Intramolecular Ligand-to-Substrate Single-Electron-Transfer

Facilitating Radical-Type reactivity on Palladium(II)

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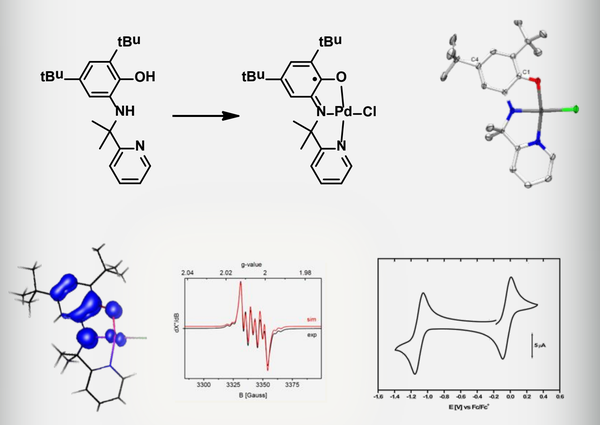
Redox-active ligands have been succesfully employed to induce two-electron reactivity upon metals that are prone to undergo single-electron reactivity.[1] Here we present how new redox-active pincer ligands are able to induce radical-type reactivity upon Pd(II) by Intramolecular Ligand-to-Substrate Single-Electron transfer.[2]

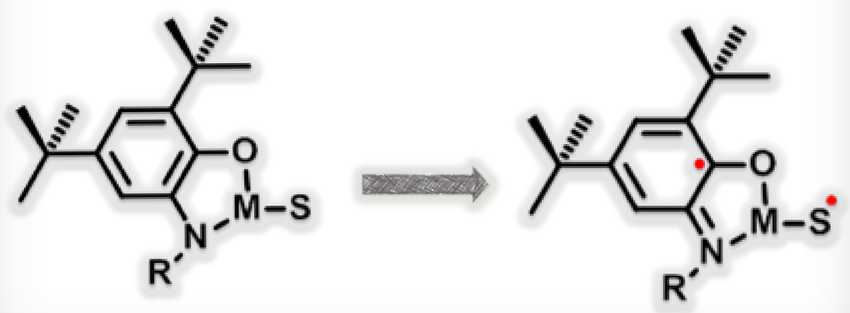
NNO Ligand



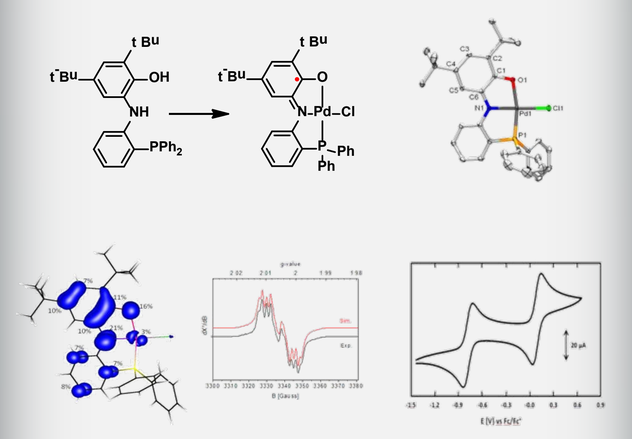
Ligand-centered radical

Fully reversible one-electron redox changes

Ligand-to-Substrate Single-Electron Transfer



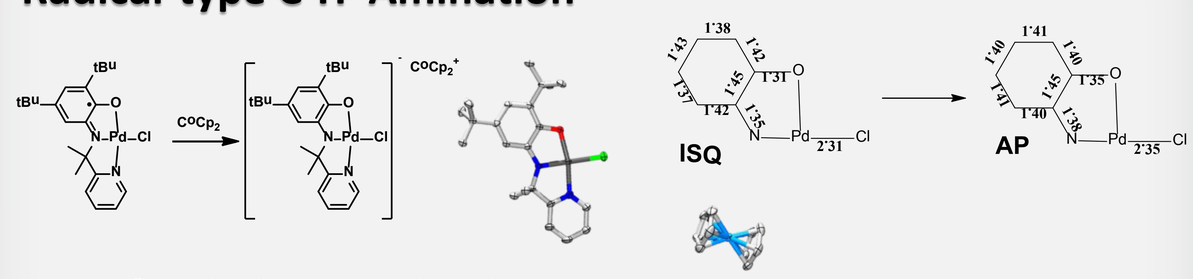
PNO Ligand



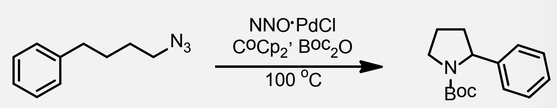
Ligand-centered radical

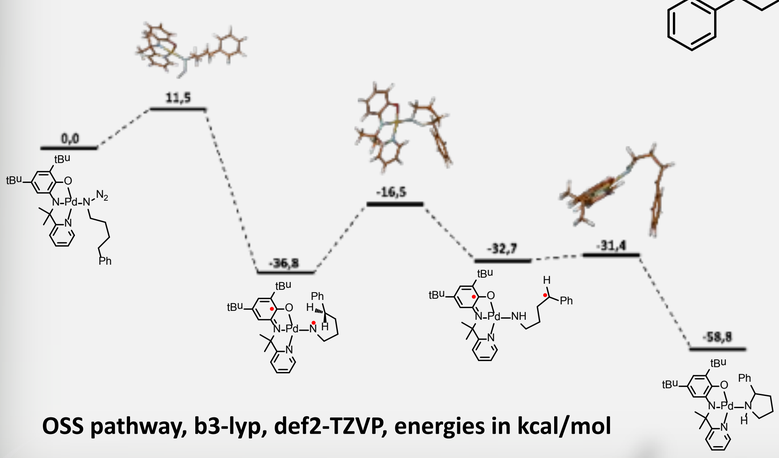
Fully reversible one-electron redox changes

Radical-type C-H Amination



Mechanistic Investigations

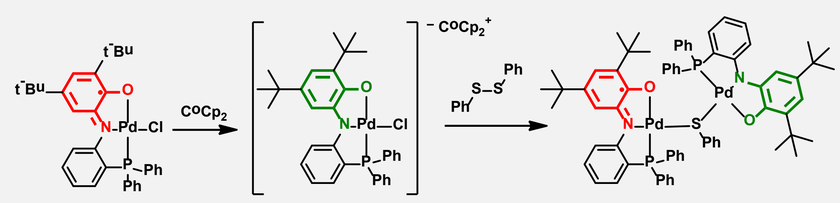




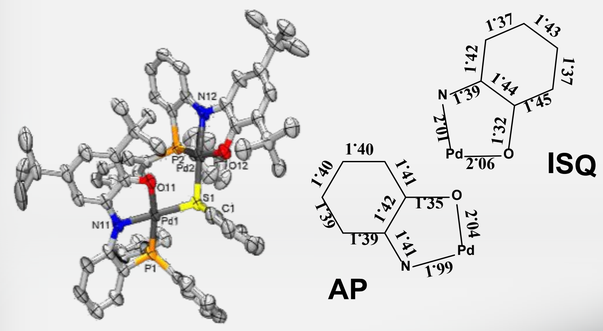
OSS pathway, b3-lyp, def2-TZVP, energies in kcal/mol

- Open-Shell Singlet pathway most favoured
- TEMPO-H inhibits reaction
- kH/kD = 3.35 (DFT 3.65)

Homolytic Bond Activation

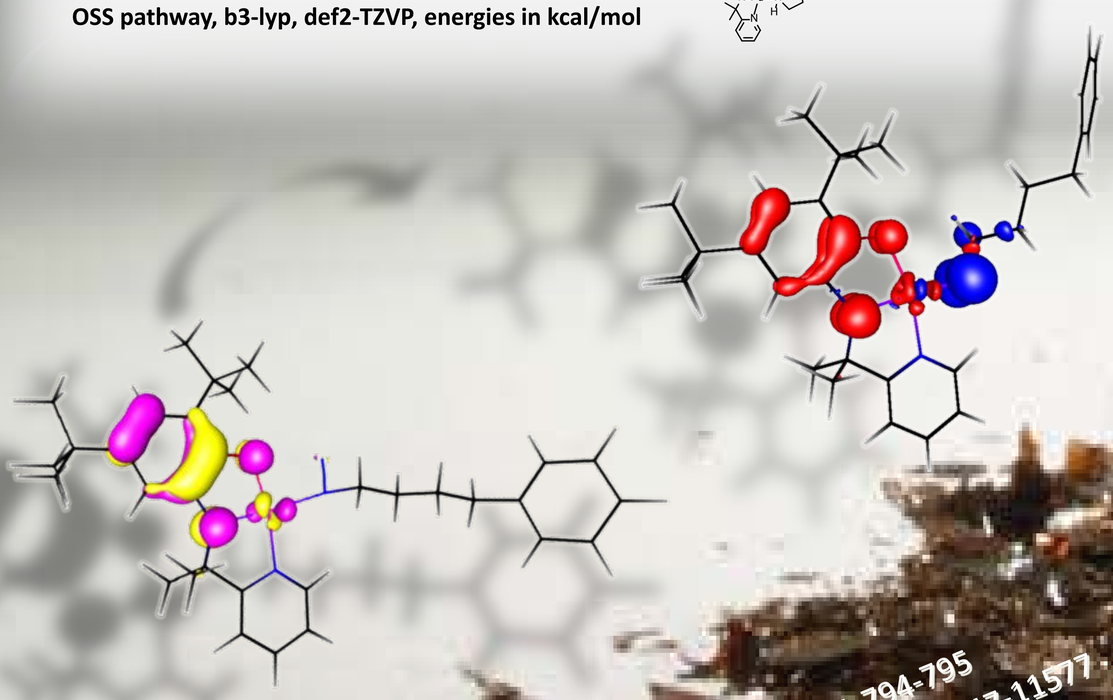


μ_{eff} = 1.90



Ligand-based mixed valence in Pd dimer

XRD



New redox-active NNO & PNO pincer ligands are able to facilitate and transfer a single electron to a bound substrate, enabling radical-type reactivity on Pd (II).

References

1. Wieghardt, K.; Chirik, P.J. Science, **2010**, 327, 794-795
2. van der Vlugt *et al.* J. Am. Chem. Soc. **2014**, 136, 11547-11577
3. Hennessy, E. T.; Betley, T. A. Science **2013**, 340, 591

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