Halogen metathesis in Pd(II) σ -butadienyl complexes

Thomas Scattolin^a, Fabiano Visentin^a, Luciano Canovese^a and Claudio Santo^a

^aDipartimento di Scienze Molecolari e Nanosistemi, Universita` Ca' Foscari, Venezia e-mail: thomas.scattolin@unive.it

Irrespectively of the involved mechanism, the formation of aryl or alkyl Pd(II) species is comparatively easier and faster when aryl- or alkyl-iodide, instead of bromide and chloride derivatives are reacted with Pd(0) substrates.¹⁻²

The substitution of I- with Cl- or Br- is usually obtained by de-halogenation of the iodo-species followed by addition of an appropriate soluble halide.³

In the present abstract, we report that σ -butadienyl palladium complexes bearing thioquinoline as spectators ligands undergo substitution of the iodide bound to Pd(II) by bromide or chloride by one pot reaction between the above complexes and the interhalogens IBr and ICl, respectively (Scheme 1).⁴

In one case we were able to substitute simultaneously the iodides bound to palladium and terminal butadienyl carbon with two bromides simply by adding bromine to complex **1a** (Scheme 2).⁴ We have explained this peculiar reactivity with a mechanistic hypothesis based on a sequence of selective processes of oxidative addition and reductive elimination involving Pd(IV) intermediates.⁴

References

- 1. Hartwig, J.F.; in " Organotransition Metal Chemistry", 2010, Chap.7, University ScienceBook.
- 2. Crabtree, R.H., in "The Organometallic Chemistry of the Transition Metals", 2005, Chap. 6, Wiley.
- 3. Tobe, M.L.; Burgess, J., in "Inorganic Reaction Mechanisms", 1991, Chap.3, Addison Wesley.
- 4. Scattolin, T.; Visentin, F.; Santo, C.; Bertolasi, V.; Canovese, L., Dalton Trans., 2016, submitted.