Investigation of Chemical Bonds of the Interactions Cation-π in Ruthenophanes

Sergio Emanuel Galembeck (PQ) and Renato Pereira Orenha (PG)

Departamento de Química, FFCLRP, Universidade de São Paulo, 14040-901, Ribeirão Preto - SP

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INTRODUCTION

The interaction between the cyclophanes and the metal cations is extremely relevant due, for example, be related the biomimetic catalysis, selectivity and transportation of ions, and molecular recognition.[1]

METHODS

From of optimized geometry of $[Ru(\eta^6\text{-}C_{16}H_{16})(NH_3)_3]^{2+}$ with the BP86/def2-TZVP computational model containing ECP-28 for the Ru atom, the NBO, QTAIM, IQA and ELF methods were used to the analysis of electron density.

RESULTS AND DISCUSSION

In the first place, the geometry parameters of compound studied (Fig. 1) shows that the most nearly carbon atoms of Ru are C(10) and C(14), followed by C(11) and C(13) (Fig. 1). Already, C(9) and C(12) has the longest r(Ru-C) bond lengths.

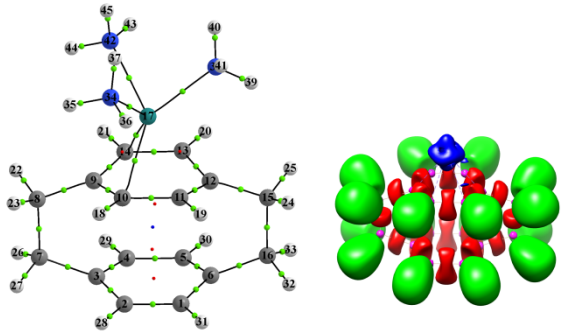

Figure 1. QTAIM topological map and 3D basins representation (ELF=0.721).

Furthermore, at the ELF method the delocalization index between the V(Ru) basins and V(C,C) disynaptic basins occurs involving, mainly, the C(10) and C(14) atoms (Fig. 1). However, the electron delocalization is more deep between the V[Ru,C(11)] and V[Ru,C(13)], monosynaptic basins localized nearly to C(11) and C(13), to V(Ru).

Besides, from of NBO method, the highest order second energy stabilization of structures arises of donation π C-C → d_π or d_z^2 Ru (Fig 2.). Since it is important highlight that the main involved are C(10) and C(14), due the highest overlap between the natural bond orbitals.

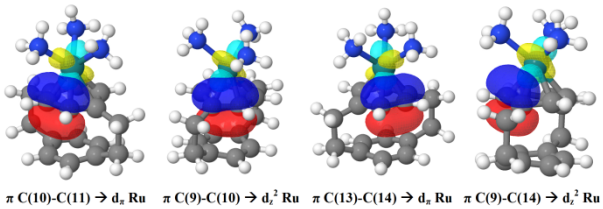

Figure 2.Main NBOs interactions (Isovalue= 0.04).

Another point, the QTAIM method shows BCPs only between Ru and C(10) or C(14) (Fig. 1). Where, the negative and nearly to zero H(r) factor indicates that there is low covalent character for these chemical bonds.

Finally, the IQA method highlighted the interactions between Ru with C(11) and C(13) as the most stabilizers due mainly the lower values of inter-electronic and inter-nuclear repulsion than the showed by Ru with C(10) and C(14), despite of higher electrons-nuclei energies.

CONCLUSIONS

Therefore, the interactions between Ru with C-C occurs main from C(10) and C(14), but, the metal establishes more stable interactions with the electron density localized in C(11) and C(13).

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[1] G. F. Caramori, L. C. Garcia, D. M. Andrada and G. Frenking, ORGANOMETALLICS, 33, 2301, (2014).