XAFS-based Structural Study of Homogeneous Catalytic Species

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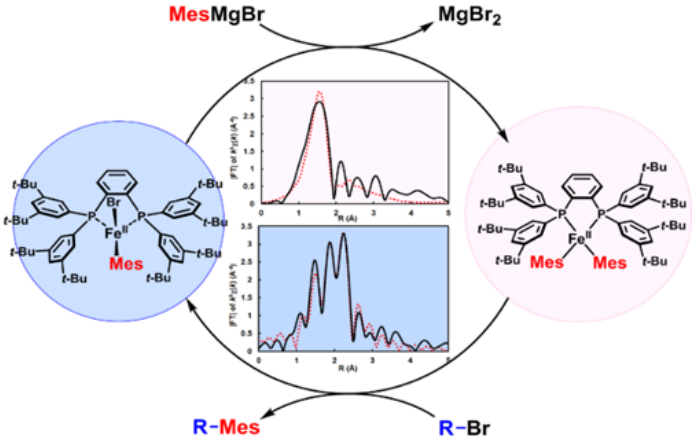
The renaissance of iron-catalyzed cross-coupling reactions in the last decade has been triggered by a standpoint of element strategy, which seeks discovery of unprecedented reactivity and selectivity apart from the conventional palladium- and nickel-catalyzed cross-coupling reactions. Despite the significant progress in cross-coupling chemistry based on 3d-transition metal catalysts including iron catalysts, there has been little detailed mechanistic studies because the large paramagnetic shifts and the related loss of spin–spin coupling information in NMR spectra hampers solution phase structural study of catalytic intermediates. The inherent chemical instabilities of 3d-metal–carbon bonds toward H_2O and O_2 further complicate the research to elucidate reaction mechanisms. We therefore attempted to apply X-ray absorption fine structure (XAFS) for structural and mechanistic investigations of paramagnetic catalytic intermediates in homogeneous iron-catalyzed cross couplings. Despite the widespread application and significant contribution of synchrotron XAFS in the research field of heterogeneous catalyst, its application to homogeneous catalysts is still underdeveloped and scarcely applied to *in-situ* structure determination of unstable and highly reactive organometallic intermediates, especially in organic reaction mixtures.

Recently, we reported that the solution phase XAFS-based identification and structure determination of some organoiron intermediates of iron-catalyzed Kumada–Tamao–Corriu (KTC)-type cross-coupling reaction as shown in Scheme 1.[1] Solution phase XAFS study at BL14B2 beamline at SPring-8 was successfully performed to determine the valency and structures of the corresponding intermediates being engaged in the $FeBr_2$(SciOPP)-catalyzed KTC-type coupling. It is noteworthy that EXAFS fitting analysis with support of DFT calculation enabled us to solve the solution phase structure of the key catalytic intermediates of FeBrMes(SciOPP) and dimestyliron $FeMes_2$(SciOPP), which formed by the stepwise reaction of MesMgBr with $FeBr_2$(SciOPP) in THF.



Scheme 1. Iron-catalyzed KTC-type coupling reaction

References

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