EXPERIMENTAL AND THEORETICAL STUDIES ON THE OXIDATION OF A "PLATINUM-BUTTERFLY" COMPLEX BY HALOCARBONS

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The oxidative addition (OA) of halocarbons (RX) to d^8 Rhodium (I) and Iridium (I) dinuclear bis-pyrazolate complexes have been widely studied yielding in many cases metal-metal bonded M_2(II,II) compounds.[1] In this regard, moving into the Platinum(II) chemistry, the activation of RX by a similar system has been recently studied in our group for the first time.[2]

Here we report the oxidation of a Pt_2(II,II) complex, [{Pt(C^C*)(μ-pz)}$_2$] (HC^C*= 1-(4-ethoxycarbonylphenyl)-3-methyl-1*H*-imidazol-2-ylidene, **A**), by halocarbons such as RX (R= CH_3, CH_2Ph; X = Br, I). Depending on the nature of RX and on the reaction's conditions, the oxidation affords the metal-metal bonded Pt_2(III,III) complexes (R-[Pt]-[Pt]-X) ([Pt] = [Pt^{III}(C^C*)(μ-pz)]; R= CH_2Ph; X = Br , I) or go further up to the Pt_2(IV,IV) derivatives [R-[Pt](μ-X)[Pt]-R]X ([Pt] = [Pt^{IV}(C^C*)(μ-pz)]; R=CH_3, X = I; R= CH_2Ph, X = Br). Experimental work and density functional theory calculations have been carried out to decipher the mechanism, the metal-metal cooperative effects and the influence of both fragments (R, X) in the oxidation reactions.

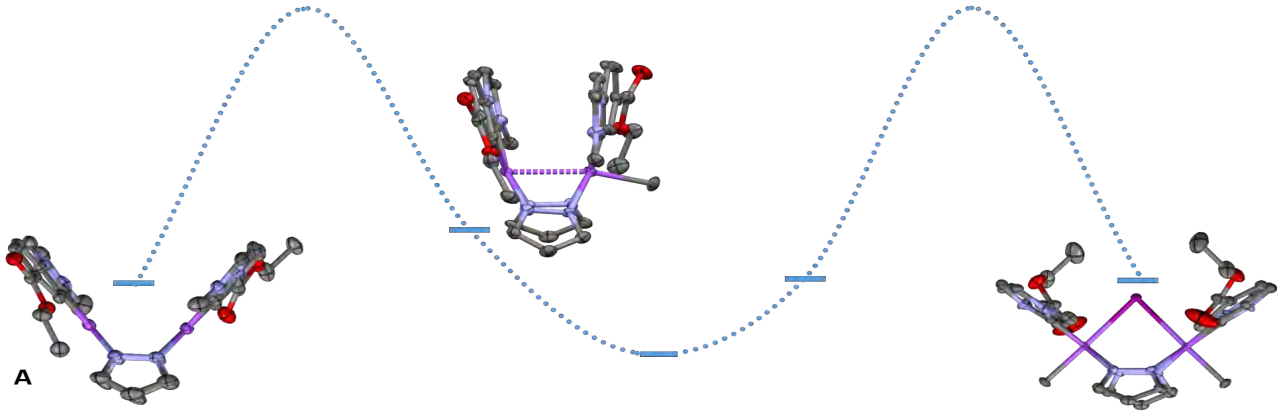

Figure: Energy profile for the oxidative addition of CH_3I to **A**

References

[1] C. Tejel, M. A. Ciriano, A. J. Edwards, F. J. Lahoz and L. A. Oro, *Organometallics* **1997**, *16*, 45-53; [2] V. Sicilia, L. Arnal, S. Fuertes, A. Martin and M. Baya, *Inorg Chem* **2020**, *59*, 12586-12594.