Coupling dinitrogen and hydrocarbons through aryl migration

The activation of abundant molecules such as hydrocarbons and atmospheric nitrogen (N₂) remains a challenge because these molecules are often inert. The formation of carbon–nitrogen bonds from N₂ typically has required reactive organic precursors that are incompatible with the reducing conditions that promote N₂ reactivity, which has prevented catalysis. Here we report a diketiminate-supported iron system that sequentially activates benzene and N₂ to form aniline derivatives. The key to this coupling reaction is the partial silylation of a reduced iron–dinitrogen complex, followed by migration of a benzene-derived aryl group to the nitrogen. Further reduction releases N₂-derived aniline, and the resulting iron species can re-enter the cyclic pathway. Specifically, we show that an easily prepared diketiminate iron bromide complex mediates the one-pot conversion of several petroleum-derived arenes into the corresponding silylated aniline derivatives, by using a mixture of sodium powder, crown ether, trimethylsilyl bromide and N₂ as the nitrogen source. Numerous compounds along the cyclic pathway are isolated and crystallographically characterized, and their reactivity supports a mechanism for sequential hydrocarbon activation and N₂ functionalization. This strategy couples nitrogen atoms from N₂ with abundant hydrocarbons, and maps a route towards future catalytic systems.

Reduction or ‘fixation’ of N₂ is accomplished by a few catalytic systems that fully reduce N₂ to ammonia (NH₃). It is difficult to adapt these processes to form C–N bonds from N₂, even though several functionalizations of N₂ are thermodynamically feasible. Efforts to form C–N bonds from N₂ generally require reduction of N₂ to make it nucleophilic enough to react with carbon electrophiles. Notable examples include synthetic cycles for C–N bond formation. A frequent difficulty is the direct reaction of the reducing agents with the carbon electrophiles.

There would be a substantial advantage if N₂ could be induced to form a C–N bond with a simple hydrocarbon, without prior functionalization of the hydrocarbon to convert it into an electrophile. Such a strategy would require C–H activation of the hydrocarbon, making use of decades of work on oxidative addition of C–H bonds by low-valent transition metal complexes. Although C–H functionalization to form cross-coupling products is well known, we know of no previous examples of cross-coupling of C–H bonds with the relatively unreactive N₂ molecule.

Here, we report an iron complex that couples N₂ and unactivated arenes at low temperature, taking advantage of silyl activation of the N₂ to produce silylated anilines in a one-pot procedure. The overall strategy (Fig. 1) begins with C–H bond activation of benzene to form a phenyl fragment, which could migrate to N₂ upon silylation to form the key C–N bond. To explore the feasibility of this pathway, we converted the iron(II) bromide complex [LFe(μ-Br)]₂ (1) into the iron(I) complex [LFe(μ-N₂)]₂ (2).
benzene complex LFe(η6-C6H6) (2). Figure 2 shows the structure of 2 and illustrates the β-diketiminate ligand L, which controls the coordination environment of iron. Reduction of 2 with KC₈ in the presence of 18-crown-6 (18c₆) at room temperature led to the isolable, purple iron(0) complex LFe(η₄-C₆H₆)K(18c₆) (3-K). When 2 was reduced with Na and 15-crown-5 (15c₅) in benzene, the product was the red iron(ii) complex LFe(H)(Ph)Na(15c₅) (4-Na), in which a C–H bond of benzene is broken to give an iron(ii) complex with phenyl and hydride groups on the iron (Supplementary Fig. 50). Thus, 3-K and 4-Na have isomeric anions (bottom of Fig. 2a). Mössbauer spectra of solid 3-K and 4-Na (Supplementary Figs. 23–25) support this difference, and density functional theory (DFT) studies indicate that the molecules have high-spin electronic configurations (spin states are S=1 for 3-K and S=2 for 4-Na). This is a rare case of room-temperature C–H activation using a high-spin iron complex.

Reduction of 2 with Na and 15c₅ in toluene similarly gave LFe(H)(Tol)Na(15c₅), from activation of the aryl C–H bonds of the solvent. The X-ray crystal structure refined best to a 61:39 mixture of meta and para isomers (Supplementary Fig. 54).

The solution ¹H nuclear magnetic resonance (NMR) spectra of 3-K and 4-Na in C₆D₆ showed a few peaks that disappeared over several hours, suggesting that these benzene or phenyl groups exchange with C₆D₆. Additionally, a minor component was observed in the ¹H NMR spectrum of the C₆D₆ solutions of 3-K that resembled those of 4-Na, and vice versa. These observations suggested that the arene-bound iron(0)
complex 3 and the C–H activated iron(ii) complex 4 are in equilibrium with one another, and the iron(0) arene isomer (3) predominates with K(18c6)−, whereas the oxidatively added iron(1) phenyl hydride isomer (4) predominates with Na(15c5)− (see Supplementary Tables 7, 8). This hypothesis was supported by solution studies in tetrahydrofuran (THF), a solvent that can disrupt the interactions with the alkali metal. Dissolving either purified 3–K or purified 4–Na in THF gave mixtures with characteristic peaks of both isomers 3 and 4 in 1H NMR and Mössbauer spectra (Supplementary Figs. 9, 26). The ability of each isomer to produce the other one demonstrates that there is reversible oxidative addition of the aryl C–H bond of 3 to form 4.

Purple THF solutions of LFe(H)(Ph)Na(15c5) (4–Na) turned green after standing at room temperature for several hours, and 1H NMR spectra showed formation of the iron(ii) phenyl complex [LFePh][Na(15c5)] (6–Na) (Fig. 2b). Although the formation of 6–Na from 4–Na corresponds to formal loss of H+, the spectroscopic yield of 6–Na from 4–Na in THF was only 18% (Supplementary Fig. 17), and the best yield of 6–Na (44%) came from addition of excess 15c5 and Na to 2 in diethyl ether (Supplementary Fig. 18). These results suggest that the reaction could proceed through a disproportionation pathway. In a mechanistically revealing experiment, 4–Na transferred the hydride to triphenylborane (BPH3) to give the previously characterized5 and [Na(15c5)][HBPH3] (Supplementary Figs. 19, 20) in a higher yield of 75%. Therefore, it is possible that in the presence of excess reducing agent, 4–Na can similarly lose hydride to give 5, which is subsequently reduced by 3 or by Na to give the observed 6–Na.

Next, we explored N2 binding. Cooling a solution of 6–Na in THF under an atmosphere of N2 led to changes in the electronic absorption (ultraviolet–visible; UV–vis) spectrum (Fig. 3a) and the Mössbauer spectrum (Fig. 3b) that did not occur in control experiments under argon. Van’t Hoff analysis of the UV–vis data for 6–Na gave ΔH = −17 ± 2 kJ mol−1 and ΔS = −55 ± 10 J K−1 mol−1 (Supplementary Fig. 40; ΔH is the enthalpy change, ΔS is the entropy change; uncertainties represent standard deviations), which are consistent with the binding of N2. To obtain crystallographic verification of N2 binding, we cooled a concentrated sample of the potassium analogue 6–K at −78 °C for 3 h, which led to crystals of the N3 complex 7–K. The X-ray crystal structure of this potassium salt of 7 (Fig. 4, bottom) demonstrates end-on binding of the N2 unit and a pseudotetrahedral geometry at the iron(i) site, and the spectroscopic similarity to the Na system (Supplementary Figs. 36–39) indicates that 7–Na has a similar structure.

Next, we silylated the N2 ligand that had been activated through Fe coordination. Treating a cold solution of 7–K with 2 equivalents (equiv.) of Me3SiX (X = Br, I) formed the hydrazido complex LFe(N(Ph)N(SiMe3)2) (8). To our knowledge, the transformation of 7 to 8 is the first crystallographically verified example of the migration of a hydrocarbyl group from a metal to the α position of N2 (refs. 24, 25). This is the key C–N bond–forming step during the formation of silylated anilines (Fig. 1), which differs from the previously used attacks on bound N2 by carbon electrophiles.

Although we did not detect any intermediates during the conversion of 7 to 8, the treatment of a cold solution of 7–K with 0.5 molar equivalents of the bulkier triisopropylsilyl triflate (TIPSOTf; OTf = SO3CF3) gave the formally iron(ii) diazenido complex 9, in which the N2 is singly silylated while the phenyl group remains bound to the iron (Supplementary Fig. 55). The conversion of 7 to 9 is accompanied by a similar yield of the iron(ii) complex 5, which results from half of 7 acting as a reducing agent. Considering this stoichiometry, the formation of 9 occurs in 67% yield. The isolation of 9, in which the phenyl has not migrated, suggests that the initial silylation of the β position of the coordinated N2 in 7 takes place before the migration of the aryl group. It is likely that the second silylation induces the aryl migration, because a recent study27 reported the migration of H from an iron center to the α position of a doubly silylated N2 group to form an iron dicyanohydrazido complex. Accordingly, addition of excess trimethylsilyl triflate (Me3SiOTf) and excess Na to 9 gave a 14% yield of PhN(SiMe3)2, showing that addition of a second silyl group can initiate C–N bond formation. This could be because the second silylation leads to a formally iron(iv) complex with an Fe=N double bond, a migration that is reminiscent of alkyl migration to N in an imidoiron(iv) complex28.
The conversion of \( \text{8} \) to the silylated aniline and amine occurred upon the addition of 1 equiv. KC8 and 2 equiv. Me3SiX (X = Br, I) to solutions of \( \text{8} \); this treatment led to mixtures containing PhN(SiMe3)2, PhN(SiMe3)N(SiMe3)2 and N(SiMe3)3 within 30 min, either at room temperature or at −100 °C. By contrast, \( \text{8} \) did not react with 2 equiv. Me3SiBr alone within 3 days at room temperature. This result suggests that reduction precedes the electrophilic attack of silyl groups on \( \text{8} \); alternatively, this final step could involve the formation of Me3Si• radicals. Other studies have also reported on the reductive silylation of disilylhydrazido complexes.

After release of the silylated nitrogen products from \( \text{8} \), the large excess of bromide is expected to give iron(ii) bromide species that are poised to be reduced with further arene binding. This suggests the feasibility of a cyclic process (Fig. 4) in a single pot, which forms silylated anilines from arenes and N2. However, the C–H activation and hydride loss to reform complex \( \text{6} \) requires room-temperature treatment with Na, and at this temperature Na degrades Me3SiBr. Further, \( \text{N} \) binds to \( \text{6} \) at low temperatures. Thus, we treated \( \text{8} \) with Na (25 equiv.), benzene (20 equiv.), Me3SiBr (6 equiv.) and 15c5 (5 equiv.) at −100 °C in diethyl ether, then warmed it to room temperature for 1 h, then cooled it again and treated it with additional Me3SiBr (6 equiv.). To verify that the overall process is indeed cyclic, \( \text{8} \) was treated under the same conditions with added toluene in place of benzene. Analysis of the organic reaction products after two cycles of Me3SiBr addition showed a 163% yield of N(SiMe3)3, a 62% yield of PhN(SiMe3)2 and a 16% yield of (tolyl)N(SiMe3)2 (both \( \text{meta} \) and \( \text{para} \) isomers). The ability of the phenylhydrazido complex to give products from tolueneamination demonstrates that the iron-containing products of the hydrazido reduction can activate toluene and continue to another reaction cycle, although the yields are low.

To test the overall cycle, we reacted the easily prepared iron(ii) complex \( \text{1} \) with 30 molar equivalents (equivalents relative to \( \text{[Fe]} \)) of Na, 20 equiv. C6H6 and 5 equiv. 15c5 at ambient temperature in diethyl ether.
followed by addition of 6 equiv. trimethylsilyl bromide (Me₃SiBr) at −108 °C, which afforded Ph(N(SiMe₃))₂ in a yield of 24% per iron atom, as determined by gas chromatography. The yield of the reaction could be increased by adding Me₃SiBr in one portion per temperature cycle. First, a mixture of 1, 35 equiv. Na, 35 equiv. benzene and 5 equiv. 15c5 in diethyl ether was stirred vigorously for 1.5 h at room temperature until it became green, corresponding to the colour of 6. Cooling the mixture to −108 °C under 1 atm N₂ resulted in a colour change to dark red, corresponding to 7. Then, addition of 2 equiv. Me₃SiBr (per iron atom) to this cold solution and warming to room temperature for 1 h resulted in another green reaction mixture, suggesting that 6 was regenerated. Cooling again caused the same colour change to red (7), and more Me₃SiBr was then added in a second cycle. Repeating 10 cooling–silylation–warming cycles with 2 equiv. Me₃SiBr per cycle gave a cumulative yield of (85 ± 14)% Ph(N(SiMe₃))₂ (versus Fe; average and standard deviation of six trials; Supplementary Table 1). The ability to produce more product with repeated Me₃SiBr additions suggests a cyclic process, albeit one in which a substantial amount of the active species decomposes in each cycle. Although aniline formation was attenuated with repeated cycles, the yield of N(SiMe₃)₂ continued to increase with the number of additions of Me₃SiBr, reaching (380 ± 41)% (versus Fe) (Supplementary Figs. 1, 2). Under the same conditions but in the absence of benzene, no Ph(N(SiMe₃))₂ was produced, but a similar catalytic yield of N(SiMe₃)₂ was observed. Neither product was detected in the absence of 1. These results suggest that the iron decomposition products lose the ability to aminate benzene but remain able to silylate N₂ to N(SiMe₃)₂—a more frequent reaction that has been reported with other homogeneous catalysts and decomposition products.

Isotope labelling experiments were used to verify that the aniline product arises from benzene and N₂. When performing the reaction under an atmosphere of 15N₂, gas chromatography coupled with mass spectrometry indicated the formation of Ph₁₅N(SiMe₃)₂ and 15N(SiMe₃)₃ (Fig. 5a), demonstrating that N₂ is the source of the N atoms. Performing the reaction with C₆D₆ as the arene substrate gave (C₆D₅)N(SiMe₃)₂, showing that benzene is the source of the phenyl group. The reaction with an equimolar mixture of C₆H₆ and C₆D₆ gave a 1:1 mixture of (C₆H₅)N(SiMe₃)₂ and (C₆D₅)N(SiMe₃)₂ (Supplementary Fig. 5), but partially deuterated 1,3,5-d₋ₓ-xylene was used, a (12 ± 2)% yield of Nₓ,N₋ₓ-bis (trimethylsilyl-3,4-xylylene) was observed. These silylated aniline products could be hydrolysed to the deprotected anilines with weak aqueous acid when desired. Arenes with easily reducible functionalities—such as aryl halides, aryl ethers and polycyclic aromatics—did not give aminated products. Formation of the silylated aniline and N(SiMe₃)₂ also occurred when Me₆SiX reagents (X = Cl, I, OTf) were used, although the reaction gave the highest yields with Me₃SiBr.

Other arene substrates were also tested using 5 cycles of Me₃SiBr addition (Fig. 5b), with a yield of benzene to Ph(N(SiMe₃))₂ of (68 ± 4)% per iron. Toluene gave a mixture of (p-tolyl)N(SiMe₃)₂ and (p-tolyl)N(SiMe₃)₃ in a 3:1 ratio with a total yield of (61 ± 7)% per iron. The overall yield is similar to that for benzene, and the ratio of isothers is comparable to that observed in the crystal of LFe(H)(Tol)Na(15c5) (Supplementary Fig. 54). When o-xylene was used, a (12 ± 2)% yield of Nₓ,N₋ₓ-bis (trimethylsilyl-3,4-xylylene) was observed. These silylated aniline products could be hydrolysed to the deprotected anilines with weak aqueous acid when desired. Arenes with easily reducible functionalities—such as aryl halides, aryl ethers and polycyclic aromatics—did not give aminated products. Formation of the silylated aniline and N(SiMe₃)₂ also occurred with other Me₆SiX reagents (X = Cl, I, OTf), although the reaction gave the highest yields with Me₃SiBr.

The strategy outlined here differs fundamentally from previously described strategies for the formation of C–N bonds from N₂. Typically, carbon electrophiles have been used to create C–N bonds, either from N₂ (refs. 31,33,42–44) or nitrides that result from cleavage of N₂ (refs. 35–37,46). In the proposed reaction, silylation plays a key part by making the coordinated N₂ sufficiently reactive to accept the migrating aryl group from the metal centre. The silylated amines that are formed can be used in further synthetic steps or can be deprotected to the parent anilines using mild aqueous acid. In this method, the C–N bond comes from the migration of a hydrocarbyl from a metal to a N₂-derived group, a strategy that has been used in few stoichiometric C–N bond formation reactions.38–42 The ability of these iron complexes to generate a hydrocarbonyl group on the iron through C–H activation, and then transfer it to an activated N₂, provides a new tactic for coupling hydrocarbons to N atoms from atmospheric N₂, combining the powers of these bond-cleaving reactions.

Online content
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**Data availability**

Materials and methods, experimental procedures, useful information, spectra and mass spectrometry data are available in Supplementary Information. Raw data are available from the corresponding author on reasonable request. The crystallographic datasets generated during the current study are publicly available from the Cambridge Crystallographic Data Centre (CCDC) repository at https://www.ccdc.cam.ac.uk/structures/ with CCDC numbers 1937999, 1978000, 1938001, 1938002, 1939265, 1939266 and 1966313.

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**Author contributions**

S.F.M., D.L.J.B. and P.L.H. conceived the ideas and designed the experiments. S.F.M., D.L.J.B., C.J.V.H. and S.M.B. performed the experiments. B.Q.M. performed crystallographic measurements and interpretation. S.F.M., D.L.J.B. and P.L.H. wrote the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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