

# Pd-Sn Bond Enables the Formation of Pd-Aryl Bonds through Oxidative

## Addition of Aryl Halides

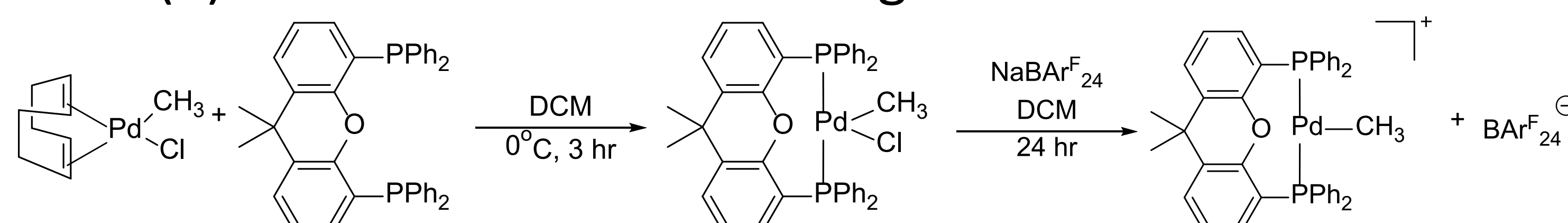
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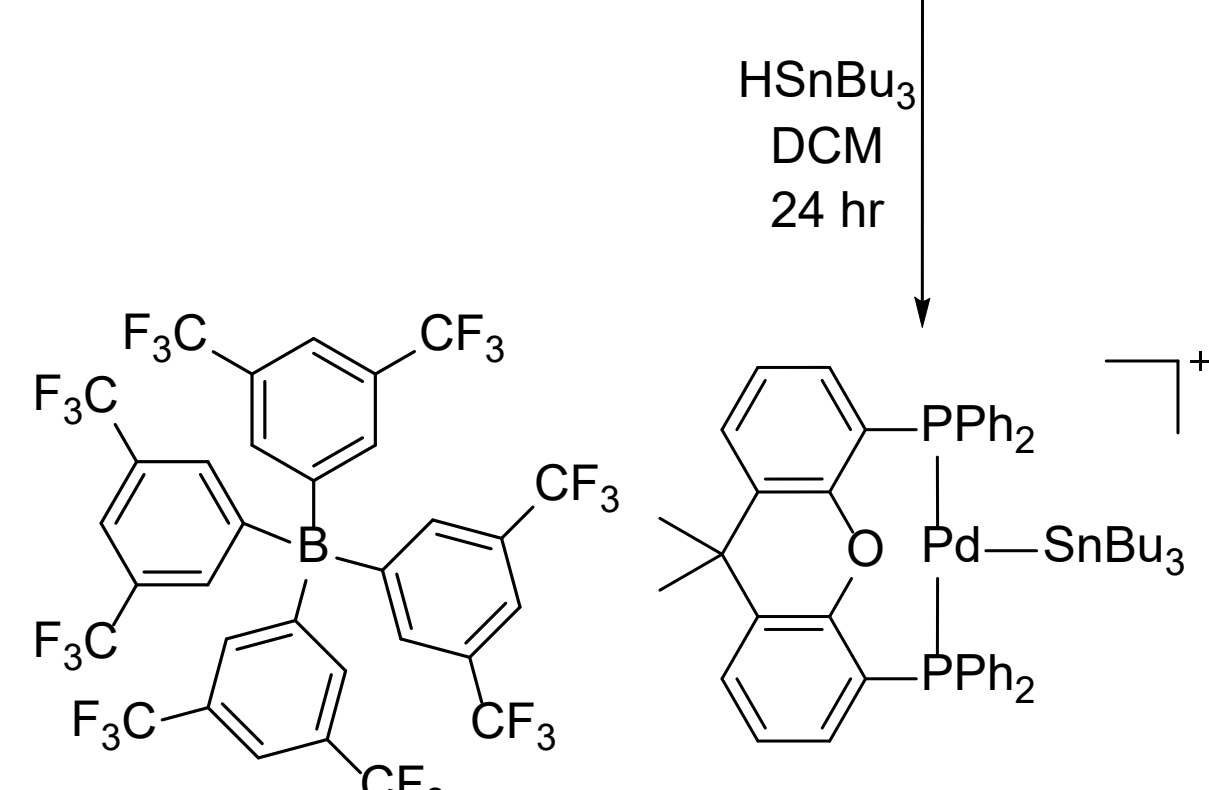
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### Background

- The Gagne Lab recently developed a palladium silyl cation catalyst which cleaves carbon-oxygen bonds
- Tin is the next highest electronegative atom behind silicon in the Group 4 elements
- Pd(II) oxidation state can undergo oxidative addition

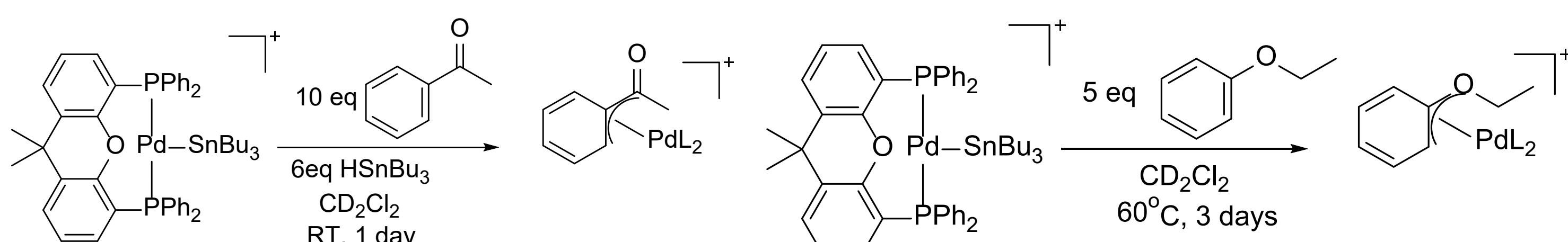


- A (XantPhos)Pd-SnBu<sub>3</sub> complex was synthesized with a BAR<sup>F</sup><sub>24</sub> counterion to determine if an air-stable species could be formed, and perform this the bond reduction



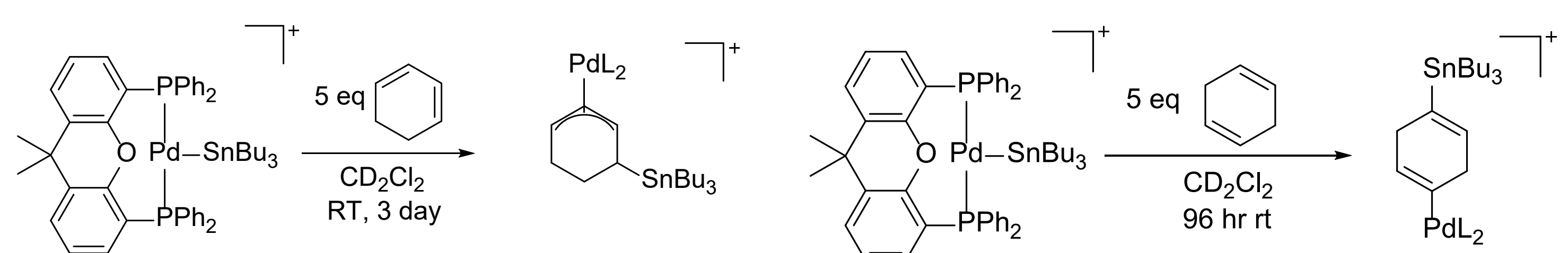
### Oxygen and Carbon as Nucleophiles

- Tin has a lower oxophilicity than silicon



Time	% Conversion
24 hours	Slight Decomposition
48 hours	Slight Decomposition

Time	% Conversion
24 hours	0%



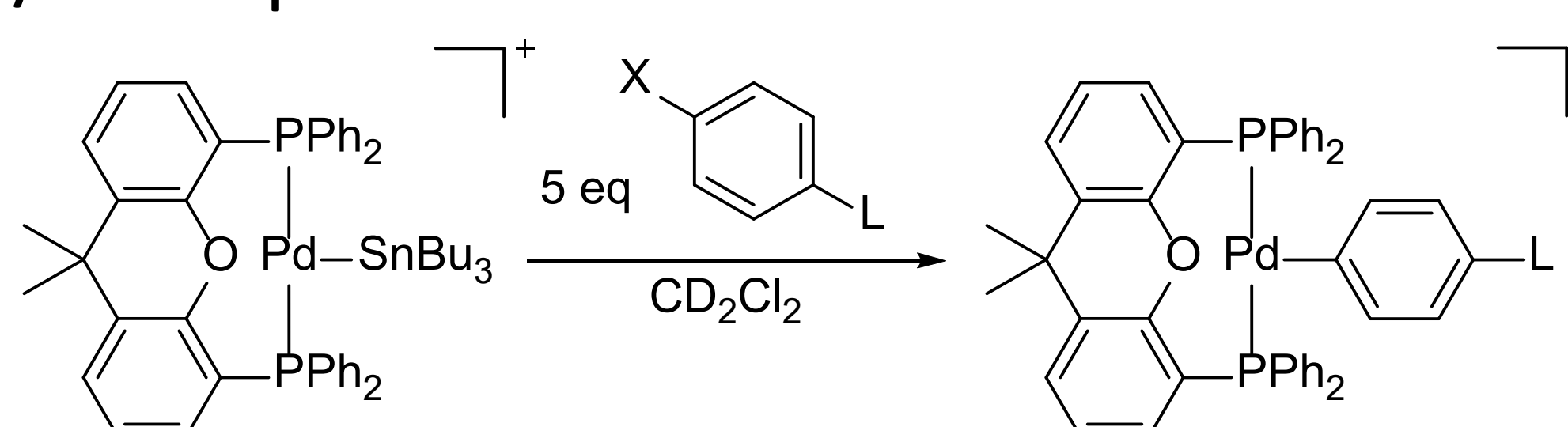
Time	% Conversion
24 hours	69%
48 hours	80%
72 hours	94%

Time	% Conversion
24 hours	4%
96 hours	56% conversion with decomposition

- The Sn-O bond doesn't form
- Carbon nucleophiles better cleaves the Pd-Sn bond
- Palladium is haptically bound to carbon and donates more electron density into the sigma bond

### Oxidative Addition

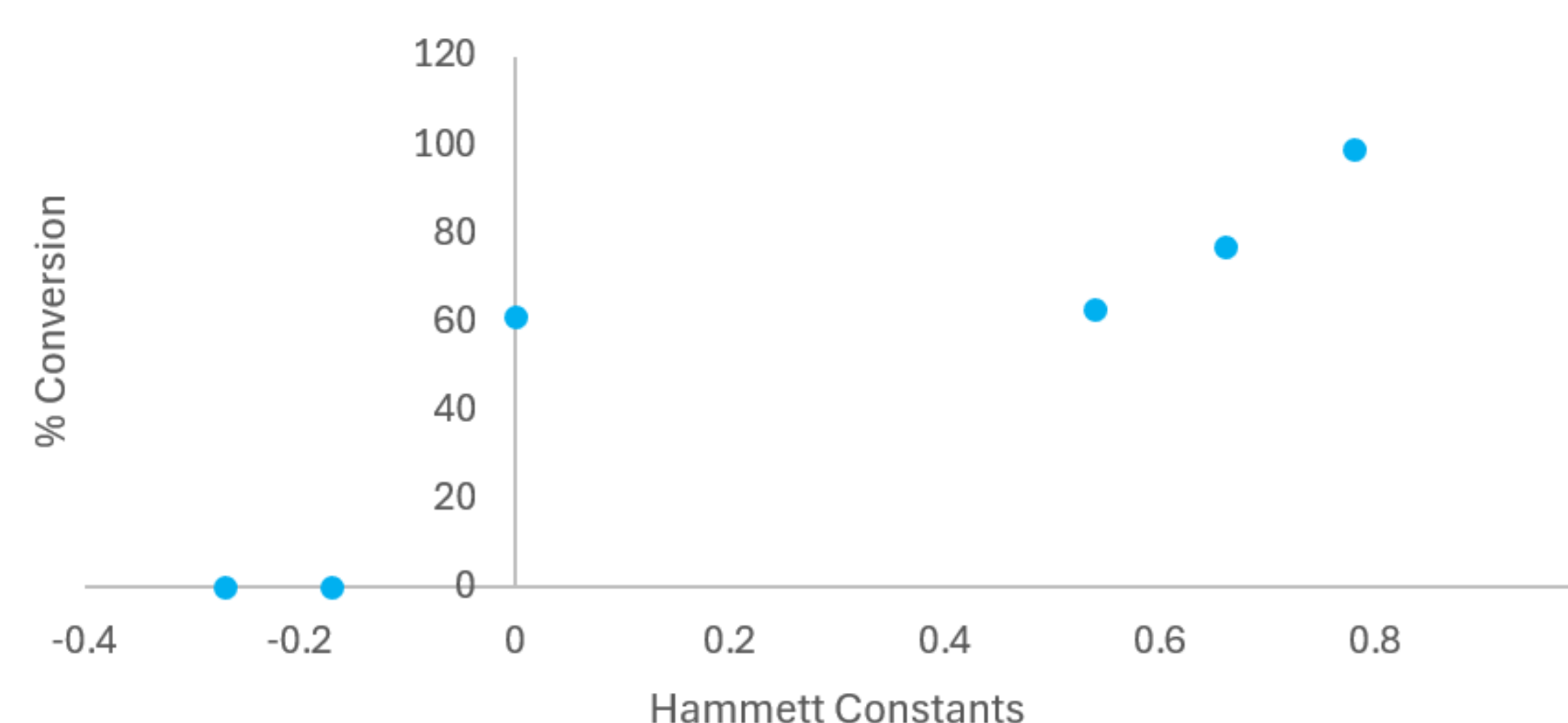
- Oxidative addition and subsequent reductive elimination can form Pd-Aryl complexes.
- Hammett Constants are a measure of the Electron Donating/Withdrawing ability of a substituent in the para/meta position on a benzene.



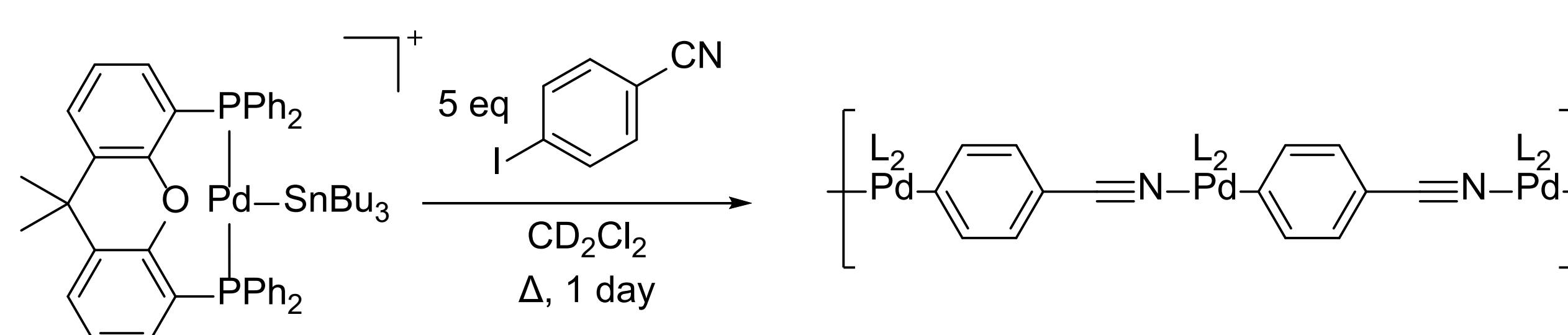
Reaction	X	L	Hammett Constant	% Conversion
1	Br	H	0	85%
2	I	H	0	61%
3	Cl	H	0	0%

Reaction	X	L	Hammett Constant	% Conversion
4	Br	Methoxy	-0.27	0%
5	Br	CH <sub>3</sub>	-0.17	0%
6	I	NO <sub>2</sub>	0.78	99%
7	I	CN	0.66	77%
8	I	CF <sub>3</sub>	0.54	63%
9	I	Methyl Ester	-	99%
10	Br	Methyl Ester	-	71%

Percent Conversion vs Hammett Constants of Substituents

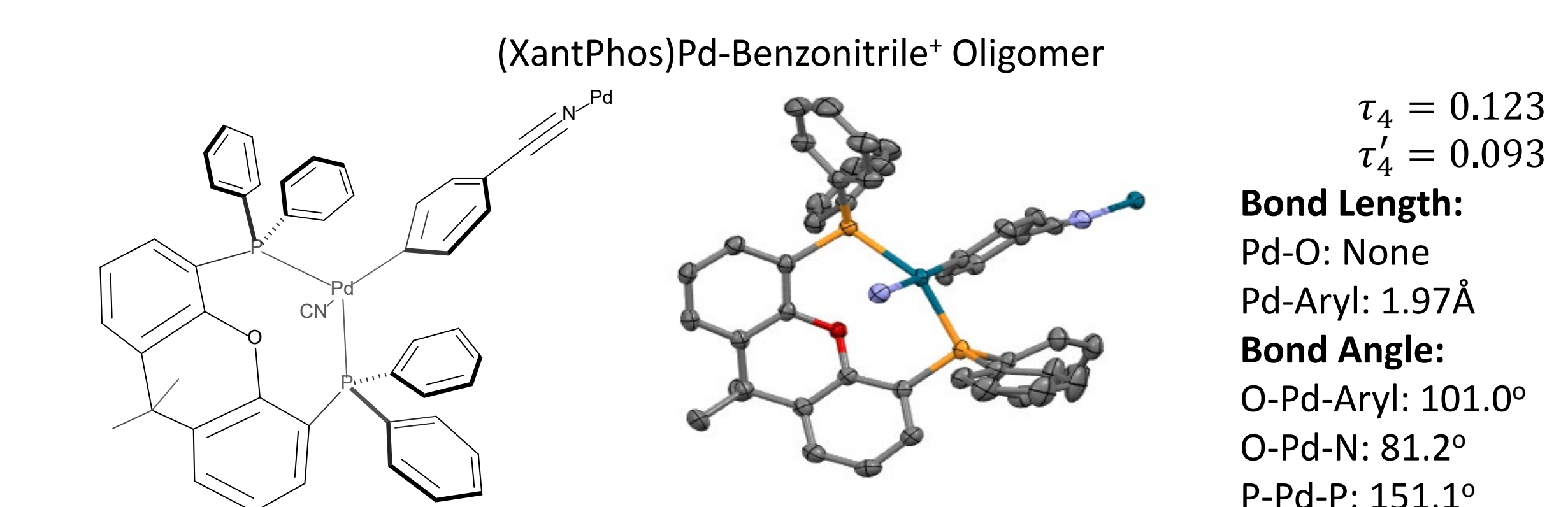
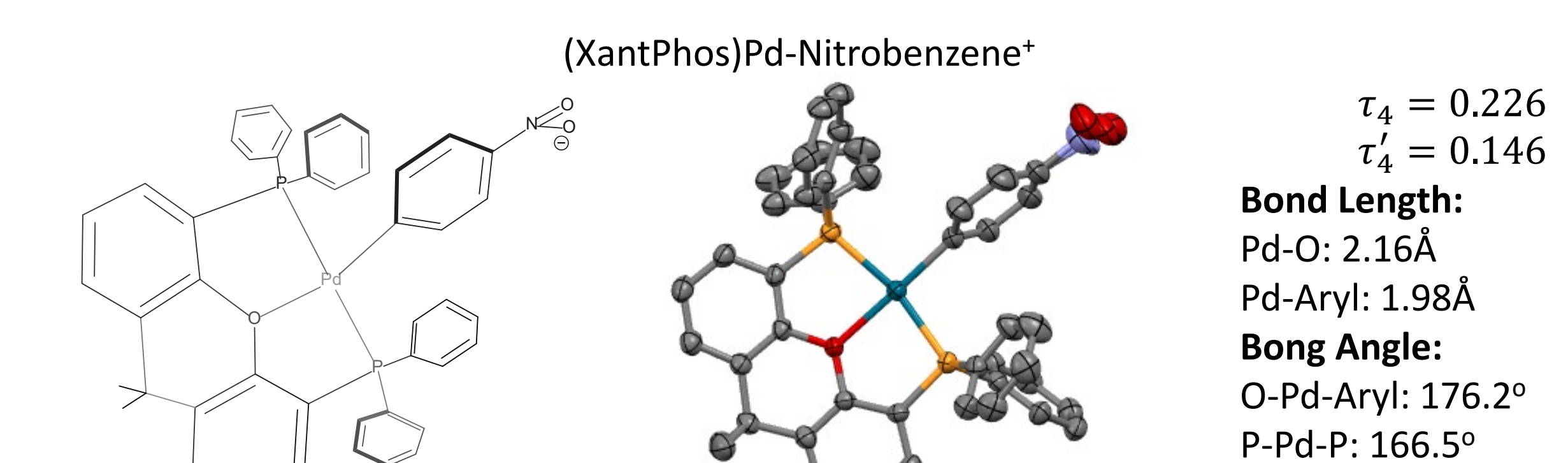
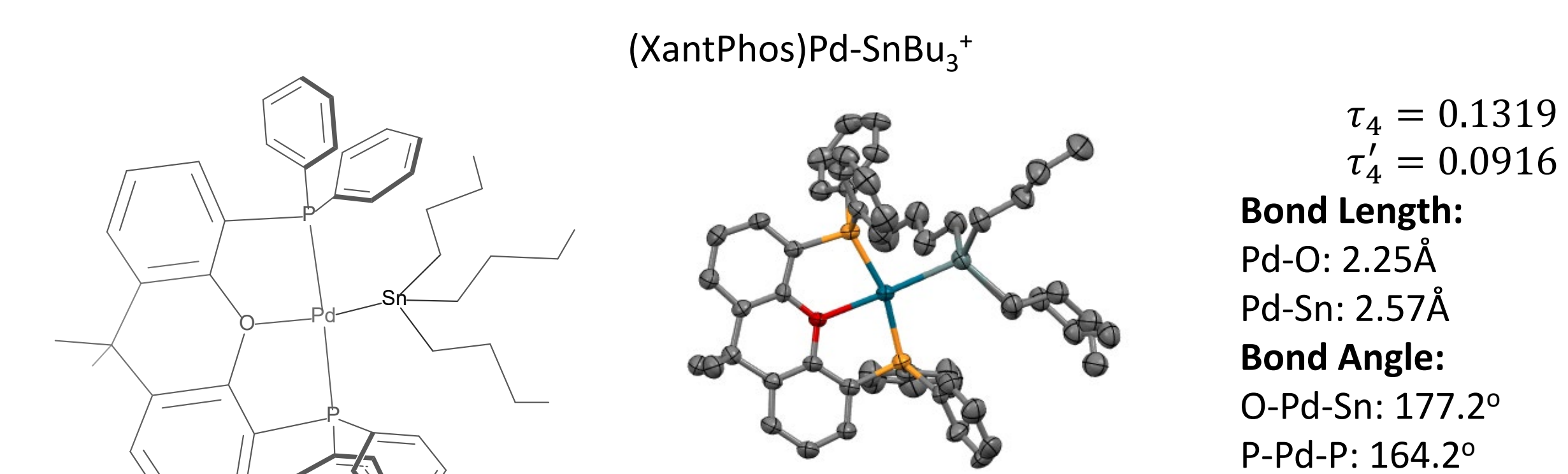


- Electron Donating substituents do not perform this oxidative addition reaction.
- The more withdrawing the group, the better the oxidative addition occurs.
- The formation of the Pd-Aryl bond is strong enough to cleave the Pd-Sn bond.



- Oligomer formed in Solid-State with nitrile
- Nitrile readily attacks the palladium as a nucleophile

### Crystal Structures



### Conclusions and Future Work

- Development of an air-stable Pd-Sn species
- Formation of Pd-C bonds produces enough energy to cleave Pd-Sn bonds, where the palladium has a lower electron density as compared to when its bond with tin
- Calculations for the electron density in the Pd-C and Pd-Sn bonds by Pascale Hunter
- Expand substrate scope for the aryl halides
- Explore nucleophilic addition of amines to the palladium

#### Acknowledgements

- Pascale Hunter for calculations for the (XantPhos)Pd-SnBu<sub>3</sub><sup>+</sup> with BAR<sup>F</sup><sub>24</sub> counterion
- William Hearne for acquiring and solving all crystal structures

