In recent work, we showed that unusual pyridylidene complexes can play an active role in catalysis, in this case C-H functionalization of pyridine. While exploring the reactivity of a catalyst deactivation product in this system (2) we uncovered some unexpected, but exciting reactivity. Reaction of 2 with a range of electrophilic fluorinating agents leads to the formation of [3]+ via an unprecedented outer-sphere electrophilic fluorination (OSEF) mechanism. This contrasts strongly with related Pd-based electrophilic fluorination reactions, which typically proceed via the formation of a metal-fluoride intermediate. Subsequent work in York has shown that a range of metal alkynyl and alkenyl complexes undergo fluorination (and trifluoromethylation) via OSEF. A detailed discussion of the mechanistic features of these systems and the reactivity of the fluorinated organometallic species will be presented, based on the results of both experimental and computational studies. This fundamental work has significant potential to underpin the development of novel metal-mediated fluorination methodologies and preliminary results in this direction will also be discussed.

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