

Oxidative Addition of Aryl Halides and Phenol Derivatives to a Prototypical Nickel(0) Complex

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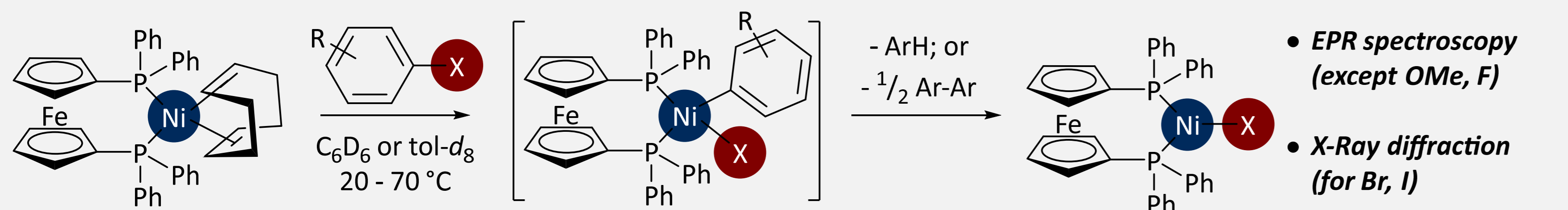
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Understanding the Reactivity of Nickel(0)

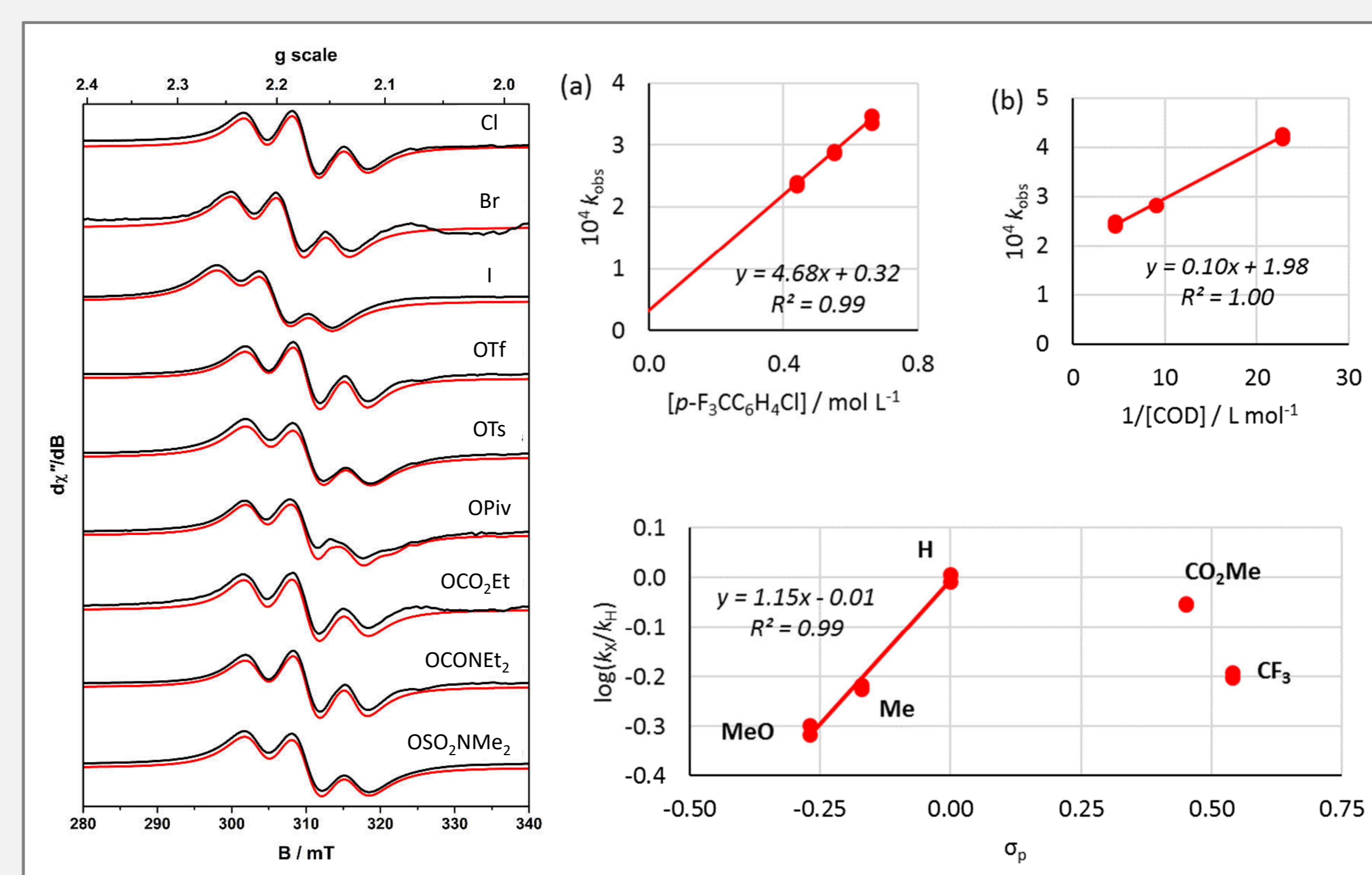
- Oxidative addition is a process where the reactivity of nickel and palladium diverge; nickel reacts with a much wider range of electrophiles, potentially leading to selectivity issues; the oxidative addition of aryl halides to Ni⁰ complexes can lead to Ni^I complexes
- A detailed, quantitative, and fundamental understanding of reactivity is important to enable advances in nickel catalysis

Oxidative Addition Mechanism

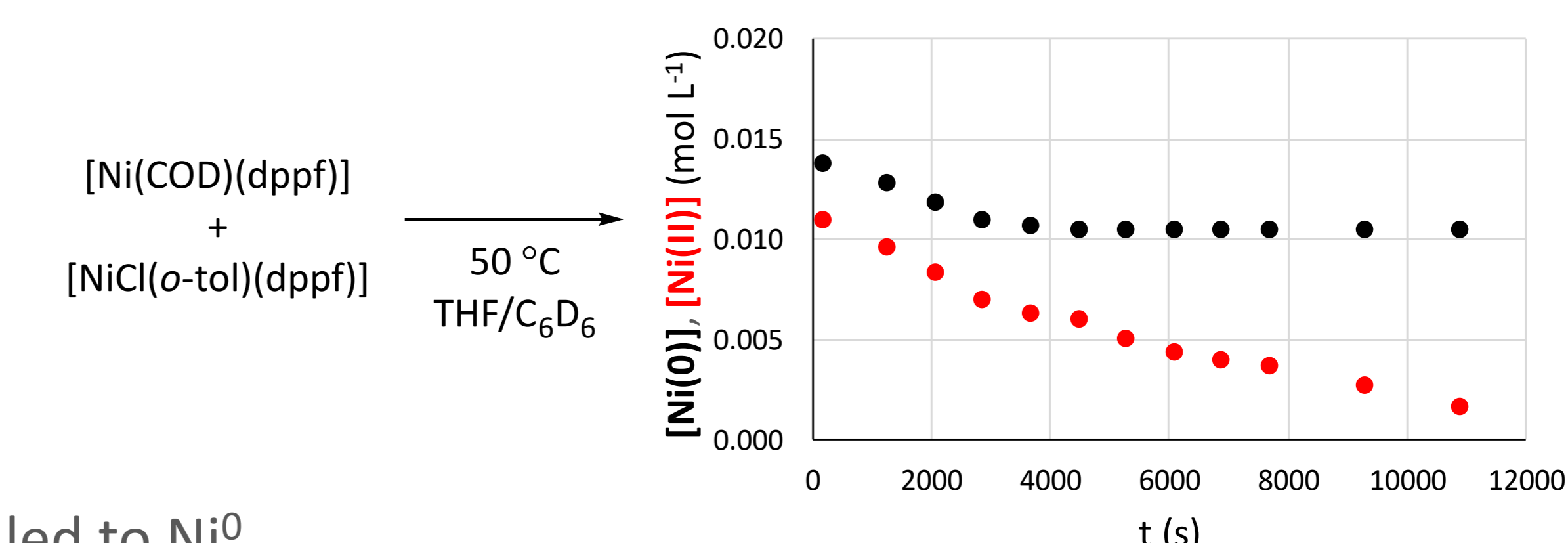
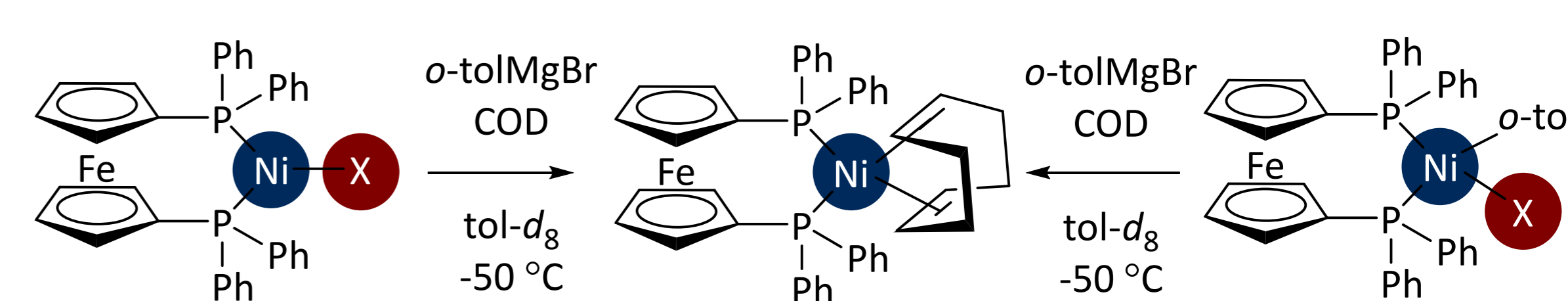
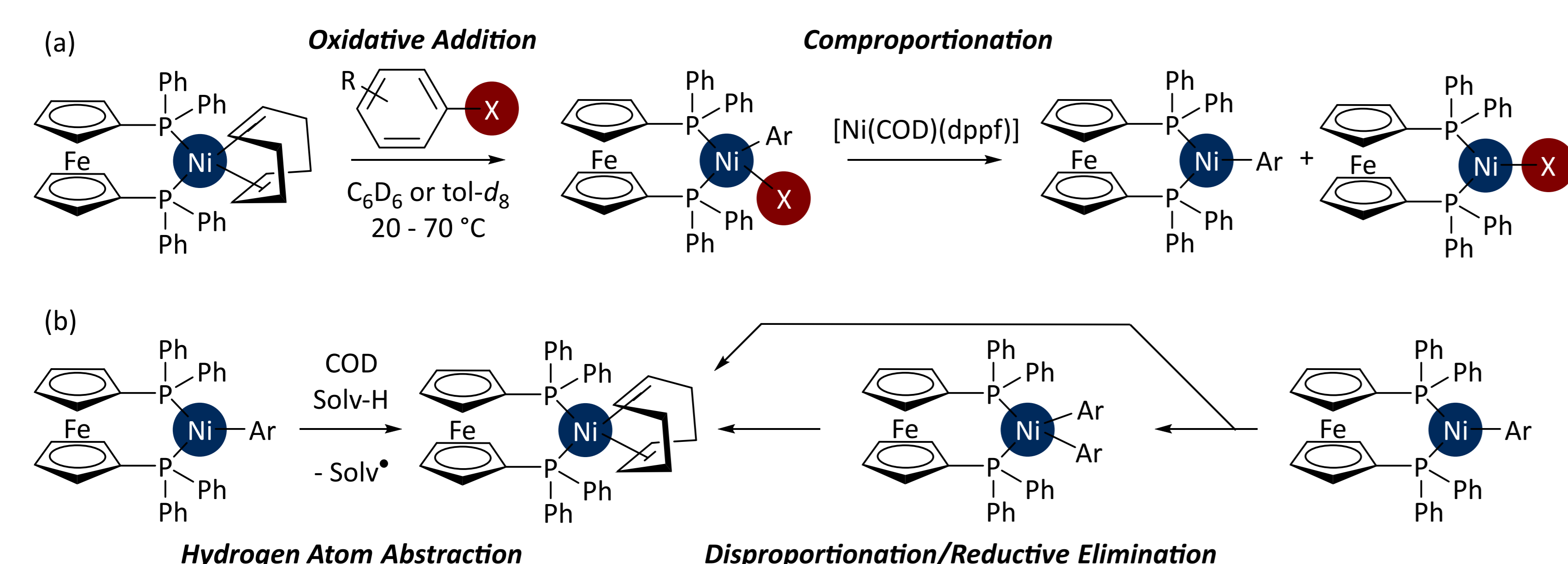


• Kinetic experiments monitored by ³¹P NMR spectroscopy (≥20 equiv. ArX)

- First order in ArX, and inhibited by COD; bound COD does not exchange with free COD (no EXSY cross-peaks), so ligand exchange proceeds *via* an interchange mechanism
- The final product is Ni^I, with Ni^{II} intermediates observed with *ortho*-substituted aryl halides, or in low temperature experiments with other aryl halides
- Substrates with alkenes rapidly form well-defined intermediates
- Hammett plot is not simple, suggesting two processes with very different ρ values
- Entropy and enthalpy of activation determined for *p*-F₃CC₆H₄X where X = Br, OTs, OTf
 - ΔH[‡]: Br: 24(1) kcal mol⁻¹ OTs: 28(2) kcal mol⁻¹ OTf: 31(2) kcal mol⁻¹
 - ΔS[‡]: Br: 0(3) cal K⁻¹ mol⁻¹ OTs: 8(5) cal K⁻¹ mol⁻¹ OTf: 16(7) cal K⁻¹ mol⁻¹



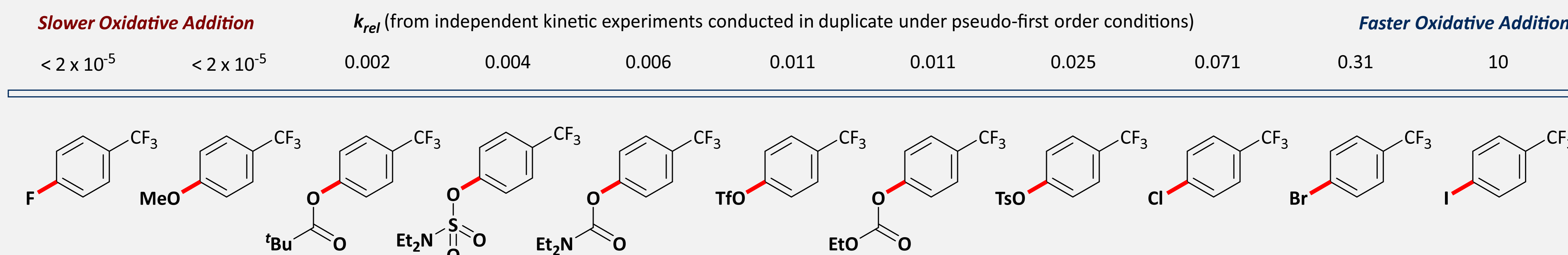
The Origin of Nickel(I) in Oxidative Addition Reactions



- Attempts to synthesise [Ni(*o*-tol)₂(dppf)] or [Ni(*o*-tol)(dppf)] in toluene-*d*₈, even at -50 °C, led to Ni⁰
- [NiCl(*o*-tol)(dppf)] stable: 9% decomp. after 24 h in THF/benzene at 50 °C; *unstable* in the presence of [Ni(COD)(dppf)]: 100% decomp. after 4 h at 50 °C
- Comproportionation is almost catalytic in Ni⁰; biaryl and arene both detected by GC in various experiments

A Reactivity Scale for Oxidative Addition

- Kinetic experiments at 50 °C in benzene-*d*₆ and 70 °C in toluene-*d*₈ allow the construction of the first reactivity scale that includes a range of aryl halides and phenol derivatives; this covers *ca.* 6 orders of magnitude of reactivity, and reveals the scope of Ni-dppf catalysts for cross-coupling
- Unexpectedly, tosylates and carbonates undergo reaction more quickly than triflates; fluorides and ethers undergo very slow reaction at 70 °C in toluene-*d*₈ (25% conversion in *ca.* 48 h) so rates are estimated



Conclusions and Next Steps

- This work** shows that the oxidative addition of aryl halides to [Ni(COD)(dppf)] initially yields well-defined [Ni(Ar)X(dppf)] intermediates, which then undergo comproportionation to form Ni^I products. Most of these products have been characterised by EPR spectroscopy
- Future work** focuses on a number of themes, including (i) exploiting our reactivity scale in chemoselective organic synthesis; (ii) exploring some substrates that allow us to change this reactivity trend; and (iii) extending our studies to new substrates and new model catalyst complexes

Further Information: Please see our recently published manuscript: *Organometallics* 2017, *In Press*, DOI: 10.1021/acs.organomet.7b00208



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