

XAS- and DFT-based Mechanistic Study on Homogeneous Iron Catalysis in Organic Synthesis

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In this decades, iron catalysis has received intensive research interests from a standpoint of “element strategy” criteria, where the use of earthly abundant, low price, and environmentally friendly metals for catalyst development is strongly required. In this context, renaissance of cross-coupling reactions has been achieved by replacing the conventional palladium- and nickel-catalyzed cross-coupling reactions by iron-catalyzed ones and this trends is accelerated by discoveries of unprecedented reactivity and selectivity of iron-catalyzed coupling reactions being inaccessible by other metals. However, the origin of unique catalytic properties of iron has not been well clarified yet because of the significant difficulty for structural determination of organoiron catalytic intermediates. The large paramagnetic property of organoiron species hampers NMR-based solution-phase structural study which is the most established method for mechanistic study of homogeneous catalytic reactions. We therefore conducted solution-phase XAS-based investigation of catalytic intermediates in iron-catalyzed cross-coupling reactions to elucidate the precise reaction mechanism.¹

In this research, we developed specially designed cells for solution-phase XAS, bearing chemical resistance PEEK-made body and ultra-thin Si₃N₄ X-ray window. The XAS measurement was carried out at BL14B2 and BL27SU beamlines in SPring-8 with the appropriate settings for the target reactions and absorbing atoms. The atomic coordinates for FEFF-based EXAFS-fitting structural analysis of catalytic intermediates were obtained by DFT calculation with suitable functionals and basis sets using Gaussian09 and 16.

We found that various iron complexes bearing bisphosphine and *N*-heterocyclic carbene ligands showed excellent catalytic activities toward Corriu-Kumada-Tamao-type cross-coupling reactions.^{2,3} DFT-based theoretical study of these reactions indicated formations of aryliron or alkyliron complexes as key catalytic intermediates. XANES observation of stoichiometric steps of the calculated catalytic cycles enabled us to determine oxidation states and coordination geometries of the proposed catalytic organoiron intermediates of FeArX(Bisphosphine), FeAr₂(Bisphosphine), and FeRX_n(SIPr) (X = Cl, Br) formed by the transmetalation reactions of catalyst precursors and Grignard reagents (ArMgX or RMgX). EXAFS-fitting analysis using atomic coordinates obtained from DFT calculation adequately proved the formation of these intermediates with accurate molecular structures.

In conclusion, combination use of solution-phase XAS and DFT calculation has been demonstrated to be highly effective to elucidate the reaction mechanisms of homogeneous iron-catalyzed cross-coupling reactions, being inaccessible by the conventional NMR analysis.

References

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