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

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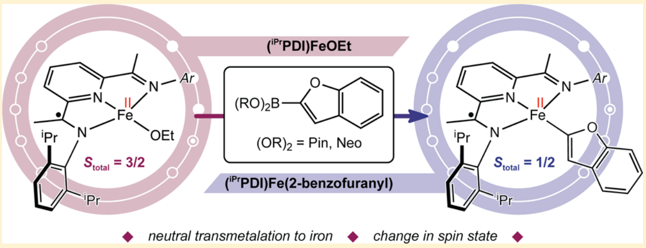
Supporting Information

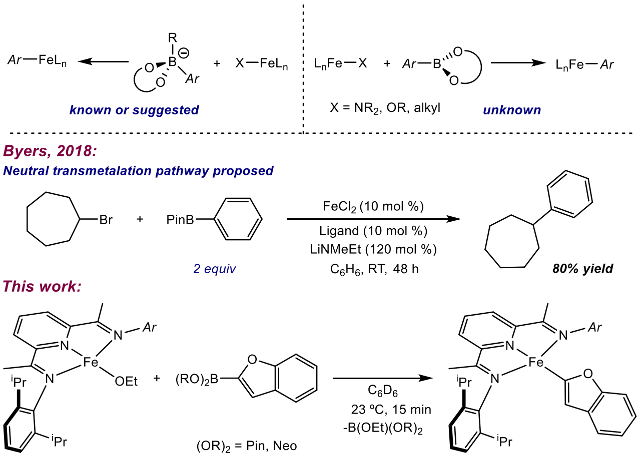


ABSTRACT: Transmetalation of the neutral boronate esters, (2-benzofuranyl)BPin and (2-benzofuranyl)BNeo (Pin = pinacolato, Neo = neopentylglycolato), to a representative pyridine(diimine) iron alkoxide complex, (^{iPr}PDI)FeOEt (^{iPr}PDI = 2,6-(2,6-^{i}Pr$_2$−C$_6$H$_3$N═CMe)$_2$C$_5$H$_3$N; R = Me, Et, SiMe$_3$), to yield the corresponding iron benzofuranyl derivative was studied. Synthesis of the requisite iron alkoxide complexes was accomplished either by salt metathesis between (^{iPr}PDI)FeCl and NaOR (R = Me, Et, SiMe$_3$) or by protonation of the iron alkyl, (^{iPr}PDI)FeCH$_2$SiMe$_3$, 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 (^{iPr}PDI)FeOR compound as an essentially planar, high-spin, $S = 3/2$ compound where the iron is engaged in antiferromagnetic coupling with a radical anion on the chelate ($S_{Total} = 3/2$; $S_{Fe} = 2$, $S_{PDI} = -1/2$). The resulting iron benzofuranyl product, (^{iPr}PDI)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 ($S_{Fe} = 1$, $S_{PDI} = -1/2$). These findings may be relevant to further development of iron-catalyzed Suzuki−Miyaura cross-coupling with neutral boronate esters and alkoxide bases.

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 1940s[2] 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 SMC. 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(sp^2)−C(sp^3) bond formation.[4a] Lithium aryl borate species have also been shown by Bedford and co-workers to be nucleophiles for directed C(sp^2)−C(sp^2) 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(sp^2)−C(sp^3) 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

Scheme 1. Transmetallation of Boron Nucleophiles to Iron



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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]

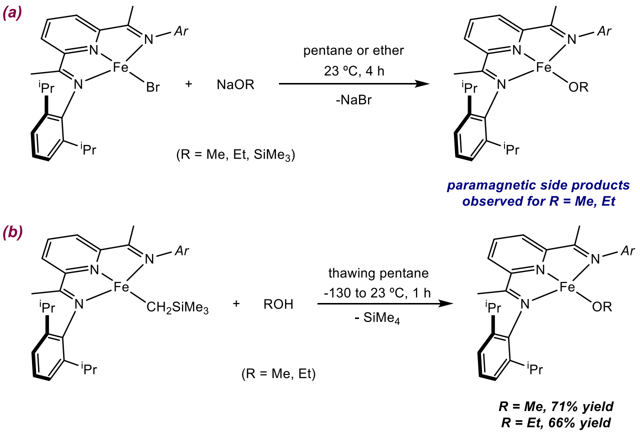
Examples of boron-based stoichiometric transmetalation to generate an iron aryl complex are primarily limited to lithium aryl borate nucleophiles.[7] Neidig and co-workers demonstrated that the reaction of (SciOPP)FeCl$_2$ (SciOPP = spin-control-intended o-phenylene bisphosphine) with lithium phenylborate 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 transmetalation.

To explore the possibility of transmetalation 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.[11−13] More germane to iron-catalyzed cross coupling, both iron aryl, (^{iPr}PDI)Fe(Ar) (Ar = phenyl; ^{iPr}PDI = 2,6-(2,6-^{i}Pr$_2$−C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N)),[14] and alkoxide (^{iPr}PDI)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 transmetalation, similar to observations previously reported by our group in cobalt-catalyzed SMC.

Suzuki-type transmetalation of a neutral aryl boronic acid or ester nucleophile to an iron amide or alkoxide complex has yet to be demonstrated in a stoichiometric reaction and could provide key mechanistic insights on optimal bases, iron precursors, and spin states for promoting this essential fundamental organometallic transformation. Here we describe the observation of stoichiometric transmetalation 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 transmetalation 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 (^{iPr}PDI)FeBr[17] with various alkoxide sources was initially studied. Addition of NaOR (R = SiMe$_3$, Me, Et) to a diethyl ether solution of the iron bromide complex generated the corresponding (^{iPr}PDI)FeOR derivatives (Scheme 2a). Pure (^{iPr}PDI)FeOSiMe$_3$ was isolated in 57% yield following recrystallization from pentane. However, using NaOCH$_3$, the salt metathesis protocol yielded paramagnetic iron-containing side products in addition to the targeted (^{iPr}PDI)FeOCH$_3$ complex. Because protonolysis of iron alkyls by free alcohols is a known method for the preparation of iron alkoxide complexes,[18,19] pentane solutions of (^{iPr}PDI)Fe(CH$_2$SiMe$_3$) were independently treated with methanol and ethanol, and, following filtration and removal of volatiles, (^{iPr}PDI)FeOCH$_3$ and (^{iPr}PDI)FeOEt were obtained in 71% and 66% yields, respectively, as green solids (Scheme 2b).

Scheme 2. Synthesis of (^{iPr}PDI)FeOR Complexes by (a) Salt Metathesis and (b) Solvolysis of Iron Alkyls



These iron alkoxide compounds exhibit the number of ^{1}H NMR resonances consistent with overall C_{2v} symmetry. As has been previously reported for (^{iPr}PDI)FeX (X = Cl, Br) compounds,[22] ^{1}H NMR resonances for (^{iPr}PDI)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 (^{iPr}PDI)FeOEt) and imine methyl CH_3 resonances (−209.74 ppm for (^{iPr}PDI)FeOEt) are diagnostic. For (^{iPr}PDI)FeOSiMe$_3$, a benzene-d_6 magnetic moment of 4.0 μ_B was measured (Evans method),[20] consistent with the spin-only value of 3.87 μ_B for three unpaired electrons and an overall S = 3/2 iron complex.

The solid-state structures of (^{iPr}PDI)FeOSiMe$_3$, (^{iPr}PDI)FeOEt, and (^{iPr}PDI)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 = SiMe$_3$: 360.43(17)°, R = Et: 360.20(13)°, R = Me: 359.96(4)°). Near linear N(2)−Fe(1)−O(1) bond angles of 174.39(11)° ((^{iPr}PDI)FeOSiMe$_3$), 177.30(6)° ((^{iPr}PDI)FeOEt), and 175.46(2)° ((^{iPr}PDI)FeOCH$_3$) were observed in all cases, suggesting some degree of π-donation from the alkoxide oxygen to iron.

Two representative pyridine(diimine) iron alkoxide compounds, (^{iPr}PDI)FeOSiMe$_3$ and (^{iPr}PDI)FeOEt, were also characterized by solid-state ^{57}Fe Mössbauer spectroscopy. (Figure 1). Isomer shifts of 0.75 and 0.74 mm/s were obtained for (^{iPr}PDI)FeOSiMe$_3$ and (^{iPr}PDI)FeOEt, respectively, with quadrupole splittings, $|\Delta E_Q|$, of 1.20 and 1.21 mm/s. Both isomer shifts are comparable with the previously reported value of δ = 0.74 mm/s for (^{iPr}PDI)FeCl, although there is a slight increase in quadrupole splitting when the X-type ligand is changed from Cl to OR. ($|\Delta E_Q|$= 0.73 mm/s for (^{iPr}PDI)FeCl).[22] Both the magnetic moment and Mössbauer isomer shift support high spin iron(II) complexes, in analogy to (^{iPr}PDI)FeCl and related complexes assigned previously.[21,22]

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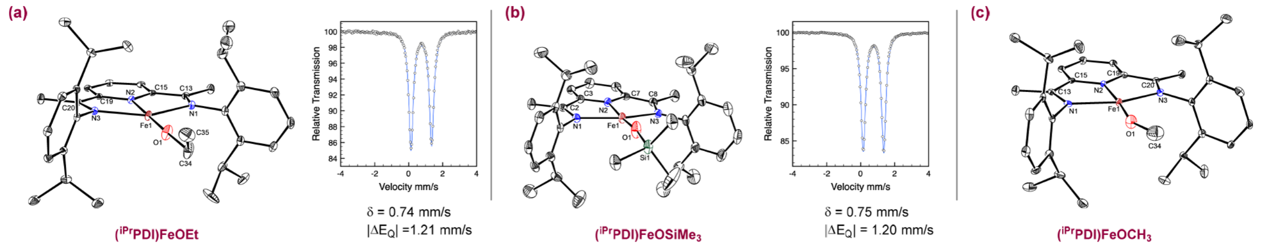


Figure 1. Solid-state structures of (a) (^{iPr}PDI)FeOEt, (b) (^{iPr}PDI)FeOSiMe$_3$ and (c) (^{iPr}PDI)FeOCH$_3$ at 30% probability ellipsoids, with hydrogen atoms omitted for clarity. Zero-field ^{57}Fe Mössbauer spectra of (a) (^{iPr}PDI)FeOEt and (b) (^{iPr}PDI)FeOSiMe$_3$ at 80 K in the solid state. Gray circles represent the experimental spectrum, while the blue line indicates the best fit of the data.

To provide additional support for the electronic structure assignment of the (^{iPr}PDI)FeOR compounds (R = Et, SiMe$_3$), 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 S7. This electronic structure is comparable to the electronic structure of (^{iPr}PDI)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 $|\Delta E_Q| = 1.23$ mm/s for (^{iPr}PDI)FeOEt and $\delta = 0.64$ mm/s and $|\Delta E_Q| = 1.28$ mm/s for (^{iPr}PDI)Fe(OSiMe$_3$), in good agreement with experimentally determined data.

With pyridine(diimine)iron alkoxide complexes in hand, their transmetalation reactivity with neutral aryl boronic esters was studied. Addition of PhBPin to a benzene-d_6 solution of (^{iPr}PDI)FeOEt produced no reaction at ambient temperature or upon heating to 80 °C for 24 h. Taking inspiration from previous work on transmetalation to cobalt,[10] the transmetalation 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) transmetalation at 23 °C in C$_6$D$_6$ as judged by an immediate color change from light to dark green and observation of (^{iPr}PDI)Fe(benzofuranyl) by ^{1}H NMR spectroscopy. In each case, a second, paramagnetic iron compound, tentatively assigned as the iron-boryl, (^{iPr}PDI)Fe(BPin) or (^{iPr}PDI)Fe(BNeo), accompanied formation of the benzofuranyl transmetalation product. Recrystallization of the product of the reaction with (2-benzofuranyl)BNeo from diethyl ether resulted in isolation of (^{iPr}PDI)Fe(2-benzofuranyl) as dark green crystals in 90% yield. Attempted transmetalation with (2-benzofuranyl)B(OH)$_2$ and (^{iPr}PDI)FeOEt generated an intractable mixture of products with just trace quantities of (^{iPr}PDI)Fe(2-benzofuranyl) (see SI).

Single crystals of (^{iPr}PDI)Fe(2-benzofuranyl) were obtained from a concentrated solution of (^{iPr}PDI)Fe(2-benzofuranyl) in diethyl ether at −35°, and the solid-state structure confirmed the generation of the iron heteroaryl complex (Figure 2). The bond distances observed in (^{iPr}PDI)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 (^{R}PDI)$^{1-}$. 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.

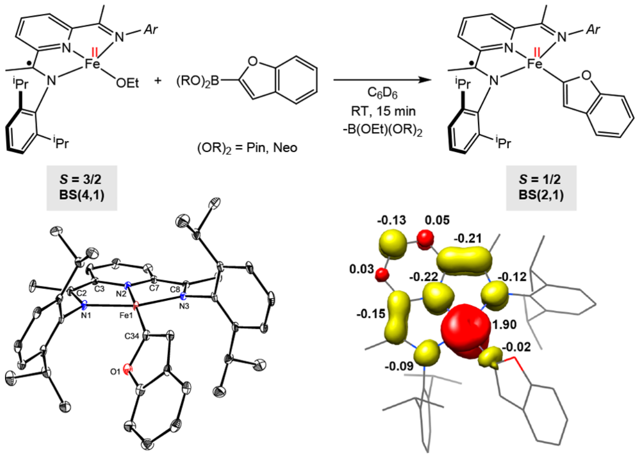
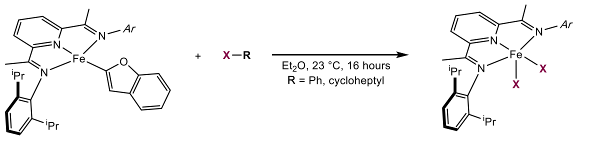


Figure 2. Top: A spin state change accompanies transmetalation. Bottom: Solid-state structure (left) of (^{iPr}PDI)Fe(benzofuranyl) at 30% probability ellipsoids, with hydrogen atoms omitted for clarity. Mulliken spin density plot (right) of (^{iPr}PDI)Fe(2-benzofuranyl).

Experimental and full-molecule DFT studies (B3LYP) on (^{iPr}PDI)Fe(2-benzofuranyl) support an intermediate spin iron(II) center 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 (^{iPr}PDI)Fe(2-benzofuranyl) established, the flow of electrons during transmetalation reaction can be discussed. The starting iron alkoxides, (^{iPr}PDI^{1-})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 transmetalation reaction between (^{iPr}PNP)CoOR (PNP = bis(phosphino)-pyridine, R = iPr or CH(Ph)Me), where a spin-state change from $S = 1$ (tetrahedral) to $S = 0$ (planar) accompanies the

Scheme 3. Reaction of (^{iPr}PDI)Fe(2-Benzofuranyl) with Electrophiles



Major iron-containing species detected
+ other unidentified products

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transmetalation step.[10] Likewise, the propensity of 2-benzofuranyl boronate esters to undergo transmetalation as compared to the phenyl variant suggests that initial π-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 (^{iPr}PDI)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 blue solids identified as the pyridine(diimine) iron dihalide, (^{iPr}PDI)FeX$_2$ (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 transmetalation of a neutral boron nucleophile to an iron alkoxide complex was demonstrated. In contrast to previous examples of transmetalation to iron, boronic acid ester nucleophiles commonly employed for palladium SMC are capable of promoting transmetalation. A net spin state change from $S = 3/2$ to $S = 1/2$ occurs during transmetalation, which was previously observed for cobalt and may assist in transmetalation. These results suggest that Suzuki-type transmetalation from boron to iron may be a viable pathway for iron-catalyzed cross coupling.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00733.

NMR spectra (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 1953963, 1953965, 1954249, and 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 emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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