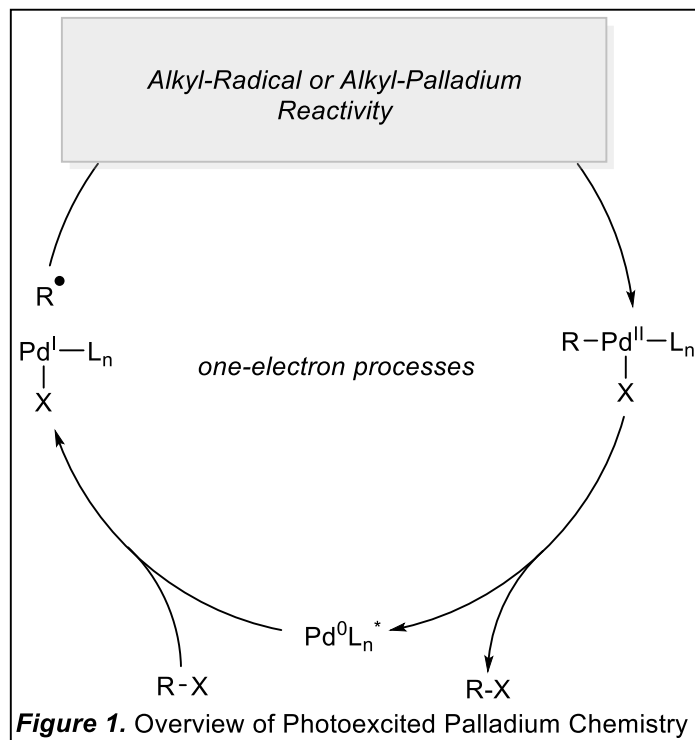


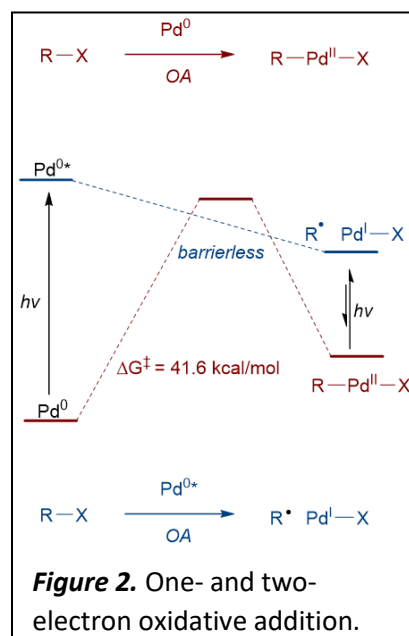
**Introduction** – Two-electron chemistry of palladium catalysts is a well-developed field and has allowed for the efficient, controlled formation of carbon-carbon as well as carbon-heteroatom bonds. This



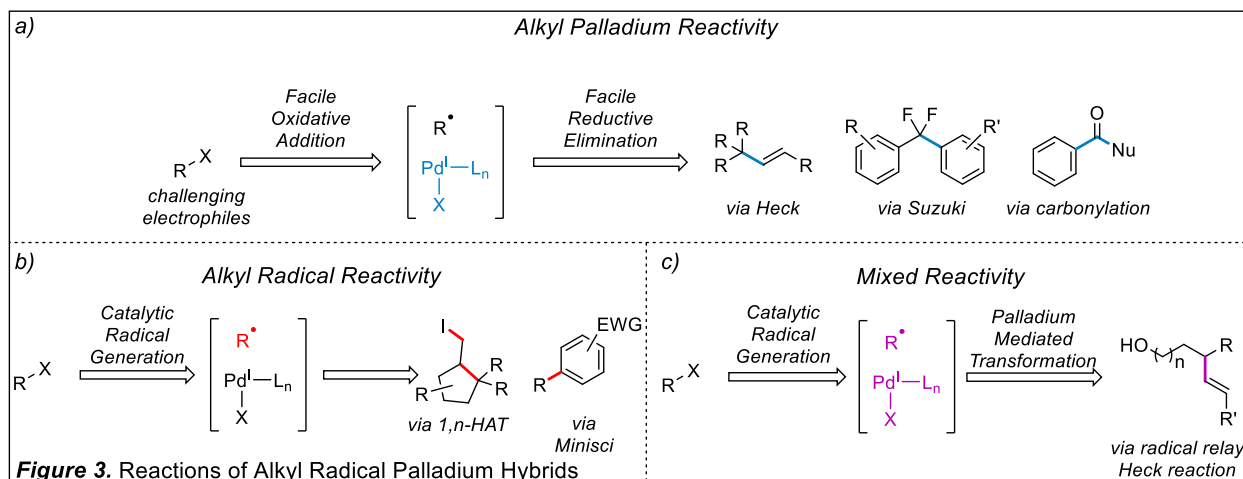
chemistry has been utilized not only in the environment of total synthesis, but also in pharmaceutical chemistry owing to its reliability and scalability.<sup>1</sup> One-electron chemistry of palladium complexes is significantly less studied, and as a result, less utilized in synthetic organic chemistry. One method that has seen a recent increase in popularity is the photoexcitation of palladium complexes to an excited state and utilization of these photoexcited complexes for single-electron oxidative addition into carbon-halogen bonds. Shown in figure 1 is a generic

catalytic cycle of a photoexcited palladium catalyst. Oxidative addition *via* a single electron pathway yields alkyl radical palladium hybrid **XX**. There are two main reactivity paradigms with which this alkyl radical palladium hybrid may behave. The first is via palladium mediated processes, where the alkyl radical palladium hybrid has similar reactivity to a classic Pd(II) species. The other type of reactivity is akin to an alkyl radical.<sup>2</sup>

**Alkyl Palladium Reactivity** – Reacting as an alkyl palladium species allows this alkyl radical palladium hybrid to undergo a variety of different cross coupling reactions such as Heck reactions, Suzuki cross couplings, or carbonylation reactions. Importantly, due to the excited nature of the palladium(0) catalyst, the oxidative addition of the photoexcited palladium catalyst into a carbon-halogen bond is barrierless (figure 2).<sup>3</sup> This allows for the utilization of electrophiles



which are challenging to engage in cross coupling reactions *via* two-electron mechanisms such as tertiary halides, or trifluorotoluene (figure 3a).



**Alkyl Radical Reactivity** – The alkyl radical palladium hybrid may also react as an alkyl radical. Under this mechanistic umbrella, an alkyl radical can be generated catalytically from an alkyl halide and the photoexcited palladium catalyst. With this catalytically generated radical, a number of typical radical reactions can be achieved: remote unsaturation, 1,5-HAT and cyclization reactions to name a few (figure 3b).

**Mixed Reactivity** – The final regime of reactivity blends the two previous ones. Catalytic generation of an alkyl radical allows first for typical radical reactivity (diene addition, 1,5-HAT) followed by radical polar crossover to generate a Pd(II) species. This Pd(II) species reacts the same as if it were generated *via* a two-electron mechanism and can undergo  $\pi$ -allyl substitution or a Heck cross coupling (figure 3c).

**Outlook** – Despite the utility of these transformations catalyzed by a photoexcited palladium species, there are still many shortcomings of this chemistry. First, the generation of an alkyl radical palladium hybrid *via* a single-electron transfer oxidative addition prevents the development of stereospecific methods. Additionally, the development of nickel catalysis<sup>4</sup> and the unanswered mechanistic questions regarding the nature of the active Pd(I) species prevent the widespread application of this chemistry.

## References –

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