Computational investigations on the unexpected extrusion of molecular iodine in Pd(II) σ-butadienyl complexes.

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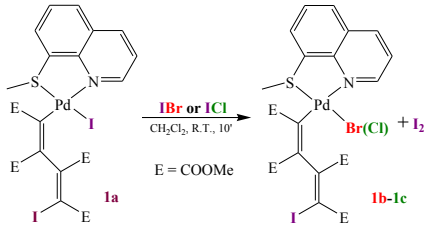
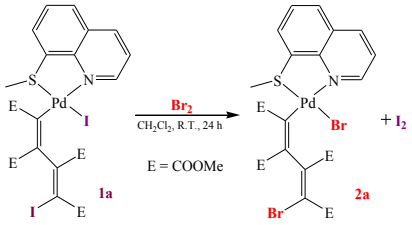
We have experimentally and theoretically studied the stoichiometric addition of halogens or interhalogens to σ-butadienyl Pd(II) complexes bearing thioquinolines as spectator ligands.[1]
The observed reactions do not involve the expected elimination of the butadienyl fragment[2] but rather the unpredictable extrusion of molecular iodine (Schemes 1-2).[1]

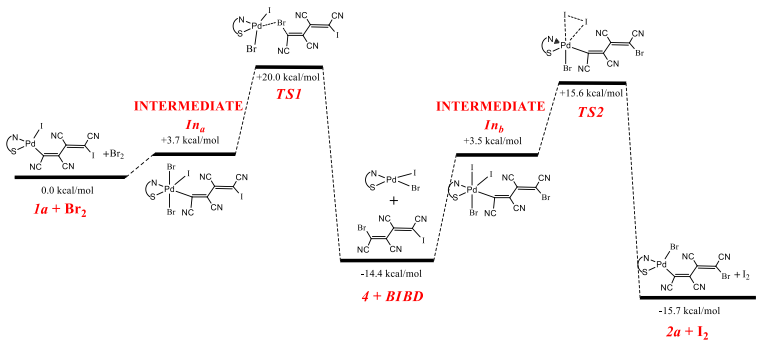


Scheme 1

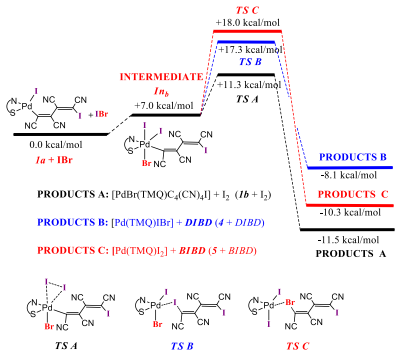


Scheme 2

We have explained this peculiar reactivity with a mechanistic hypothesis (Scheme 3) involving Pd(IV) intermediates (to save computer time, the COOMe was substituted with CN group).[1]
In the case of the reaction between complex ***1a*** and IBr, it is apparent from the computational output (Scheme 4) that I_2 and complex ***1b*** represent the favored reaction products from both kinetic and thermodynamic points of view (the energy values are expressed as ΔG° at 298K).



Scheme 3



Scheme 4

The geometrical optimization of the complexes was carried out using the hyper-GGA functional MO6 [3] in combination with the LAN2TZ(f) [4] basis set for the Pd atoms, the LANL2DZdp basis set[5] for the halogen atoms and the 6-31G(d,p) basis set for the other elements. Solvent effects (dichloromethane, ε =8.93) were included using CPCM[6]. The thermodynamic parameters were obtained by means of the stationary points characterized by IR simulation.

References

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