C–H amination is a very elegant, atom-efficient and potentially versatile approach to forge C–N bonds. Catalytic pathways that involve bioinspired odd-electron mechanisms have gained momentum in the last few years, with much emphasis currently on open-shell transition metal species as the locus of radical reactivity. This approach requires the use of paramagnetic metal ions (e.g. high-spin Fe$^{II}$, Co$^{II}$) to generate metal-bound substrate radicals. Redox-active ligands have been overlooked as a tool to invoke radical character onto metal-bound substrates. Palladium(II) is normally not disposed to induce odd-electron chemistry onto bound substrates, e.g. organoazides. Employing a novel redox-active pincer ligand, we have recently reported the first example of stoichiometric ligand-to-substrate single-electron transfer, utilizing the coordination sphere of redox-inert Pd(II) as substrate-binding platform. This concept proved competent for the intramolecular benzylic C–H amination of organoazides via nitrene radicals. This contribution will discuss the overall strategy of ligand-mediated odd-electron mechanisms for C–H amination on Pd as well as Fe, based on experimental and computational insight.

References