

1 A SIMPLIFIED OVERVIEW OF THE CHEMONT0 METHODOLOGY

1.1 Reaction is Heck reaction as shown below:



Steps to construct CHEMONT0 knowledge:

Step: (1) Read the setup file in XYZ format. Step: (2) SUI Identification. Step: (3) Chemical Unit Identification, Step: (4) Reaction Center Identification, Step: (5) Constructing the hybridization of atoms.

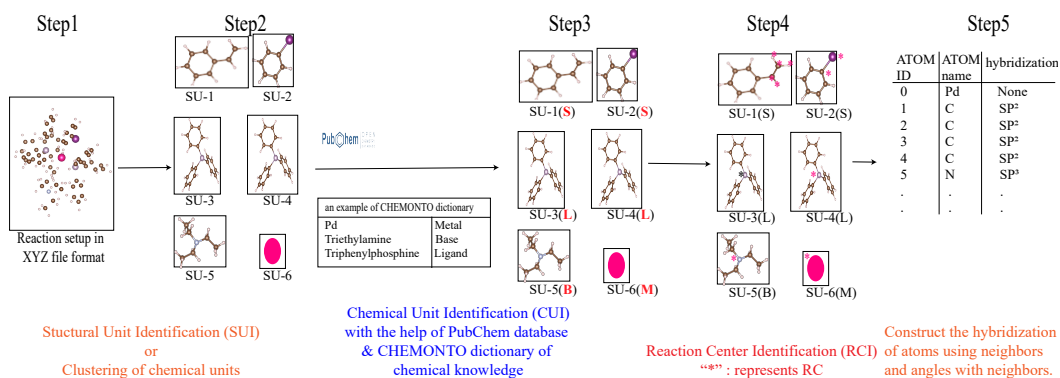
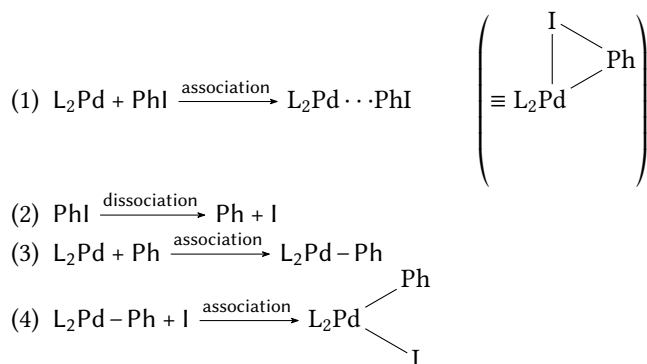


Fig. 1. The five basic steps of CHEMONT0. Step 1 corresponds to reading the setup file. Steps 2 and 3 address SUI and CUI, respectively. There are a total of six SUs. Step 3 further includes RCI; for example, the substrate PhI contains two RCs, styrene contains five RCs, while a ligand, a base, and a metal each contain one RC. The label M represents metal, L represents ligand, B represents base, and S represents substrate.

1.2 An example of ERPO of oxidative addition which provides paths to AFIR



In all the steps, it is assumed that both the Ls are attached to Pd. Steps (3) and (4) can be interchanged.

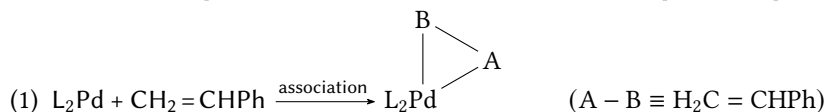
Figure 1, step 4 shows that the substrate PhI has two RCs and the metal Pd has one RC. If Pd_{Id} , Ph_{Id} , and I_{Id} are the reaction centers of Pd, Ph, and I, respectively, and $d(\text{X}, \text{Y})$ measures Euclidean distance between X and Y, then the following conditions have to be fulfilled for defining the oxidative addition.

1.3 The use of ERPO in section 1.2 to find oxidative addition from reaction network:

- (1) In ERPO definition of oxidative addition (section 1.2), the first option is not required for checking the completion of oxidative addition.
- (2) $d(I_{Id}, Ph_{Id}) > \delta$,
- (3) $d(Pd_{Id}, Ph_{Id}) < \delta$,
- (4) $d(Pd_{Id}, I_{Id}) < \delta$.

$\delta = 3.0 \text{ \AA}$. During the evaluation of the above distance criteria, atomic hybridizations are additionally considered to verify the validity of each SU through the `allowed_changes` option. For further details, please refer to the main manuscript.

1.4 Another example of ERPO of olefin insertion which provides paths to AFIR



1.5 The use of ERPO in section 1.4 to find olefin insertion from reaction network:

- (1) $d(Pd_{Id}, C1_{Id}) < \delta$,
- (2) $d(Pd_{Id}, C2_{Id}) < \delta$,

where C1 and C2 represent atom IDs of two olefin carbon atoms.

Similarly, other ERPOs can be built. Since the conditions for oxidative addition and olefin insertion are checked separately, their overlap leads to the idea of overlapping ERPOs.