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# IL21 – The Evolution from FLPs to Electrophilic Phosphonium Cations and Hydrodefluorination and C–F Functionalization

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Suitably selected combinations of main group Lewis acids and bases constitute frustrated Lewis pairs (FLPs) were shown to activate hydrogen. This has allowed the development of unprecedented metal-free catalytic hydrogenations of C=N bonds, anilines, *N*-heterocycles, olefins, polyaromatic hydrocabons and most recently ketones and aldehydes.[1] This conceptual advance has been furthered leading to the development of electrophilic phosphonium cations (EPCs).[2] These species prove to be highly Lewis acidic species that can effect CF bond hydrodefluorination catalysis. In addition, these Lewis acids are useful for hydrosilylations,[3] dehydrocouplings,[4] ketone deoxygenation[5] and in FLP hydrogenations.[6] More recently, we have extended the reactivity of EPCs to effect the catalytic Fiedel-Crafts arylation of $CF_3$ groups[7] as well as benzyl fluorides. Such reactivity has little precedent and provides a new and highly variable approach to organic derivatizations. The implications of these findings for applications of main group species in catalysis is considered in this lecture.

## References

1. Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 10018-10032.
2. Caputo, C. B.; Hounjet, L. J.; Dobrovetsky, R.; Stephan, D. W. *Science* **2013**, *341*, 1374-1377.
3. Pérez, M.; Hounjet, L. J.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 18308-18310.
4. Pérez, M.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W. *Proc. Nat. Acad. Sci.* **2014**, *111*, 10917-10921.
5. Mehta, M.; Holthausen, M. H.; Mallov, I.; Perez, M.; Qu, Z. W.; Grimme, S.; Stephan, D. W. *Angew. Chem. Int . Ed.* **2015**, *54*, 8250-8254.
6. vom Stein, T.; Pérez, M.; Dobrovetsky, R.; Winkelhaus, D.; Caputo, C. B.; Stephan, D. W. *Angew. Chem. Int . Ed.* **2015**, *54*, 10178-10182.
7. Zhu, J.; Pérez, M.; Caputo, C. B.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2016**, *55*, 417-421.