

Theoretical Investigation of a Di-Rhenium Bis (Triphenylphosphine) Carbonyl Cluster Containing Sulfuric and Hydrido Bridge: QTAIM analysis

Nadia Ezzat Al-kirbasee¹, Manal A. Mohammed Al-Jabery², Murtadha Hussein Hasan³, Ahlam Hussein Hassan^{4*} and Muhsen A. Muhsen Al-Ibadi⁴

¹Department of Chemistry, College of Education for Women, University of Kufa, Iraq.

²Department of Basic Medical Science, College of Dentistry, University of Kerbala, Iraq.

³Department of Physics, College of Science, University of Kufa, Iraq.

⁴Department of Chemistry, College of Science, University of Kufa, Iraq.

**Corresponding author: ahlamh.aitufaily@student.uokufa.edu.iq*

Abstract

Scientists used the quantum theory of atoms in molecules (QTAIM) to calculate and interpret various electron density parameters for a di-rhenium bis(triphenylphosphine) carbonyl cluster containing sulfuric and hydrido bridge: $[\text{Re}_2(\text{CO})_6(\mu\text{-S})(\mu\text{-H})(\text{PPh}_3)_2]$. They compared data from previous organometallic system studies to the bond critical points. The researchers could compare the topological processes of various atom-atom interactions based on these findings.

The calculations showed that there were no bond critical points or identical bond paths between Re-Re in the core of the cluster. The electron density distribution was affected by the position of bridging hydride and sulfur atoms coordinated to Re-Re, which significantly affected the bonds between these transition metal atoms. However, the calculations did confirm the presence of a 6c–8e bonding interaction delocalized over HRe_2SP_2 in the cluster.

The scientists found that the Re-H and Re-S bonds in this cluster exhibited typical closed-shell interactions, with small values for $\rho(\text{b})$ and Laplacian $\nabla^2\rho(\text{b})$ above zero and small positive values for total energy density $H(\text{b})$. Similarly, the bond interactions between phosphine metal atoms and the C atoms of the phenyl ring ligands showed properties similar to open-shell interactions in the QTAIM classification.

Keywords: AIM approach, Bonding analysis for the di-rhenium cluster, DFT calculation, and Topological properties.

Introduction

The investigation of transition metal clusters holds significant importance in the realm of organometallic chemistry as they play a crucial role in the activation of inert substances, thereby facilitating synthetic reactions. Over the past decade, considerable attention has been directed towards rhenium organometallic compounds due to their potential practical applications, including the development of novel materials, optically responsive materials, molecular sensors, radiopharmaceuticals, medical imaging, biological assaying, and biomarking [1-3].

In order to comprehend the bonding within organometallic systems, the Quantum theory of atoms in molecules (QTAIM) serves as a vital approach [4,5]. This methodology enables the characterization of chemical bonds by identifying bond critical points (bcp) along atomic interaction lines in an equilibrium geometry known as the bond bath [6-8]. Topological parameters, such as electron density, Laplacian, and electronic energy density calculated at the bcp, offer valuable insights into the bonding nature of organometallic systems [9,10].

This study specifically focuses on examining the bonding scenarios among various atomic interactions, including Re-Re, Re-H bridged, Re-S, and Re-P bonds within the dirhenium cluster $[\text{Re}_2(\text{CO})_6(\mu\text{-S})(\mu\text{-H})(\text{PPh}_3)_2]^{11}$. This particular complex has been chosen for investigation as there have been no prior QTAIM studies conducted on a diRhenium cluster compound containing bridging hydride and sulfur ligands. Consequently, studying this compound will allow for a comprehensive comparison of

diverse topological properties associated with different interactions involving metal-metal and metal-ligand bonds.

Theoretical Methods

The Rhenium cluster's structure in the gas phase was optimized through Density Functional Theory (DFT) calculations. Frequency calculations were performed to confirm that the structure represents a minimum on the potential energy surface. The Gaussian 09 program [12] was employed, utilizing the PBE1PBE functional [13] along with the 6-31G(d,p) [14] basis set for S, P, H, C, and O atoms. For Re atoms, the SDD [15] effective core potential (ECP) basis set was used. To compute the topological parameters, the AIM2000 program package was employed, with the PBE1PBE /WTBS [16] level of theory for Re and the 6-31G (d, P) basis set for the other atoms [17].

Results and Discussion.

The QTAIM method, utilizing the AIM2000 program, plays a pivotal role in determining the structures and bonding scenarios of molecules and nanoclusters through the calculation of the metal-metal bond critical point (rc) [7,18,19]. The critical points provide valuable insights into various types of bonding, such as open and closed-shell interactions. A bond critical point (bcp) (labeled as (3,-1)) signifies the existence of bonding, characterized by a decrease in electron density in two directions and concentration in the third direction. Conversely, a ring critical point (rcp) (labeled as (3,+1)) exhibits a decrease in electron density in one direction and an increase in two directions [20,21]. Furthermore, certain structures possess a cage critical point (ccp) (labeled as (3,+3)), which entails an increase in charge density in all three directions. As mentioned earlier, a chemical bond within the compound is identified by a bond path that connects the two nuclei, passing through their corresponding bond critical point [22,23]. Based on these descriptions, the chemical structure of the system is represented

by a topological graph generated from the network of bond paths and the maxima of charge densities. In the cluster's graph (Figure 2), we observe a collection of bond critical points, ring critical points, and the bond paths that bind the nuclei.

Specifically, bond critical points and bond paths are present for the Re-H, Re-P, and Re-S bonds. Notably, it is crucial to highlight the absence of direct bonding between the nuclei of the transition metal atoms in the cluster, as evidenced by the lack of bond critical points and bond paths connecting them. Additionally, multiple ring critical points were identified.

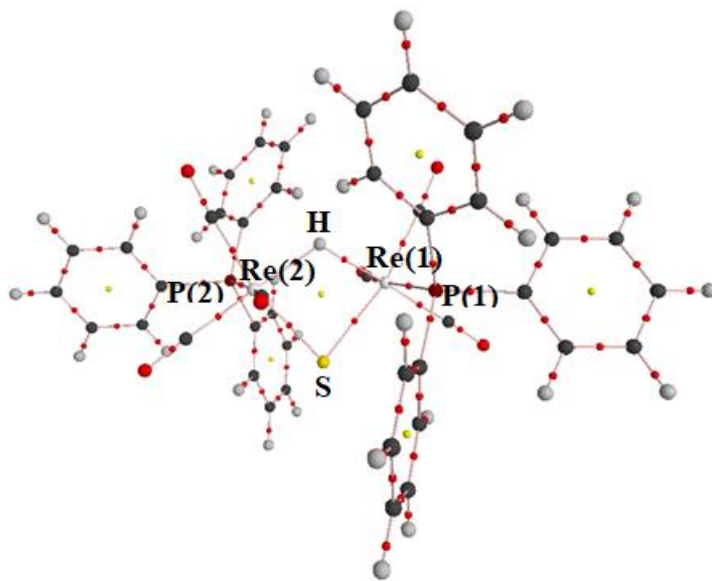


Figure. 2: The Molecular graph of the dirhenium cluster 1 is represented by a graph that highlights gray lines (bond paths BPs) with small red circles (bond critical points BCPs between two atoms), and yellow circles (ring critical points RCPs).

A gradient trajectory map, shown in Figure 3, shows both Re-H-Re-S planes with their atomic basins, but no such corresponding bcps and bps were found between Re-Re. Also, the bond critical points and bond paths were found between H with Re(1) and

Re(2) metals, S with Re(1) and Re (2) metal, Re(1) with P(1) and Re (2) with P(2), atoms can be observed.

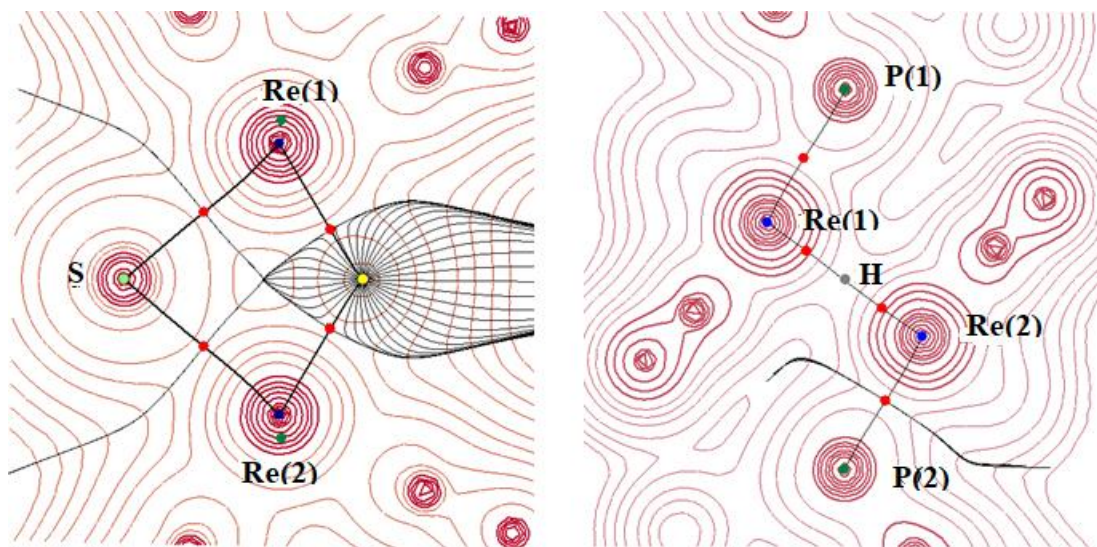


Figure. 2: Gradient trajectories in the P(1)-Re(1)-H-S-Re(2)-P(2) plane mapped on an electron density plot, with atomic basins (BP's) and (BCP's), are indicated.

The nature of the interactions in the core:

The interactions within the core can be classified based on the sign of $(\nabla^2\rho_b)$ at a bond critical point, which provides insights into shared shell or closed shell interactions between atoms. A negative sign of $(\nabla^2\rho_b)$ indicates the sharing of electrons by both nuclei, indicating covalent interactions. On the other hand, a positive sign of $(\nabla^2\rho_b)$ suggests concentrated electrons in each atom, representing closed shell interactions such as ionic bonds. Moreover, additional information about the bonding can be obtained from the sign and values of $G(r)$, $V(r)$, and $H(r)$ [10,24,25]. The topological properties calculated for the cluster are summarized in Table 1.

Table. 1: The topological parameters at BCPs [(ρ_b) electron density, ($\nabla^2\rho_b$) Laplacian, (H_b) ratio of total energy density, (G_b) ratio of kinetic energy density, (V_b) virial energy density, and (ϵ_b) ellipticity].

Bond	$\rho_b(\text{e}\text{\AA}^{-3})$	$\nabla^2\rho_b(\text{e}\text{\AA}^{-5})$	$G_b(\text{he}^{-1})$	$H_b(\text{he}^{-1})$	$V_b(\text{he}^{-1})$	ϵ_b
(Re1-H84)	0.069	0.1892	0.064	-0.016	-0.080	0.024
(Re2-H84)	0.069	0.1888	0.064	-0.016	-0.080	0.020
(Re1-S)	0.069	0.1924	0.062	-0.014	-0.076	0.119
(Re2-S)	0.069	0.1924	0.062	-0.014	-0.076	0.118
(Re1-P)	0.055	0.156	0.048	-0.009	-0.057	0.037
(Re2-P)	0.055	0.156	0.048	-0.009	-0.057	0.062

Regarding Re-Re interactions, a noteworthy observation is the absence of bond critical points or bond paths between the bridged transition metal atoms, which are connected by a hydride and N groups. This indicates the lack of localized electron density between the transition metal atoms. According to the QTAIM theory [9], the presence of bond critical points between atoms indicates the existence of bonding [10,11]. Consequently, we can conclude that there is no direct bonding between any pair of transition metal nuclei in the studied cluster [12]. The strong ligand bridging interaction has disrupted the topological Re-Re bonding. However, bond critical points between metal atoms have been observed in unsupported M-M interactions, such as $\text{Co}_2(\text{CO})_6(\text{Asph}_3)_2$ [26] and $\text{Mn}_2(\text{CO})_{10}$ [27], as well as in cases of strong ligand bridging interactions, such as $[\text{Mo}_3(\mu_2\text{-S})_3(\mu_2\text{-S})\text{Cl}_3(\text{PH}_3)_6]^+$ [28].

In the case of Re-H interactions, the electron density values (as shown in Table 1) are significantly above zero ($0.069 \text{ e } \text{\AA}^{-3}$), while the Laplacian values are positive (ranging from 0.1888 to $0.1892 \text{ e } \text{\AA}^{-5}$). As discussed in the literature [29], the negative values of $H(r)$ (-0.016 h e^{-1}) indicate characteristics typical of open-shell interactions [29]. Additionally, the calculated AIM ellipticities of the Re-H bonds are slightly greater than zero, suggesting a nearly linear bonding between the transition metals and the hydrogen atom.

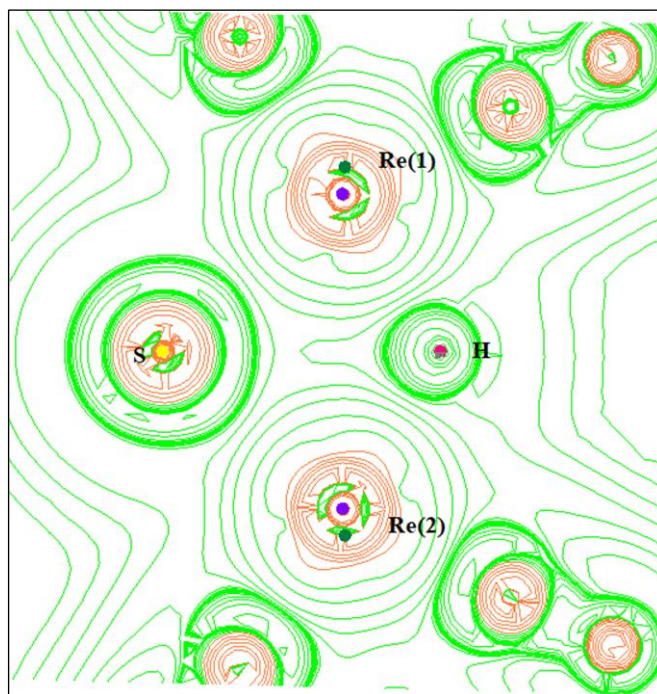


Figure. 5: Laplacian map showing the electron density of the P(1)-Re(1)-H-S-Re(2)-P(2) plane in the trinuclear cluster 1.

The bonding characteristics of the core portion (Re₂HS) can be examined by analyzing the contour plot presented in Figure 4. This graphical representation of the Laplacian offers insights into the Re-Re, Re-H, and Re-S interactions. The valence shell charge concentration of Re atoms is slightly directed towards the bridged Re-Re atoms, while the bridging hydrogen ligands exhibit a shift in valence shell charge concentration towards the interatomic surface of the transition metal edges, similar to previous observations for other bridging hydrogen atoms.

An interesting comparison can be made between the topological properties of the Re-S bonds and the Re-H bonds. As indicated in Table 1, the topological property values for Re-S bonds are identical. The calculated data reveals that Re-S bonds exhibit open-shell topological properties, characterized by a low positive $\nabla^2\rho(b)$, a low value for $\rho(b)$ above zero, and a value close to zero for $H(b)$. Remarkably, the bridging S ligands demonstrate topological parameter values similar to those of the bridging H ligands, including the electron density ($0.069 \text{ e } \text{\AA}^{-3}$), the Laplacian (0.1924 vs. $0.1888 \text{ e } \text{\AA}^{-5}$), and the kinetic energy density ratio (0.062 vs. 0.064 he^{-1}), with some differences in ellipticity (0.119 vs. 0.024). Furthermore, the topological local properties of the bridging H and S ligands closely resemble those reported in the literature for other bridging ligands, such as bridging CO, H, and CH ligands in [FeCo(CO)₈] [30], [Cr₂(μ -H)(CO)₁₀] [31], and [Ru₃(μ -H)₂(μ ₃-MeImCH)(CO)₉] [32], respectively.

In terms of the Re-P bonds, the topological property values are also equal. These bonds exhibit typical characteristics of closed-shell interactions, with a large value for $\rho(b)$ above zero ($0.055 \text{ e } \text{\AA}^{-3}$), a positive value for $\nabla^2\rho(b)$ ($0.156 \text{ e } \text{\AA}^{-5}$), and a significantly negative $H(b)$ value (-0.009 he^{-1}). These topological properties align with those reported in the literature [29] for Re-P bonds.

Conclusions

To investigate bonding in the trinuclear heterometallic tetrahydrido $[\text{Re}_2(\text{CO})_6(\mu\text{-S})(\mu\text{-H})(\text{PPh}_3)_2]$, the Quantum Theory of Atoms-in-Molecules (QTAIM) approach is used.

The metal-ligand and metal-metal bond critical points (BCPs) properties the electron density (ρ_b), Laplacian ($\nabla^2\rho_b$), total energy density (H_b), kinetic energy density (G_b), virial energy density (V_b), and ellipticity (ϵ_b).

Most intriguingly, the presence of bridging hydride ligands affects the electron density distribution of metal...metal interactions. No direct bonding has been observed due to the absence of BCPs and their BPs between these transition metals. The topological properties of the Re-H and Re-S bonds indicate that they are all typical open-shell bonds.

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