TOPOLOGICAL ANALYSIS OF THE BONDING IN
[\text{Ru}_5(\mu_5-C_2)L(CO)_{13}] \text{ AND } [\text{Ru}_4(\mu_4-C_2)L(CO)_{10}] \text{ COMPLEXES}

(L = (\mu\text{-SMe})(\mu\text{-PPh}_2)_2)

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The nature of metal-metal and metal-carbon bonding interactions within the penta- and tetra-ruthenium acetylide complexes [\text{Ru}_5(\mu_5-C_2)L(CO)_{13}] (1) and [\text{Ru}_4(\mu_4-C_2)L(CO)_{10}] (2) respectively are investigated using the present topological theories of the chemical bond: AIM and ELF. The electron density analysis within the framework of Atoms in Molecules (AIM) indicates that, in the first complex, only one bond path exists between the Ru4 and Ru5 metal atoms, whereas there is no direct bonding between ruthenium atoms in the second complex. On the other hand, the ELF analysis reveals that in both complexes, all Ru–C bonds belong to closed-shell type interactions and leads to the conclusion that the Ru–Ru bond is predominantly covalent. Moreover, the presence of trisynaptic basins in the first complex points out a three-center bond connecting ruthenium atoms.

Keywords: topological analysis, atoms in molecules (AIM), electron localization function (ELF), metal acetylide.

INTRODUCTION

Metal acetylide complexes are of both theoretical and practical interest, in particular, as their potential to form molecular wires [1-3], liquid crystals [4], electrical conductors [5], and other nanoelectronic devices [6, 7]. In this context, Chris J. Adams et al. [8] reported the synthesis and structural determination of penta- and tetra-ruthenium acetylide complexes [\text{Ru}_5(\mu_5-C_2)L(CO)_{13}] (1) and [\text{Ru}_4(\mu_4-C_2)L(CO)_{10}] (2) respectively, where L denotes the (\mu\text{-SMe})(\mu\text{-PPh}_2)_2 group. The acetylide ligand C_2 in complex (1) (Fig. 1a) bridges one edge of the Ru_3 core and the isolated Ru–Ru bonded fragment in a \(\mu_1\), \(\mu\eta^1\), \(\eta^2\) mode, albeit with asymmetric Ru–C_2 \(\pi\) interactions [8], whereas that of (2) bridges all the four metal atoms (Fig. 1b).

The first attempts to address theoretically the bonding properties in these compounds, in practical within the subunit Ru_3C_2 of (1) and Ru_4C_2 of (2), are due to the work of Frapper and Halet [9] who used a EH calculation and the effective atomic number formalism. Depending on whether the acetylide ligand acts as a four- or six-electron donor, this method provides two tautomeric forms for (1) (Fig. 2a, b) and at least three others for (2) (Fig. 2c-e).

In order to further probe the bonding rearrangement of this complexes, two methods that have proved to be less arbitrary than the traditional Mulliken population based schemes were employed [10]: atoms in molecules (AIM) and the electron localization function (ELF).
The main goal of the present study is to examine topologically the possible existence and the nature of each metal-metal and metal–C\(_{\text{acetylide}}\) bond, combining the AIM theory with the analysis of the ELF.

**COMPUTATIONAL METHODOLOGY**

All DFT calculations were carried out using the Amsterdam Density Functional (ADF) program package [11]. To get the best relation between a reliable model and computer time, the total structure was reduced only to a minimal degree [12]: the phenyl rings were replaced by four hydrogen atoms. The geometry of each simplified model, [Ru\(_5\)(\(\mu_4\)-C\(_2\))L’(CO)\(_{13}\)] and [Ru\(_4\)(\(\mu_4\)-C\(_2\))L’(CO)\(_{10}\)], L’=(\(\mu\)-SMe)(\(\mu\)-PH\(_2\))\(_2\), were fully optimized at LDA [13], PB86 [14] and BLYP [15] levels of theory. Triple-\(\zeta\) Slater-type valence orbitals (STO) augmented by one set of polarization functions (TZP) were used for all atoms, with the core orbital being kept frozen throughout; [1s] cores of C and O, [1s-2p] core of P and S, and [1s-4p] core of Ru. Relativistic effects have been considered at the scalar level using the method of zeroth-order regular approximation (ZORA) [16]. The X-ray atomic coordinates of both complexes (1) and (2) were obtained from the Cambridge Crystallographic Data Center (CCDC) with reference codes REXPIT [8] and REXPOZ [8] respectively.

The topological analysis of ELF and of the electron density according to Bader’s Atoms in Molecules (AIM) scheme was performed using the DGrid/Basin program [17]. The molecular structure, molecular graphs, and ELF isosurfaces were achieved by the Chemcraft 1.4 program [18].