

Despite the ready availability and ease of synthesis, primary phosphines remain underutilized as synthons in preparation of value-added organophosphines. Herein, we report the catalytic synthesis of phospholes with an iron catalyst  $\text{CpFe}(\text{CO})_2\text{Me}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ). Reaction of primary aryl or alkyl phosphines with either diene or 2 equiv. of alkyne yields the corresponding phosphole in modest to high yields. This work provides a compliment to recent reports of catalytic phosphole syntheses with palladium by use of an earth-abundant catalyst and avoiding pre-fabricated P–C bonds in the substrate as well as previous work where electrophilic, metal-supported phosphinidenes allowed stoichiometric access to phospholes. The observed reactivity is most akin to  $\alpha$ -elimination, or the extrusion of a low-valent fragment. Indeed, reaction of primary phosphine with catalytic  $\text{CpFe}(\text{CO})_2\text{Me}$  in the absence of unsaturated substrate afford dehydrocoupling products. Exploration of catalysis scope and mechanism will be presented.