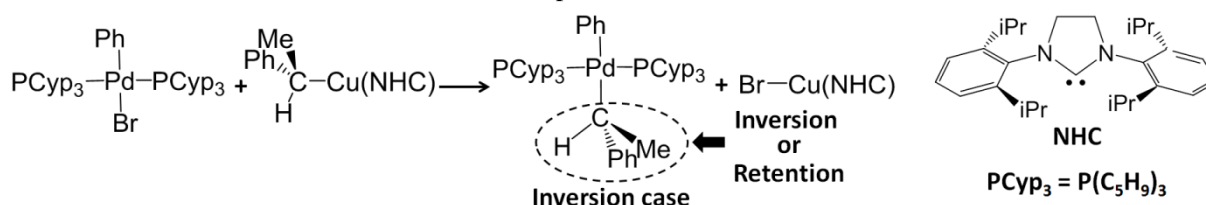


Characteristic Features of Transmetalation of Pd(II)-Ph Complex with Cu(I)-alkyl Complexes: Theoretical Study

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[Introduction] Recently a new kind of reductive cross-coupling reaction of aryl bromides with 1-arylalkenes was succeeded by cooperative Pd/Cu catalysis.¹ In this reaction, the transmetalation is involved as one of the most important steps (Scheme 1) but the mechanism is unclear. In this work, we theoretically investigated the transmetalation reaction between Pd(II)-Ph and Cu(I)-R complexes to elucidate the reaction mechanism and electronic process.



Scheme 1. Transmetalation between Pd(II)-Ph and Cu(I)-CHMePh complexes.

[Computations] All calculations were performed by DFT method with the wB97XD functional. In geometry optimization, the LANL2DZ basis sets were employed for Pd, Cu, and Br atoms. The 6-31G* basis sets were used for other atoms. In energy evaluation, the SDD (Stuttgart-Dresden-Bonn) basis sets were employed for the Pd, Cu, and Br atoms. The 6-311G(d) basis sets were used for other atoms. In both basis sets, a d-polarization function was added to Br.

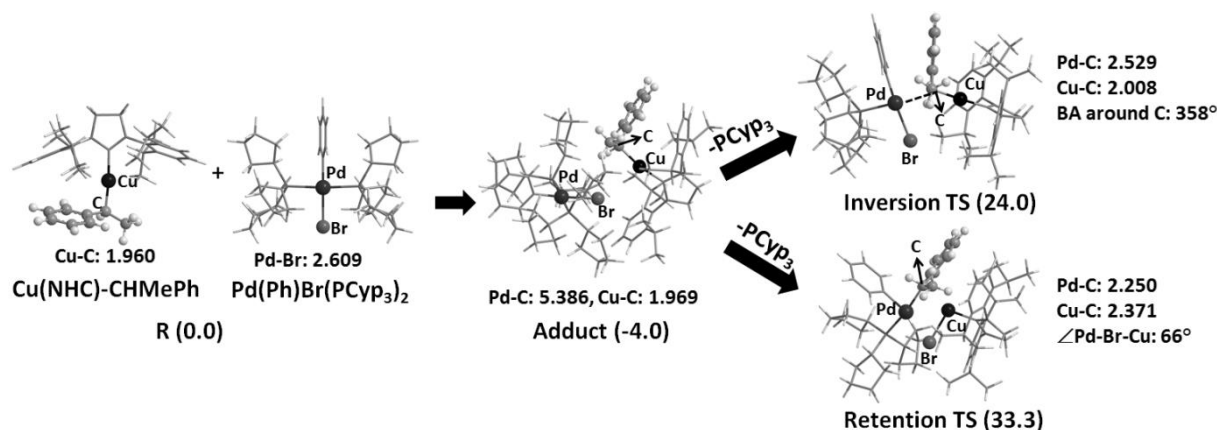


Figure 1. Changes in geometry and Gibbs energy (in kcal/mol) in the transmetalation of CHMePh group.

[Results and Discussion] In the transmetalation of CHMePh group, the four-coordinated Pd(II)-Ph and two-coordinated Cu(I)-CHMePh complexes firstly form a weak contact adduct (Figure 1). One of the PCyp₃ is dissociated prior to the transmetalation because the geometry of the adduct is too congested

around Pd. Two types of mechanisms are possible in the transmetallation: one is inversion mechanism and another is retention one. In the inversion mechanism, the CHMePh group becomes planar around the sp^3

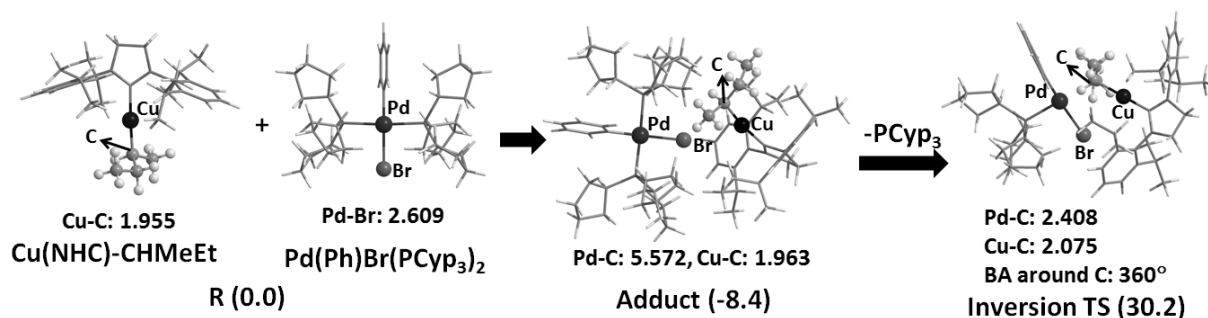


Figure 2. Changes in geometry and Gibbs energy (in kcal/mol) in the transmetallation of CHMeEt group.

carbon in a transition state (TS) and its configuration changes. In the retention mechanism, CHMePh changes its direction in TS and the configuration of CHMePh is reserved. The activation energy for retention TS (37.3 kcal/mol) is much larger than that for inversion TS (28.0 kcal/mol), as shown in Figure 1. Therefore, the inversion mechanism is favorable in this transmetallation, which agrees with experimental observations.

In the transmetallation of CHMeEt group, $PCyp_3$ dissociation also occurs. The CHMeEt group becomes planar around the sp^3 carbon in the inversion TS (Figure 2) with an activation energy of 38.6 kcal/mol. On the other hand, the reaction in retention mechanism occurs with no barrier, indicating that the retention mechanism is favorable in the CHMeEt case.

To understand the reason why the reaction mechanism is different between CHMePh and CHMeEt groups, we analyzed the $(CHMeX)^-$ ($X=Ph, Et$) anion with the same geometry as in the reactant and TS. As going from the reactant to TS, the $(CHMePh)^-$ moiety becomes more stable, as shown in Table 1. This is because orbital conjugation occurs between the lone-pair (LP) orbital of the sp^3 carbon and the π^* MO of Ph group (Figure 3); actually, the energy destabilization of the LP orbital is small (0.30 eV). In contrast, the $(CHMeEt)^-$ group becomes more unstable, as going from the reactant to TS. This is because no orbital conjugation occurs between the Et group and the LP orbital.

Reference

- 1) K. Semba, K. Ariyama, H. Zheng, R. Kameyama, S. Sakaki, Y. Nakao, *Angew. Chem., Int. Ed.* **2016**, *55*, 6275-6279.

Table 1. Deformation energy (DE, in kcal/mol) and energy destabilization ($\Delta\epsilon$) of lone-pair (LP) orbital of $(CHMeX)^-$ anion.

	DE ^a /kcal/mol	$\Delta\epsilon^b$ /eV
$(CHMePh)^-$	-3.4	0.30
$(CHMeEt)^-$	11.6	0.82

^a DE = E(TS) - E(R); ^b $\Delta\epsilon$ = LP(TS) - LP(R)

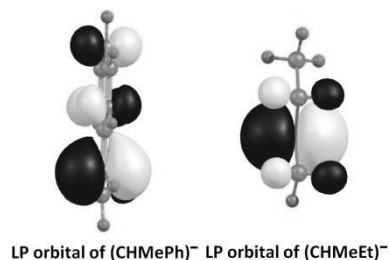
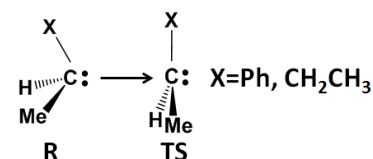


Figure 3. LP orbitals of $(CHMePh)^-$ and $(CHMeEt)^-$ anions with TS geometries.