Shuttle hydrogen atom transfer (HAT) for mild alkene transfer hydrofunctionalization

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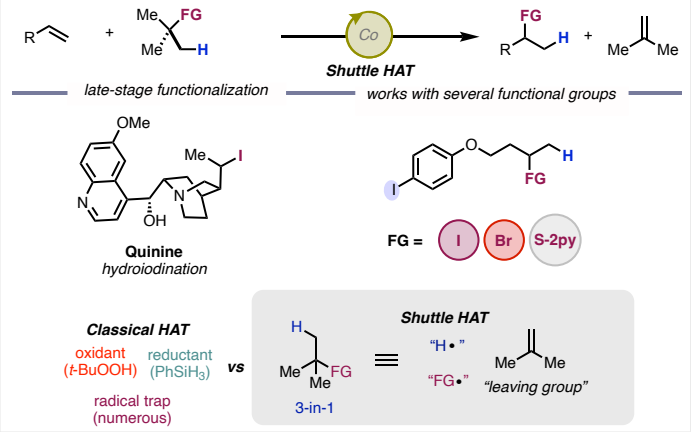
Hydrogen atom transfer (HAT) from a metal-hydride is a reliable and powerful method for functionalizing unsaturated C–C bonds in organic synthesis.[1, 2] Cobalt hydrides (Co–H) have garnered significant attention in this field, where the weak Co–H bonds are most commonly generated in a catalytic fashion through a mixture of stoichiometric amounts of peroxide oxidant and silane reductant. Here we show that the reverse process of HAT to an alkene, i.e. hydrogen atom abstraction of a C–H adjacent to a radical,[3, 4] can be leveraged to generate catalytically active Co–H species in a new application of shuttle catalysis coined shuttle HAT. This method obviates the need for stoichiometric reductant/oxidant mixtures thereby greatly simplifying the generation of Co–H under exceedingly mild reaction conditions. This approach opens the door for the introduction of functional handles (e.g., iodides) that were previously challenging through other catalytic approaches, and paves the way for new reagent design which incorporates this shuttle HAT platform. The shuttle HAT catalytic cycle can be interwoven with a reversible C–X bond forming cycle to shuttle a hydrogen atom and halogen atom between molecules. Unlike polar transfer reactions, the implementation of a radical pathway enables hydrofunctionalization to proceed with Markovnikov selectivity and prevents chain walking mechanisms.[5]



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