Published in final edited form as:

Organometallics. 2020 January 13; 39(1): 201–205. doi:10.1021/acs.organomet.9b00733.

Direct Observation of Transmetalation from a Neutral Boronate Ester to a Pyridine(diimine) Iron Alkoxide

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Abstract

Transmetalation of the neutral boronate esters, (2-benzofuranyl)BPin and (2-benzofuranyl)BNeo (Pin = pinacolato, Neo = neopentylglycolato) to a representative pyridine(diimine) iron alkoxide complex, (ⁱPrPDI)FeOEt (ⁱPrPDI = 2,6-(2,6-ⁱPr₂-C₆H₃N=CMe)₂C₅H₃N; R = Me, Et, SiMe₃), to yield the corresponding iron benzofuranyl derivative was studied. Synthesis of the requisite iron alkoxide complexes was accomplished either by salt metathesis between (ⁱPrPDI)FeCl and NaOR (R = Me, Et, SiMe₃) or by protonation of the iron alkyl, (ⁱPrPDI)FeCH₂SiMe₃, by the free alcohol R'OH (R' = Me, Et). A combination of magnetic measurements, X-ray diffraction, NMR and Mössbauer spectroscopies and DFT calculations identified each (ⁱPrPDI)FeOR compound as an essentially planar, high-spin, $S = 3/2$ compound engaged in antiferromagnetic coupling with a radical anion on the chelate ($S_{\text{Total}} = 3/2$; $S_{\text{Fe}} = 2$, $S_{\text{PDI}} = 1/2$). The resulting iron benzofuranyl product, (ⁱPrPDI)Fe(2-benzofuranyl) was characterized by X-ray diffraction and in combination with magnetic measurements, spectroscopic and computational data, was identified as an overall $S = 1/2$ compound, demonstrating that a net spin-state change accompanies transmetalation ($S_{\text{Fe}} = 1$, $S_{\text{PDI}} = 1/2$). These findings may be relevant to further development of iron-catalyzed Suzuki-Miyaura cross-coupling with neutral boronate esters and alkoxide bases.

Graphical Abstract

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NMR Spectra (PDF)

CCDC 1953963, 1953965, 1954249, 1956370 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 441223 336033.

The authors declare no competing financial interest.

The success of Suzuki-Miyaura cross-coupling (SMC) with palladium catalysts has motivated the search for similar reactivity with more Earth-abundant first row transition metals.¹ Iron is particularly attractive given its high terrestrial abundance and low toxicity. While iron-catalyzed Kumada-type coupling has been known since the 1940s² and has been performed on an industrial scale,³ iron-catalyzed Suzuki-Miyaura cross coupling is by comparison less developed. Alkyl lithium-activated arylborate nucleophiles (activated with *n*-BuLi or *t*-BuLi) are often necessary for transmetalation to iron,⁴ but these anionic nucleophiles likely function more like organomagnesium reagents applied in Kumada coupling, limiting functional group tolerance and the ease of handling and operation associated with palladium-catalyzed reactions. Achieving transmetalation to iron and using comparatively mild bases (e.g. hydroxide, carbonate, alkoxide) applied routinely in palladium catalysis remains an unmet need and attractive target toward the further development of iron-catalyzed Suzuki-Miyaura cross couplings.

Nakamura and co-workers first reported an iron-catalyzed cross-coupling with a boron nucleophile, where lithium arylborates were coupled with primary and secondary alkyl halides to achieve C(sp²)-C(sp³) coupling.^{4a} Lithium aryl borate species have also been shown by Bedford and co-workers to be nucleophiles for directed C(sp²)-C(sp²) coupling.^{4c} In both cases, formation of the borate nucleophile was essential for a successful catalytic reaction and is likely required for transmetalation. Byers and co-workers have recently reported that amide bases enabled C(sp²)-C(sp³) cross coupling promoted by a cyano bis(oxazoline)-supported iron(II) precatalyst (Scheme 1).⁵ A key finding in this study was that no coupling was observed when the amide-borate complex was preformed prior to the reaction, suggesting transmetalation occurred from a neutral, rather than anionic, boron nucleophile. Alkoxide bases were ineffective due to aggregation of the resulting iron complexes. Such a pathway is analogous to that proposed for palladium SMC, whereby transmetalation from a neutral boron nucleophile to a hydroxy palladium intermediate is kinetically preferred over the alternative involving a hydroxide-coordinated borate.⁶

Examples of boron-based stoichiometric transmetalation to generate an iron aryl complex are primarily limited to lithium aryl borate nucleophiles.⁷ Neidig and co-workers demonstrated that the reaction of (SciOPP)FeCl₂ (SciOPP = spin-control-intended ophenylene bisphosphine) with lithium phenylborate resulted in two successive transmetalation events to form (SciOPP)Fe(Ph)₂, which undergoes reductive elimination to form (SciOPP)Fe(η^6 -biphenyl).⁸ Other examples include the reaction of triarylboranes with iron alkyl complexes, forming the corresponding iron aryl complex.⁹ In these examples, it is

proposed that initial alkyl abstraction by the borane forms an activated borate, which becomes the nucleophile for transmetallation.

To explore the possibility of transmetallation from a neutral boron reagent to iron, pyridine(diimine) iron complexes were selected for study using an approach previously applied by our group for cobalt.¹⁰ This class of iron compounds exhibits a rich and diverse catalytic chemistry as well as the potential for electronic metal-ligand cooperativity, giving rise to a high density of states.^{11, 12, 13} More germane to iron-catalyzed cross coupling, both iron aryl, (*i*PrPDI)Fe(Ar) (Ar = phenyl; *i*PrPDI = 2,6-(2,6-*i*Pr₂-C₆H₃N=CMe)₂C₅H₃N),¹⁴ and alkoxide (*i*PrPDI)Fe(OR) (R = Et, allyl, etc.) derivatives have been synthesized with the latter class of compounds isolated following C–O bond cleavage in esters and ethers.¹⁵ Notably, the pyridine(diimine) iron aryl complexes possess different magnetic ground states from the iron alkoxides,¹⁶ suggesting that a spin-state change may occur during transmetallation, similar to observations previously reported by our group in cobalt-catalyzed SMC.

Suzuki-type transmetallation of a neutral aryl boronic acid or ester nucleophile to an iron amide or alkoxide complex has yet to be demonstrated in stoichiometric reaction and could provide key mechanistic insights on optimal bases, iron precursors and spin states for promoting the essential fundamental organometallic transformation. Here we describe the observation of stoichiometric transmetallation of furanyl-substituted, neutral boron reagents with iron alkoxide derivatives (Scheme 1). The electronic structure implications associated with conversion of an iron alkoxide to the corresponding iron heteroaryl complexes are elucidated and the potential for iron to undergo palladium-like SMC transmetallation reactivity is demonstrated.

Because conversion of a metal-halide to the corresponding alkoxide derivative is a key step in palladium-catalyzed SMC, the salt metathesis of (*i*PrPDI)FeBr¹⁷ with various alkoxide sources was initially studied. Addition of NaOR (R = SiMe₃, Me, Et) to a diethyl ether solution of the iron bromide complex generated the corresponding (*i*PrPDI)FeOR derivatives (Scheme 2a). Pure (*i*PrPDI)FeOSiMe₃ was isolated in 57% yield following recrystallization from pentane. However, using NaOCH₃, the salt metathesis protocol yielded paramagnetic iron-containing side products in addition to the targeted (*i*PrPDI)FeOCH₃ complex. Because protonolysis of iron alkyls by free alcohols is known method for the preparation of iron alkoxide complexes,^{18, 19} pentane solutions of (*i*PrPDI)Fe(CH₂SiMe₃) were independently treated with methanol and ethanol, and, following filtration and removal of volatiles, (*i*PrPDI)FeOCH₃ and (*i*PrPDI)FeOEt were obtained in 71% and 66% yields, respectively, as green solids (Scheme 2b).

These alkoxide compounds exhibit the number of ¹H NMR resonances consistent with overall C_{2v} symmetry. As has been previously reported for (*i*PrPDI)FeX (X = Cl, Br) compounds,²² ¹H NMR resonances for (*i*PrPDI)FeOEt were observed over a wide chemical shift range (–300 to 300 ppm) at 23 °C. Specifically, the pyridine 4-CH resonance (371.51 ppm for (*i*PrPDI)FeOEt) and imine methyl CH₃ resonances (–209.74 ppm for (*i*PrPDI)FeOEt) are diagnostic for these types of complexes. For (*i*PrPDI)FeOSiMe₃, a

benzene- d_6 magnetic moment of $4.0 \mu_B$ was measured (Evans method)²⁰, consistent with the spin-only value of $3.87 \mu_B$ for three unpaired electrons and an overall $S = 3/2$ iron complex.

The solid-state structures of (*i*PrPDI)FeOSiMe₃, (*i*PrPDI)FeOEt, and (*i*PrPDI)FeOMe were determined by single crystal X-ray diffraction and representations of the molecular structures are presented in Figure 1. For all three compounds, a distorted square planar geometry was observed around the iron center with the sum of the bond angles approximating 360° in each case (R = SiMe₃: $360.43(17)^\circ$, R = Et: $360.20(13)^\circ$, R = Me: $359.96(4)^\circ$). Near linear N(2)-Fe(1)-O(1) bond angles of $174.39(11)^\circ$ ((*i*PrPDI)FeOSiMe₃), $177.30(6)^\circ$ ((*i*PrPDI)FeOEt) and $175.46(2)^\circ$ ((*i*PrPDI)FeOCH₃) were observed in all cases, suggesting some degree of π -donation from the alkoxide oxygen to iron.

Two representative pyridine(diimine) iron alkoxide compounds, (*i*PrPDI)FeOSiMe₃ and (*i*PrPDI)FeOEt, were also characterized by solid-state ⁵⁷Fe Mössbauer spectroscopy. (Figure 1). Isomer shifts of 0.75 and 0.74 mm/s were obtained for (*i*PrPDI)FeOSiMe₃ and (*i*PrPDI)FeOEt, respectively, with quadrupole splittings, $|EQ|$, of 1.20 and 1.21 mm/s. Both isomer shifts are comparable with the previously reported value of $\delta = 0.74$ mm/s for (*i*PrPDI)FeCl, although there is a slight increase in quadrupole splitting when the X-type ligand is changed from Cl to OR. ($|EQ| = 0.73$ mm/s for (*i*PrPDI)FeCl).²² Both the magnetic moment and Mössbauer isomer shift support high spin iron(II) complexes, in analogy to (*i*PrPDI)FeCl and related complexes assigned previously.^{21, 22}

To provide additional support for the electronic structure assignment of the (*i*PrPDI)FeOR compounds (R = Et, SiMe₃), full-molecule density functional theory studies were conducted at the B3LYP level of theory. The optimized electronic structures are best described as high spin Fe(II), $S = 3/2$ (broken symmetry (4,1)), with an iron-centered radical antiferromagnetically coupled to a radical anion delocalized on the pyridine diimine ligand (see SI for discussion). A qualitative d -orbital splitting diagram is shown in Figure S6. This electronic structure is comparable to the electronic structure of (*i*PrPDI)FeX (X = Cl, Br) compounds previously described, which were also computed to exhibit an $S = 3/2$ broken symmetry (4,1) ground state.²² The computed Mössbauer parameters were $\delta = 0.65$ mm/s and $|EQ| = 1.23$ mm/s for (*i*PrPDI)FeOEt and $\delta = 0.64$ mm/s and $|EQ| = 1.28$ mm/s for (*i*PrPDI)Fe(OSiMe₃), in good agreement with experimentally determined data.

With pyridine(diimine)iron alkoxide complexes in hand, their transmetallation reactivity with neutral aryl boronic esters was studied. Addition of PhBPin to a benzene- d_6 solution of (*i*PrPDI)FeOEt produced no reaction at ambient temperature or upon heating to 80°C for 24 hours. Taking inspiration from previous work on transmetallation to cobalt,¹⁰ the transmetallation of furan-type boron nucleophiles was investigated. Use of either (2-benzofuranyl)BPin or (2-benzofuranyl)BNeo (Pin = pinacolato, Neo = neopentylglycolato) resulted in rapid (<15 min) transmetallation at 23°C in C₆D₆ as judged by an immediate color change from light to dark green and observation of (*i*PrPDI)Fe(benzofuranyl) by ¹H NMR spectroscopy. In each case, a second, paramagnetic iron compound, tentatively assigned as the iron-boryl, (*i*PrPDI)Fe(BPin) or (*i*PrPDI)Fe(BNeo), accompanied formation of the benzofuranyl transmetallation product. Recrystallization of the product of the reaction with (2-benzofuranyl)BNeo from diethyl ether resulted in isolation of

(ⁱPrPDI)Fe(benzofuranyl) as dark green crystals in 90% yield. Attempted transmetallation with (2-benzofuranyl)B(OH)₂ and (ⁱPrPDI)FeOEt generated an intractable mixture of products with just trace quantities of (ⁱPrPDI)Fe(2-benzofuranyl) (See SI).

Single crystals of (ⁱPrPDI)Fe(2-benzofuranyl) were obtained from a concentrated solution of (ⁱPrPDI)Fe(2-benzofuranyl) in diethyl ether at –35°, and the solid-state structure confirmed the generation of the iron aryl complex (Figure 2). The bond distances observed in (ⁱPrPDI)Fe(2-benzofuranyl) are consistent with one-electron reduction of the chelate,²³ where N_{imine}–C_{imine} distances of 1.319 (6) Å and 1.315(6) Å, and C_{imine}–C_{ipso} bond distances of 1.445(7) Å and 1.437(7) Å are within the range expected for (RPDI)¹⁻. The benzofuranyl moiety is rotated by 51.5(4)° relative to the plane of the pyridine(diimine) chelate. It is possible that this orientation for the benzofuranyl group is stabilized by π-stacking with the aryl groups or simply sterically preferred.

Experimental and full-molecule DFT studies (B3LYP) on (ⁱPrPDI)Fe(2-benzofuranyl) support an intermediate spin iron(II) engaged in antiferromagnetic coupling with a chelate radical anion, resulting in an overall *S* = 1/2 complex (Figure 2; see SI for discussion). With the electronic structure of (ⁱPrPDI)Fe(2-benzofuranyl) established, the flow of electrons during transmetallation reaction can be discussed. The starting iron alkoxides, (ⁱPrPDI¹⁻)Fe^{II}OR, are high spin ferrous compounds with a monoreduced pyridine(diimine) chelate. Exchange of the weak field alkoxide ligand for a stronger field heteroaryl induced a spin state change at iron from *S* = 2 to *S* = 1 and the radical anion nature of the chelate is maintained throughout the reaction (Scheme 3). This behavior is comparable to the analogous transmetallation reaction between (ⁱPrPNP)CoOR (PNP = bis(phosphino)pyridine, R = *i*Pr or CH(Ph)Me), where a spin-state change from *S* = 1 (tetrahedral) to *S* = 0 (planar) accompanies the transmetallation step.¹⁰ Likewise, the propensity of 2-benzofuranyl boronate esters to undergo transmetallation as compared to the phenyl variant suggests that initial p-coordination of the furan ring facilitates formation of the oxygen boron bond, similar to the model proposed in cobalt-catalyzed SMC.¹⁰

The potential of (ⁱPrPDI)Fe(2-benzofuranyl) to participate in carbon-carbon bond-forming chemistry was evaluated with both aryl and alkyl halide electrophiles. Addition of one equivalent of cycloheptyl bromide, iodobenzene, bromobenzene, or phenyl triflate produced a blue solid identified as the pyridine(diimine) iron dihalide, (ⁱPrPDI)FeX₂ (X = Br, I, OTf) (Scheme 3). Low yields (<15%) of the cross-coupled product were obtained, and the remainder of the organic material was identified as hydrodehalogenated products (R–H) and benzofuran (Scheme 3; see Table S1 for organic product distribution).

In summary, the transmetallation of a neutral boron nucleophile to an iron alkoxide complex was demonstrated. In contrast to previous examples of transmetallation to iron, boronic acid ester nucleophiles commonly employed for palladium SMC are capable of promoting transmetallation. A net spin state change from *S* = 3/2 to *S* = 1/2 occurs during transmetallation, which was previously observed for cobalt and may assist in transmetallation. These results suggest that Suzuki-type transmetallation from boron to iron may be a viable pathway for iron-catalyzed cross coupling.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

We thank the National Institutes of Health (R01 GM121441) for financial support.

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Figure 1.

Solid-state structures of (a) $(iPrPDI)FeOEt$, (b) $(iPrPDI)FeOSiMe_3$ and (c) $(iPrPDI)FeOCH_3$ at 30% probability ellipsoids, with hydrogen atoms omitted for clarity. Zero-field ^{57}Fe Mössbauer Spectra of (a) $(iPrPDI)FeOEt$ and (b) $(iPrPDI)FeOSiMe_3$ at 80 K in the solid state. Gray circles represent the experimental spectrum, while the blue line indicates the best fit of the data.

Figure 2.

Top: A spin state change accompanies transmetalation. Solid-state structure (left) of $(iPr)_2PDI-Fe(benzofuranyl)$ at 30% probability ellipsoids, with hydrogen atoms omitted for clarity. Mulliken spin density plot (right) of $(iPr)_2PDI-Fe(2-benzofuranyl)$.

Byers, 2018:

Neutral transmetallation pathway proposed

This work:

Scheme 1.
Transmetalation of boron nucleophiles to iron.

Scheme 2.

Synthesis of (iPrPDI)FeOR complexes by (a) salt metathesis and (b) solvolysis of iron alkyls

Scheme 3.
Reaction of $(iPrPDI)Fe(2\text{-benzofuranyl})$ with electrophiles.