The C-alkyl groups of cationic triruthenium cluster complexes of the type \([\text{Ru}_3(\mu-\text{H})(\mu-\kappa_2\text{N}_1,\text{C}_2-\text{EtnMemPyHk})(\text{CO})_{10}]^+\) (EtnMemPyHk represents a generic C-alkyl-N-methyl-pyrazium species) have been deprotonated to give kinetic products that contain unprecedented C-alkylidene derivatives and maintain the original edge-bridged decacarbonyl structure. When the starting complexes contain various C-alkyl groups, the selectivity of these deprotonation reactions is related to the atomic charges of the alkyl H atoms, as suggested by DFT/natural-bond orbital (NBO) calculations. Three additional electronic properties of the C-alkyl C-H bonds have also been found to correlate with the experimental regioselectivity since, in all cases, the deprotonated C-H bond has the smallest electron density at the bond critical point (bcp), the greatest Laplacian of the electron density at the bcp, and the greatest total energy density ratio at the bcp (computed by using the quantum theory of atoms in molecules, QTAIM). The kinetic decacarbonyl products evolve, under appropriate reaction conditions that depend upon the position of the C-alkylidene group in the heterocyclic ring, towards face-capped nonacarbonyl derivatives (thermodynamic products). Theoretical calculations support the proposal that the selectivity of these deprotonation reactions is primarily determined by the atomic charge of the alkyl H atoms: the higher the charge the easier the deprotonation when the starting complexes contain various C-alkyl groups. On the other hand, although QTAIM results have been obtained here only from theoretical electron densities for the above clusters, comparisons with local and integral topological parameters derived from both experimental and theoretical electron densities for the related triruthenium complex \([\text{Ru}_3(\mu-\text{H})_2(\mu_3-\text{MeImCH})(\text{CO})_{9}]\) (Me2Im = 1,3-dimethylimidazol-2-ylidene) may easily be made.


**Keywords:** QTAIM, Ruthenium clusters, Electron density calculations