

How do Computational Methods and Relativistic Effects Influence the Study of Chemical Reactions involving Ru-NO Complexes?

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The experimental or the computational determination of binding energies in transition metal complexes is not easy. In addition, different approximations have been adopted to treat the relativistic effects of metals in theoretical calculations.^{1,2} Therefore, two possibilities for the treatment of relativistic effects, namely effective core potentials (ECP) and scalar relativistic effects (SRE), were used to calculate geometric parameters and energies for chemical reactions involving the Ru-NO complexes. The influence of ECP and SRE in the geometric parameters as well as the reaction energies of reduction (A-F), isomerization (G-I), and Cl⁻ negative *trans* influence in relation to NH₃ (J-L) were analyzed (Figure 1).

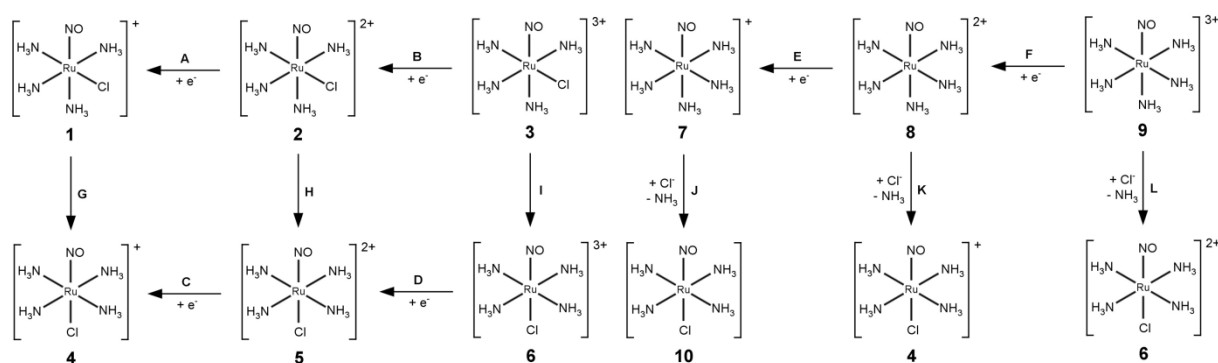


Figure 1. Reduction (A-F), isomerization (G-I), and Cl⁻ negative *trans* influence in relation to NH₃ (J-L) reactions for complexes 1-10.

Compared to the experimental values, the geometric parameters provided by ECP (or SRE) presented maximum medium absolute relative deviation of 4.0 (4.3) and 2.3 (2.6)% for bond lengths and bond angles, respectively. The geometries optimized with ECP are used to calculate the electronic energies of compounds 1-10 by means of the following computational methods: RI-MP2, RI-SCS-MP2, OO-RI-MP2, OO-RI-SCS-MP2, M06-L, M06, M06-2X, M06-HF, BP86-D3BJ, BP86, B2PLYP, LC-wPBE, B3LYP, and CCSD(T) (taken as reference). For reactions A-I, B2PLYP provided the closest results to the values obtained with CCSD(T). Additionally, LC-wPBE gave the smallest error for the energies of reactions J-L.

References

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