

Mechanistic investigation of iron-catalyzed Kumada-Tamao-Corriu-type cross-coupling reactions based on solution-phase XAFS

A renaissance of iron-catalyzed cross-coupling reactions in the last decade has been triggered in the standpoint of element strategy, the aim of which is the discovery of unprecedented reactivity and selectivity of common and ubiquitous metals apart from those of conventional precious metals. Despite the significant progress in cross-coupling technology through the use of 3d-transition metal catalysts including iron catalysts, the large paramagnetic shifts and the related loss of spin-spin coupling information in NMR spectra often hampers solution-phase structural study of catalytic intermediates in the reaction mixture. Conventional ESR spectroscopy also suffers difficulty in measuring typical Fe^{+2} and Fe^{+3} species with $S > 1/2$, as they are often invisible. In addition, the inherent chemical instabilities of 3d-metal-carbon bonds toward H_2O and O_2 complicate the conventional mechanistic study based on X-ray crystallography of isolated intermediates. We therefore attempted to apply synchrotron X-ray absorption spectroscopy (XAFS) for the structural and mechanistic investigation of paramagnetic organometallic intermediates in homogeneous iron-catalyzed reactions. Despite the widespread application and significant contribution of synchrotron XAFS in the research field of heterogeneous catalysts, its application to homogeneous catalysts is still underdeveloped and rare for *in situ* structural determination of unstable and highly reactive organometallic intermediates, especially in organic reaction mixtures.

Recently, we reported the solution-phase XAFS-based identification and structural determination of the organoiron intermediates of iron-catalyzed Kumada-Tamao-Corriu (KTC)-type cross-coupling reactions [1]. We have developed an iron bisphosphine complex, $\text{FeX}_2(\text{SciOPP})$ [2], that has proven to be highly effective toward various types of coupling reaction. For the $\text{FeX}_2(\text{SciOPP})$ -catalyzed KTC-type reaction, we proposed a formal non-redox Fe^{+2} - Fe^{+2} mechanism, as shown in Fig. 1. However, a variety of mechanisms including Fe^{+1} - Fe^{+3} , Fe^0 - Fe^{+2} , and Fe^{-2} - Fe^0 redox pathways have been proposed, and complicating the issue of the mechanism of iron-catalyzed cross-coupling reactions. Therefore, we carried out a solution-phase XAFS study at beamlines BL14B2 and BL27SU to elucidate the oxidation state and structures of the corresponding intermediates that are engaged in the $\text{FeX}_2(\text{SciOPP})$ -catalyzed KTC-type coupling. Firstly, the formation of the described organoiron intermediates of

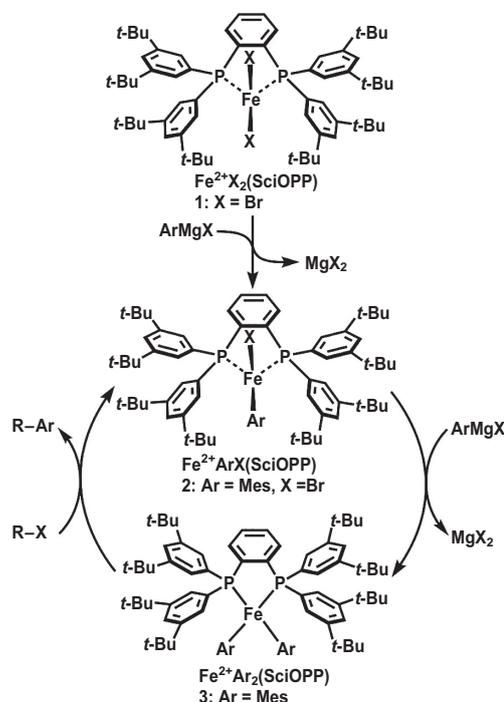


Fig. 1. Proposed mechanism of $\text{FeX}_2(\text{SciOPP})$ -catalyzed KTC-type coupling of arylmagnesiumhalide with haloalkanes.

$\text{FeBrMes}(\text{SciOPP})$ 2 and $\text{FeMes}_2(\text{SciOPP})$ 3 was examined by solution-phase XANES. The reaction of $\text{FeBr}_2(\text{SciOPP})$ 1 and MesMgBr was conducted in THF with 1:1 and 1:2 ratios at -30°C . In a glovebox, the warmed reaction mixture was transferred into a gastight cell for solution-phase XAFS, as shown in Fig. 2. The Fe K-edge XANES spectra of the THF solution of 1, and the reaction mixtures obtained from

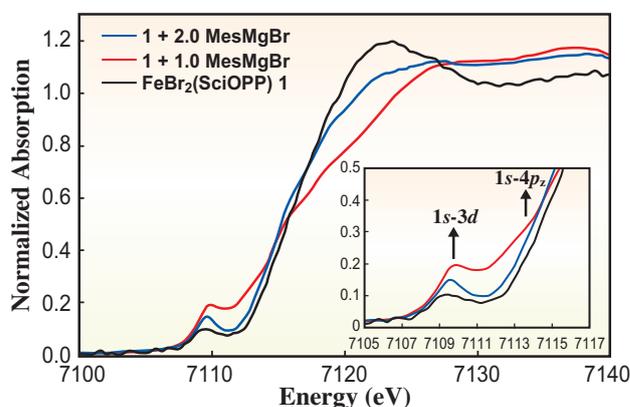
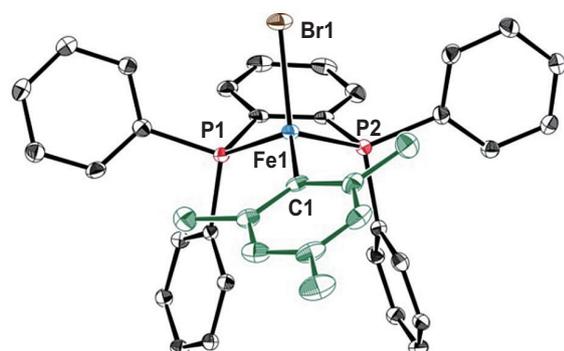


Fig. 2. A series of Fe K-edge XANES spectra of THF solution of 1 (black line) and reaction mixtures of 1 with 1.0 equiv (blue line) and 2.0 equiv (red line) MesMgBr .

1.0 and 2.0 equiv additions of MesMgBr to **1** revealed the formation of the expected divalent organoiron species of monomesityliron FeBrMes(SciOPP) **2** and dimesityliron FeMes₂(SciOPP) **3**. The observed pre-edge peak at around 7109.5 eV and the shoulder peak at 7112.3 eV can be assigned to a characteristic 1s–3d electron transition of tetrahedral iron(II) complexes and the 1s–4p_z transition of square planar iron(II) complexes, respectively.

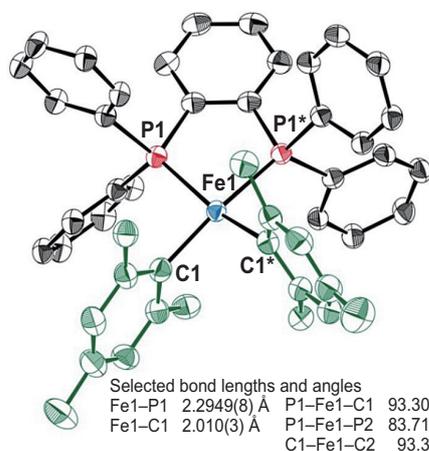
The observed organoiron intermediates were successfully isolated under strictly water- and oxygen-removed conditions and the resulting micron-size single crystals were used in low-temperature rapid single-crystal X-ray diffraction analysis at beamlines **BL40XU** and **BL02B1** to elucidate the molecular structures of **2** and **3**. As shown in Fig. 3, the tetrahedral geometry of **2** and square planar geometry of **3** are in close agreement with the geometries predicted by XAFS.

Solution-phase structure determination based on Fe K-edge XAFS was successfully performed in THF solutions of **2** and **3** and high-quality EXAFS spectra were obtained (Fig. 4). The FEFF fitting calculation



Selected bond lengths and angles

Fe1–Br1	2.4182(5) Å	P1–Fe1–C1	124.86(8)°	P1–Fe1–P2	78.33(2)°
Fe1–P1	2.4575(8) Å	P2–Fe1–C1	119.72(8)°	C2–Fe1–Br1	125.38(8)°
Fe1–P2	2.4430(7) Å	P1–Fe1–Br1	96.97(2)°		
Fe1–C1	2.046(3) Å	P2–Fe1–Br1	100.19(2)°		



Selected bond lengths and angles

Fe1–P1	2.2949(8) Å	P1–Fe1–C1	93.30(8)°
Fe1–C1	2.010(3) Å	P1–Fe1–P2	83.71(3)°
		C1–Fe1–C2	93.3(1)°

Fig. 3. Molecular structures of **2** and **3** with selected bond lengths and angles. Hydrogen atoms and *t*-Bu groups have been omitted for clarity.

using crystal-structure-based fitting models revealed that the Fe–C, Fe–Br, and Fe–P bond lengths, as well as the solution phase geometries of **2** and **3**, agree well with those of the crystal states.

Finally, the cross-coupling activity of isolated mesityliron species **2** and **3** were adequately confirmed by their reactions with 1-bromodecane under both stoichiometric and catalytic conditions. The formation of the corresponding **1** was also confirmed by *in situ* EXAFS analysis of the reaction mixture.

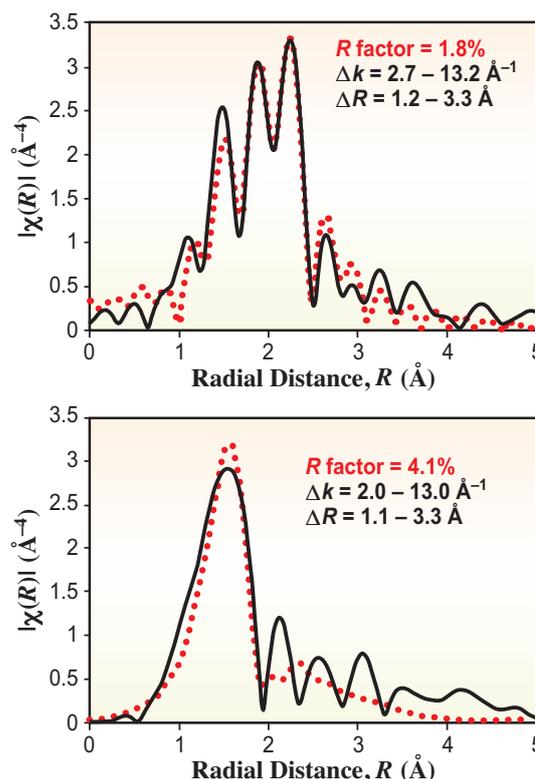


Fig. 4. EXAFS spectra of the THF solutions of **2** and **3** with fitted results.

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