate the presence of some π-electron delocalization within the five-membered ring as well as the existence of some double-bond character in the interaction of the carbene C atom with the adjacent N atoms. Thus, the AIM theory supports the proposal that the unsaturation of the carbene C atom of an imidazol-2-ylidene-type NHC ligand is alleviated by donation of electron density from the filled p-π orbitals of the N atoms to the empty p-π orbital of the carbene carbon.

Finally, to the best of our knowledge, no previous studies dealing with the bonding interaction between Picolyl and NHC ligands and triruthenium cluster have appeared in the literature. This work contributes to shed more light on these areas.

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