# A Small Mercury Drop and a Quick catalytic Stop: A Toxic Test for Homogeneity

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## Background

Our understanding of the identity of catalytic species allows us to improve the efficiency and scope of catalysts. One of the most popular tests for determining homogeneity is the mercury drop test. The test relies on the assumption that elemental $Hg^0$ will amalgamate heterogeneous $M^0$ species, reducing their catalytic ability, while leaving homogenous $M^{II}$ unaffected.

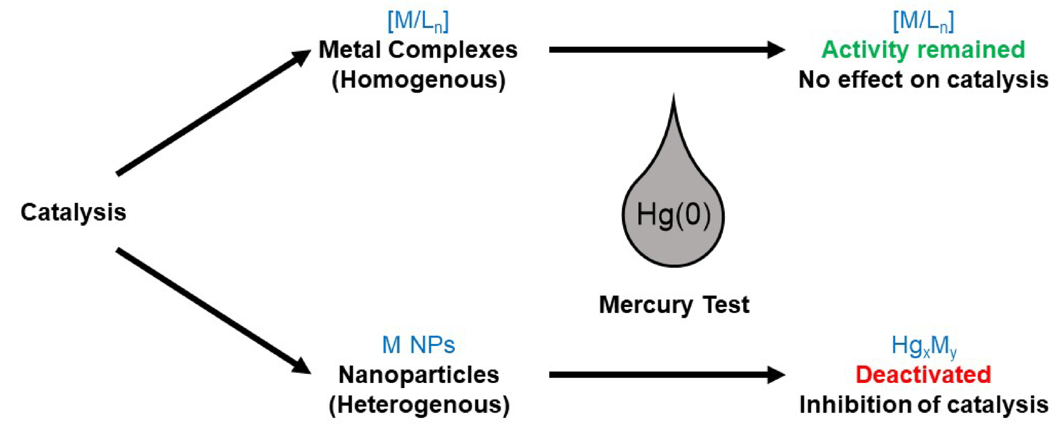



**Fig.1** Underlying principles of the mercury drop test

In contrast, recent studies have shown that elemental mercury does interact with homogenous $M^{II}$ species, casting doubt on the accuracy of this method.[1] We focused on the limitations of the mercury test during two stages of palladium catalyzed cross-coupling reactions: catalyst activation and oxidative addition.

## Methodology

Pressurized sample infusion electrospray ionization mass spectrometry (PSI-ESI-MS) was used to monitor the results of the mercury drop test in real time.

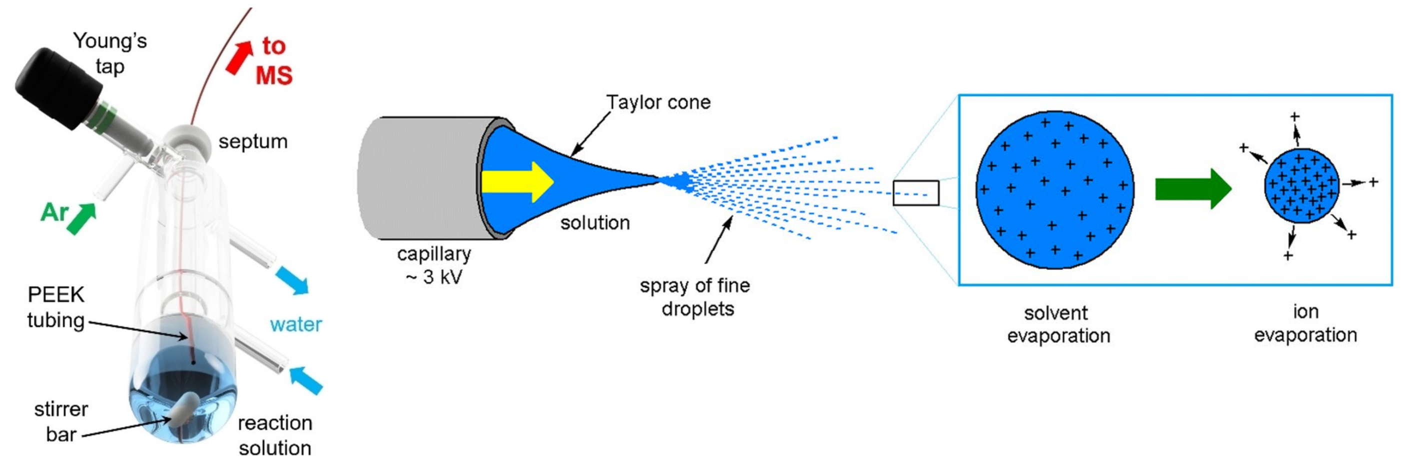
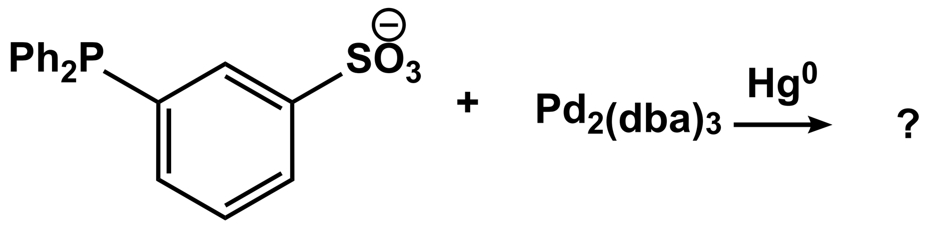



**Fig. 2** Pressurized sample infusion electrospray ionization mass spectrometry

## Catalyst Activation



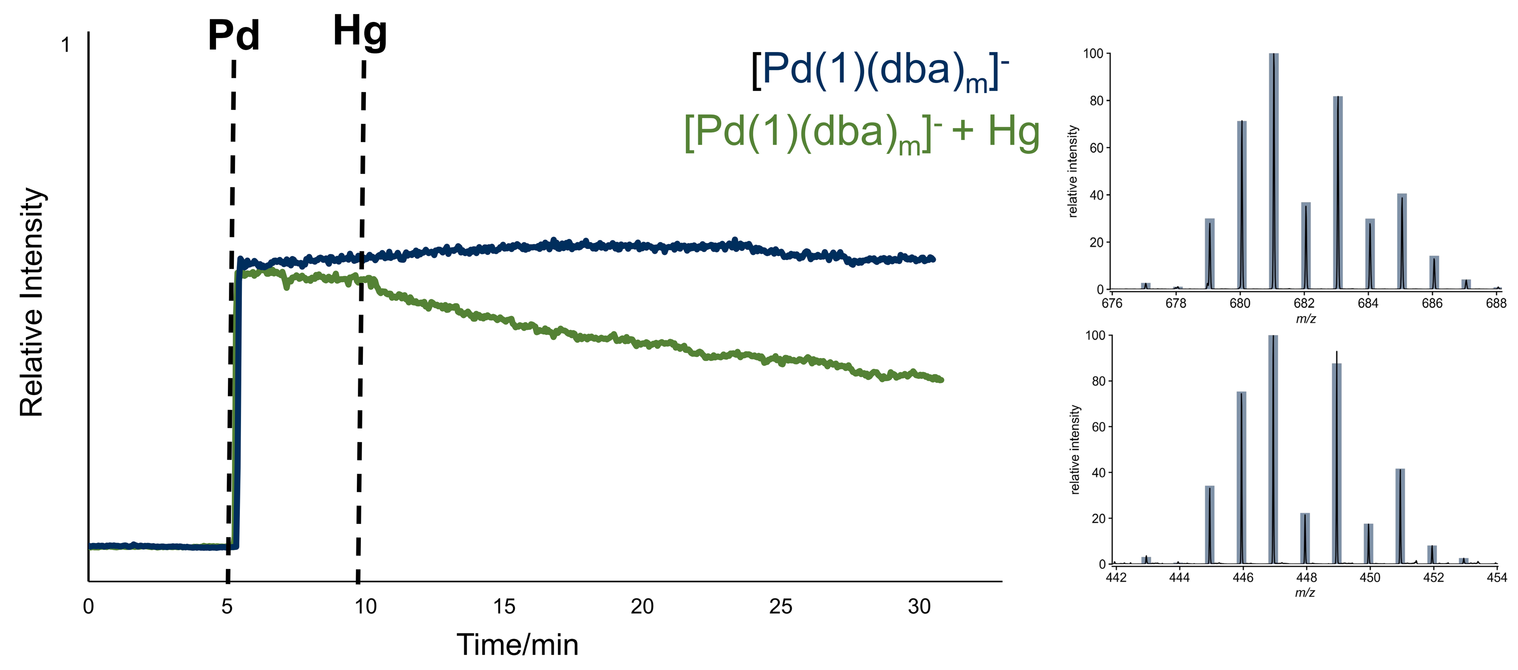
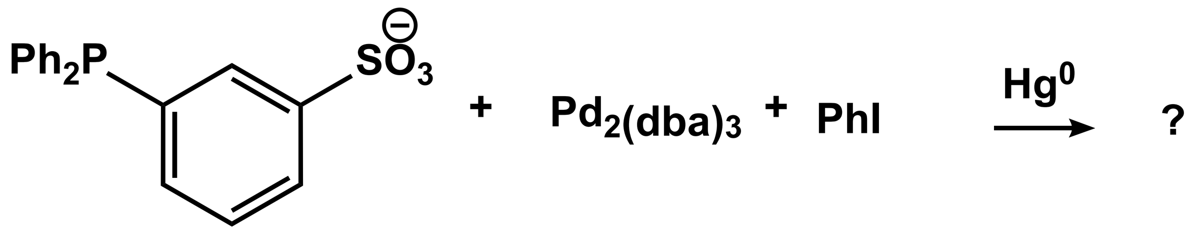




**Fig. 3** Normalized PSI-ESI-MS chromatogram showing the impact of mercury on catalyst activation of $Pd_2(dba)_3$ with [1]. m = 0-1. Isotope patterns with calculated error bars are displayed on the right.

## Oxidative Addition



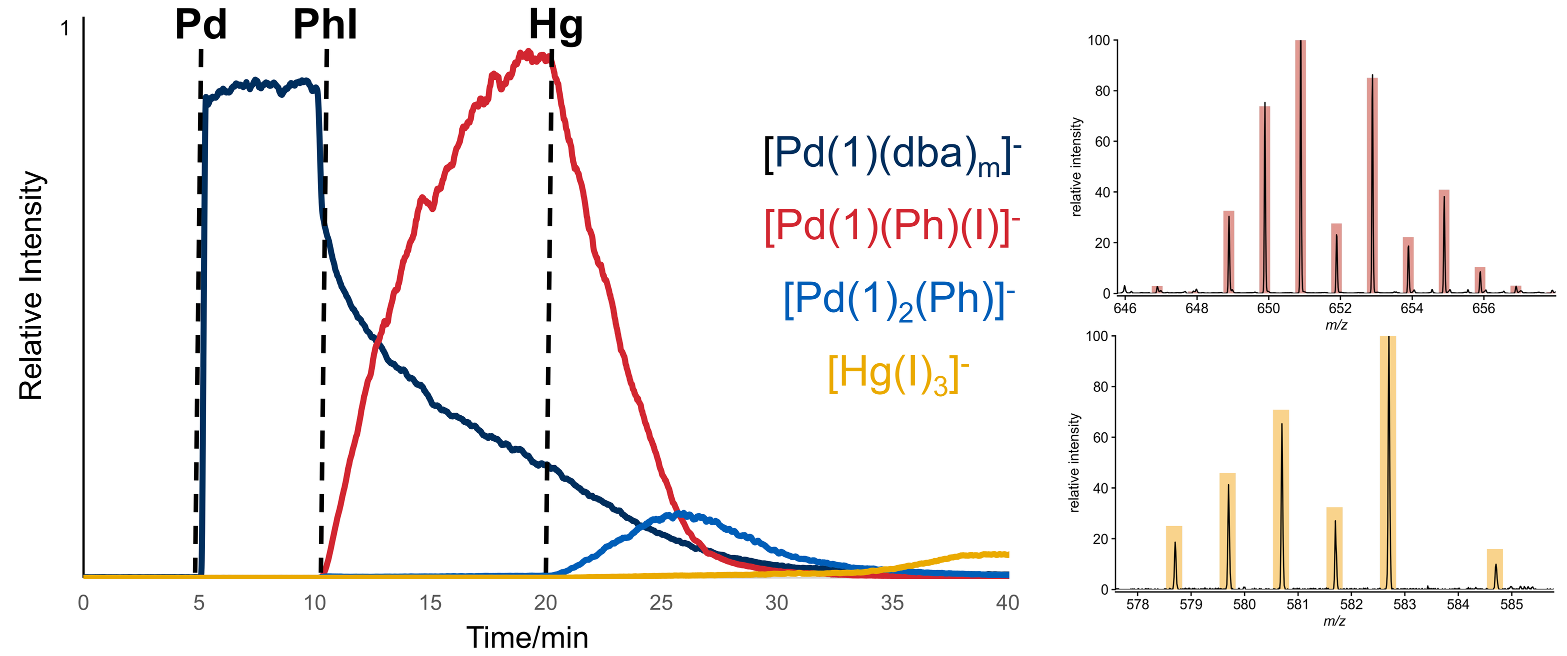
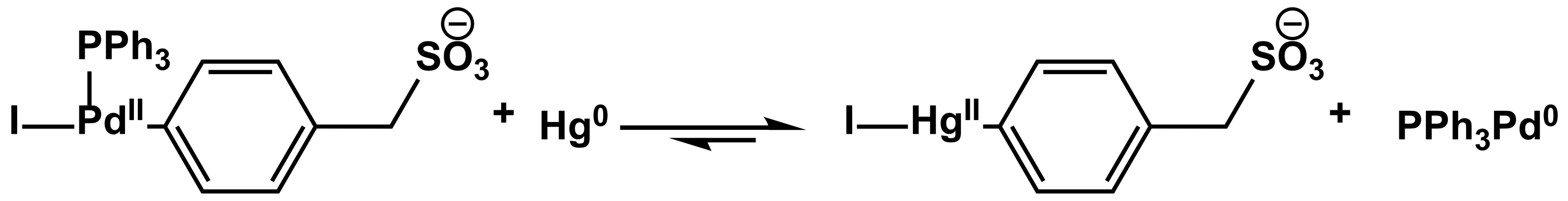




**Fig. 4** Normalized PSI-ESI-MS chromatogram of the effect caused by mercury on oxidative addition using iodobenzene. m = 0-1. Isotope patterns with calculated error bars are displayed on the right.

## Transmetalation



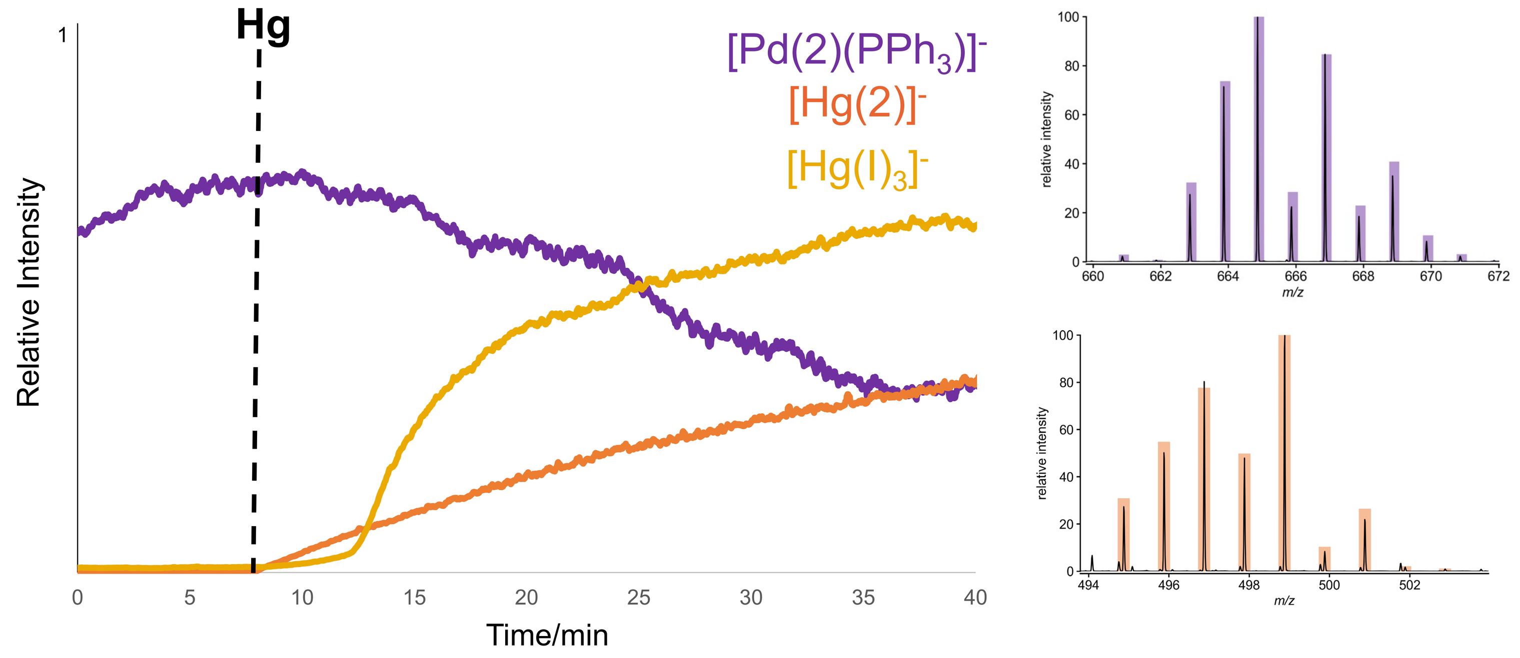
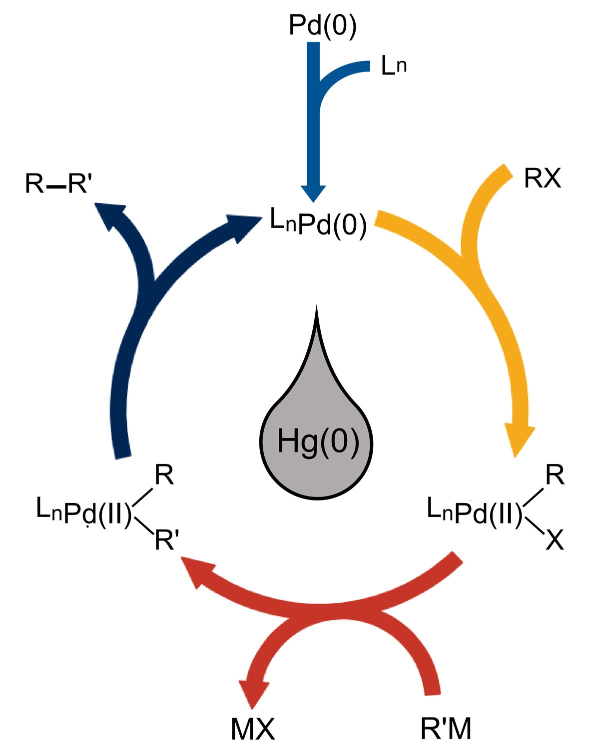




**Fig. 5** Normalized PSI-ESI-MS chromatogram. Direct observation of mercury transmetalation during oxidative addition of $Pd(PPh_3)_4$ with [2]. Isotope patterns with calculated error bars are displayed on the right.

## Discussion



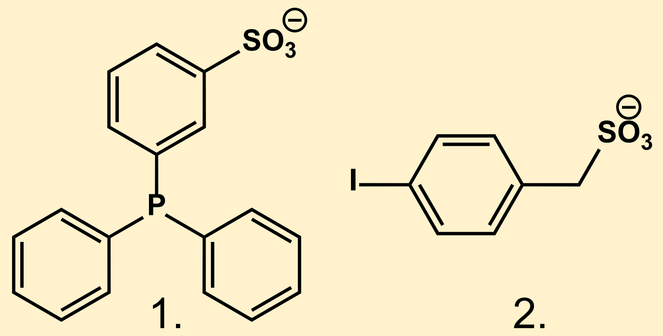

Despite the assumptions behind the test, we found that elemental mercury interacts with several homogenous species involved in catalyst activation and oxidative addition.

Using PSI-ESI-MS, we showed that there are a variety of mechanisms occurring involving elemental mercury and homogenous palladium species. The driving force of these interactions is likely the formation of mercury-palladium amalgams.

Researchers should be aware of the limitations of the mercury drop test. To avoid erroneous conclusions regarding a catalyst's identity, additional tests should be performed in combination with the mercury test.

## Charged Tags

Mass spectrometry requires analytes be charged. We used sulphonated analogues of triphenylphosphine and iodobenzene to track critical species.




1. 2.

## References

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## Acknowledgements

This research was supported by the Jamie Cassels Undergraduate Research Awards, University of Victoria, and supervised by Professor Scott McIndoe (Chemistry).

I acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC).