Chinese Chemical Letters 34 (2023) 107758

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Iron-catalyzed reductive cyclization of nitroarenes: Synthesis of aza-heterocycles and DFT calculations

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ARTICLE INFO

Article history:
Received 17 June 2022
Revised 11 August 2022
Accepted 16 August 2022
Available online 18 August 2022

Keywords:
Iron
Cyclization
Nitroarenes
Dihydrobenzo[*c*]carbazoles
Indoles

ABSTRACT

Research into environmentally friendly strategies for hydrogen transfer reduction is increasing, along with the need for more elaborate heterocyclic platforms. Within this context, we develop a new approach for substituted dihydrobenzo[*c*]carbazoles and indoles. These compounds were synthesized through an iron-catalyzed hydrogen transfer reduction of nitroarenes, followed by intramolecular cyclization. This transformation involves using a Knölker-type catalyst, Cs_2CO_3 as the base, and benzyl alcohol as the non-expensive and low volatile hydrogen donor. We synthesize 30 examples of aza-heterocycles with moderate to excellent yields by applying this strategy. Additionally, DFT calculations demonstrated that the pathway reaction could follow an anionic mechanism.

Due to their various physicochemical properties and biological activities, *N*-heterocycles represent fascinating molecules in organic chemistry [1]. These compounds constitute valuable scaffolds for numerous pharmaceuticals [2].

Although many synthetic routes to synthesize nitrogen-containing polycycles have been developed, researchers have become interested in more novel approaches during the last few decades [3–6]. With the growing awareness of global climate change, eco-friendly strategies have been widely promoted. For example, hydrogenation reactions that usually run under hydrogen pressure could be replaced by more convenient techniques, such as metal-catalyzed hydrogen transfer reduction [7,8]. This latter methodology also involves alcohols which are economical and non-toxic hydrogen transfer reagents. There is a preference for first-row transition metals, especially iron, in terms of the metal typically used [9–14]. As one of the most abundant and low-cost metals on Earth, iron has been widely employed in homogeneous catalysis since the last century [15–19].

Given these properties, reductive couplings with iron catalysts began to be used [20–23]. As such, amination reactions by hydrogen transfer with alcohols [24–26] or with Knölker-type complexes [27–30] could be performed. Nitroarenes reductions by hydrosilylation and hydrogen transfer were achieved to provide anilines and nitroso reactive intermediates [31,32]. More recently, these transformations have paved the way for new molecular syntheses of fused *N*-heterocycles [33,34]. One method, the well-known Béchamp nitroaryl reduction [35], has been applied to the one-pot synthesis of 4,7-substituted pyrrolo[1,2-*a*]quinoxalines in the presence of an excess of ethanol [36]. Bäumler and Rempe illustrated another method, the nitroarene hydrogenation using carbonyl compounds and Fe-SiCN nanocomposite catalyst to prepare benzimidazoles and quinoxalines [37]. These latter scaffolds could also be built from transfer hydrogenative condensation in the presence of sodium sulfide, an iron salt, or dppf [38,39]. Darcel and Wu described the preparation of these platforms *via* a hydrogen transfer reduction of nitrobenzene derivatives with alcohols and a Knölker-derived iron catalyst [40].

In this context, we develop an eco-compatible conception of different aza heterocycles, namely dihydrobenzo[*c*]carbazoles, and indoles. These scaffolds appear in the core of numerous biologically active products [3]. Take substituted 5,6-dihydrobenzo[*c*]carbazoles, which act as antiprotozoal agents against *Trypanosoma cruzi* [41]. The marine alkaloid Eudistomin K also presents an indole moiety, which inhibits the P-388 tumor cell line with an *in vitro* $IC_{50} = 0.01\ \mu g/mL$ (Fig. 1) [42].

With the rising importance of these frameworks, there has been conceptualization of a myriad of synthetic methods. The most common synthesis of these nitrogen heterocycles relies on the Fischer reaction, dealing with arylhydrazones and carbonyl com-

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https://doi.org/10.1016/j.cclet.2022.107758
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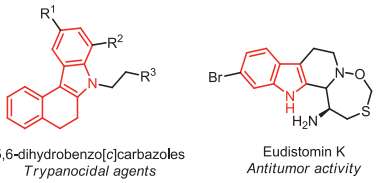


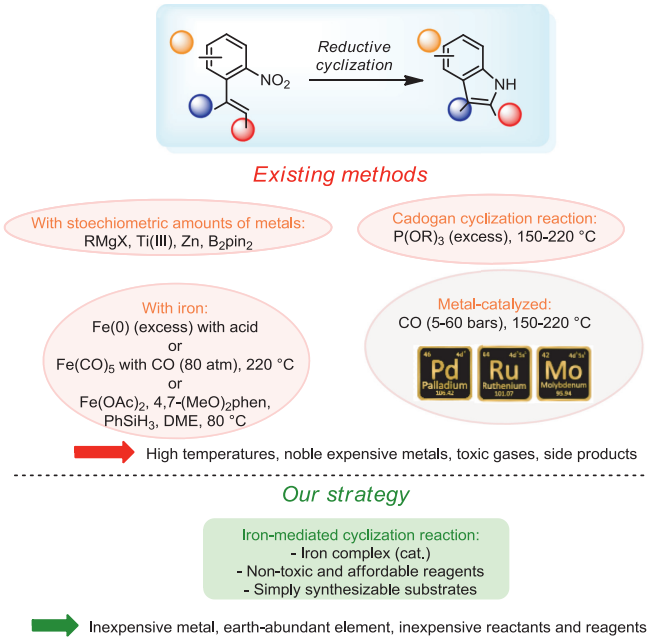
Fig. 1. Dihydrobenzo[*c*]carbazole and indole moieties in biologically active compounds.

pounds [43,44]. These transformations generally need to be implemented in harsh conditions, *i.e.*, the employment of strong acids and high temperatures. Among the other possible methodologies, the reduction of nitroarenes has also been developed to create carbon-nitrogen bonds in these structures. With their high stability and availability, nitroaryl molecules are generally the substrates of choice. At 150–220 °C, Cadogan cyclization of 2-nitrobiaryls or *o*-nitrostyrenes produces carbazoles and indoles, with an excess of triaryl or trialkylphosphines [45–47]. Nonetheless, the generation of phosphine or phosphite oxide as side products complicates the purification of the product. Variations of this reaction were thus reported with transition metals in catalytic amounts (Pd or Ru) at high pressure of carbon monoxide (5–60 bars) [48]. The reductive cyclization could also be accomplished with stoichiometric quantities of molybdenum hexacarbonyl [49], bis(pinacolato)diboron [50], Grignard reagent [51] or titanium(III) [52,53]. By iron-mediated reactions, the production of indoles could be triggered in high amounts of Fe(0) in acidic conditions or catalyzed by $Fe(CO)_5$ under carbon monoxide pressure (80 atm) at 220 °C [54]. The formation of indoles could also be achieved by iron-catalyzed reductive coupling of nitrostyrenes in the presence of a Fe(II) complex and silane as the reductant [55,56]. In light of all these harsh conditions, the applicability of these approaches is relatively narrow, namely for scale-up reactions or the construction of functionalized and complex compounds.

Hence, the development of sustainable alternative processes remains a challenge. In this perspective, we foresaw a milder strategy for forming dihydrobenzo[*c*]carbazoles and indoles from nitroarenes. This method would imply iron as an inexpensive earth-abundant metal catalyst, non-toxic and affordable reagents, and simply synthesizable nitroraryl substrates (Scheme 1).

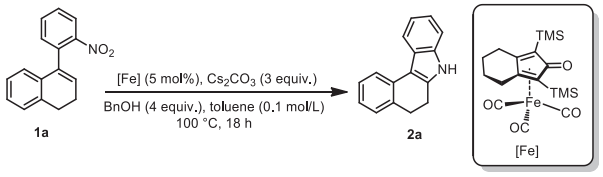
In that respect, we decided to explore a reductive cyclization reaction in different conditions (Table 1). We considered the dihydrobenzo[*c*]carbazole **2a** preparation from substrate **1a** as a model reaction. It should be highlighted that nitroarene **1a** was easily accessible from a Barluenga coupling [57] between commercial 2-bromonitrobenzene and the corresponding *N*-tosylhydrazone (Supporting information).

We first envisaged the process with an iron catalyst derived from the Knölker complex ([Fe], 5 mol%), Cs_2CO_3 as the base, BnOH as the hydrogen donor, in toluene at 100 °C for 18 h. This condition provided compound **2a** in 77% yield (entry 1). This encouraging result prompted us to look further at the reaction optimizations (see Supporting information for further details). The total conversion time was longer (40 h), with a lower yield by decreasing the temperature to 80 °C. At 140 °C, the cyclization efficiency was not affected. The suppression of base or BnOH allowed mainly the recovery of the starting material **1a**, bearing out the importance of these elements in the iron-mediated catalytic cycle (entries 4 and 5). Lowering the catalyst quantity to 2.5 mol% kept the reactivity unchanged of the Knölker-type complex, with a 75% yield. On the contrary, a sharp reduction of [Fe] contributed to longer reaction times and poor results (entry 7). The variation of the base did also not enhance the yield (Table S3 in Supporting information). The catalytic system appeared to be less efficient in polar protic and aprotic solvents, *e.g.*, acetone (entry 9).



Scheme 1. Synthetic approaches for the formation of *N*-heterocyclic scaffolds from the nitroarenes reduction.

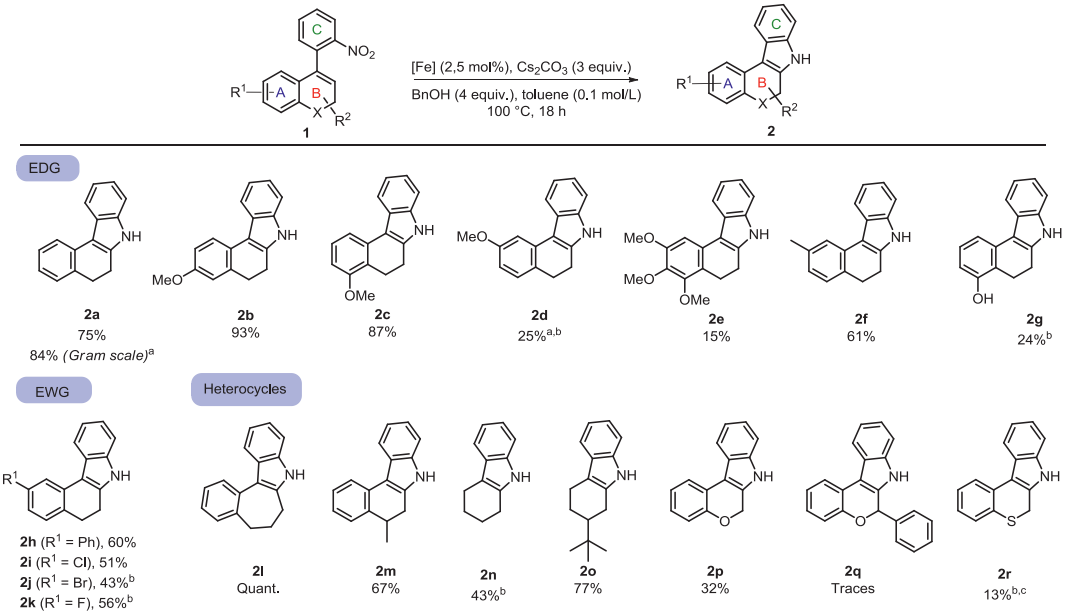
Table 1
Reaction optimizations.[a]



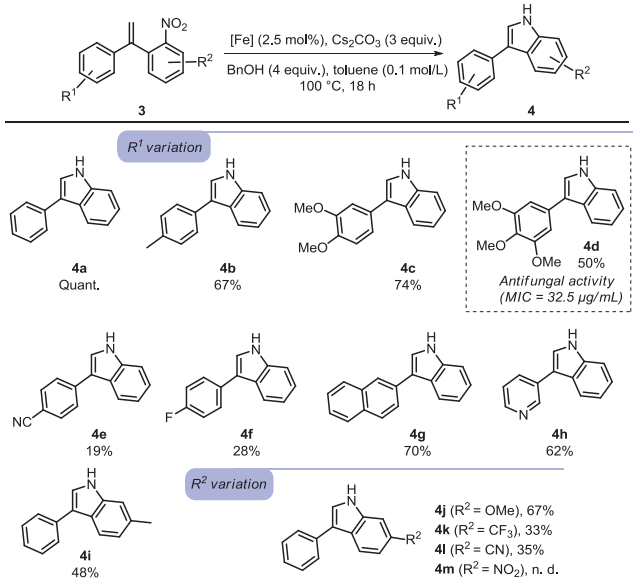
Entry	Deviation from the standard conditions	Yield of **2a** (%)[b]
1	None	77
2	80 °C	56[c]
3	140 °C	74
4	Without BnOH, at 140 °C	10
5	Without base, at 140 °C	0
6	Using [Fe] (2.5 mol%)	75
7	Using [Fe] (1.25 mol%)	70[d]
8	K_2CO_3 as the base	Traces
9	Acetone as the solvent	36
10	CPME as the solvent	73

[a] Reaction conditions: **1a** (0.2 mmol), [Fe] (2.5 mol%), Cs_2CO_3 (3.0 equiv.), BnOH (4.0 equiv.) and toluene (0.1 mol/L). All the reactions were realized in a sealed tube in an oil bath at the defined temperature.
[b] Isolated yield.
[c] The reaction was reached for 40 h.
[d] The transformation was done for 48 h.

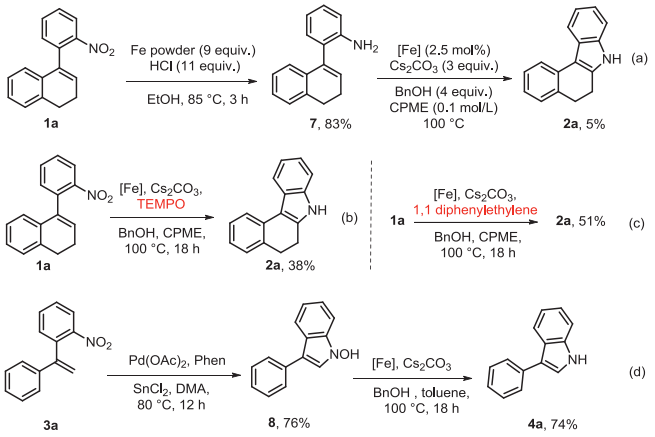
Having the best conditions in hand, we studied the scope of the reaction. As described in Scheme 2, substrates with ring A exhibiting electron-rich groups (OMe, Me and OH) provided moderate to excellent yields. Surprisingly, the *meta*-substituted product **2d** was afforded a 25% yield, a lower yield than the *para*- and *ortho*–methoxy dihydrobenzo[*c*]carbazoles **2b** and **2c**. The steric bulkiness of the trimethoxybenzene moiety caused a yield drop. The transformation was less suitable with the unprotected hydroxyl group, with only 24% yield for **2g**. In this case, the cyclization was reached in CPME since the expected product was not obtained in toluene. Electron-withdrawing substituents induced lower substrate reactivity than the electron-donor ones, with 43% to 60% yields. The reductive cyclization presented a good tolerance with seven-membered ring substrate **1l** and nitroarenes display-



Scheme 2. Scope of the reductive cyclization. Reaction conditions: **1** (0.2–0.4 mmol), [Fe] (2.5 mol%), Cs_2CO_3 (3.0 equiv.), BnOH (4.0 equiv.) and toluene (0.1 mol/L). All the reactions were realized in a sealed tube at 100 °C in an oil bath, isolated yield. [a]The reaction was carried out in a sealed reactor. [b]Reaction in CPME. [c]LC-MS yield.



Scheme 3. Indole derivatives prepared under reductive cyclization conditions. Reaction conditions: **1** (0.01–0.4 mmol), [Fe] (2.5 mol%), Cs_2CO_3 (3.0 equiv.), BnOH (4.0 equiv.) and toluene (0.1 mol/L). All the reactions were realized in a sealed tube at 100 °C in an oil bath, isolated yield.



Scheme 4. Control experiments for the mechanistic insights.

ing methyl or *tert*–butyl groups in cycle B. 2,3,4,9-Tetrahydro-1*H*-carbazole **2n** could also be prepared with our approach. In contrast, dihydrochromene and dihydrothiochromene derivatives were formed with low to moderate yields.

To validate the viability of our methodology, a gram-scale reaction was performed with **1a** (1.0 g, 4.0 mmol) under the optimized conditions defined in Table 1 in a sealed reactor vessel, and product **2a** was isolated after purification on silica gel with an 84% yield.

After the scope exploration, we examined the possibility of constructing indole derivatives (Scheme 3). The reductive cyclization was implemented with the optimal conditions in Table 1. To our pleasure, the trial with 1-nitro-2-(1-phenylvinyl)benzene **3a** (see Supporting information for the synthesis of substrates **3**), produced 3-phenyl-1*H*-indole **4a** with quantitative yield.

On the strength of this result, several nitroarenes **3b-3m** were subjected to our transformation conditions. Electron-donating substituents allowed higher yields (**4b-4d** and **4i-4j**) than the electron-poor ones (**4e**, **4f**, **4k** and **4l**). The indole **4d**, displaying antifungal activity against *Cryptococcus neoformans* (MIC = 32.5 μg/mL) [58], was delivered with a moderate yield. By bearing a strong electron-withdrawing group, molecule **4m** was not detected. Instead, a mixture of non-identified compounds was observed in the ^{1}H NMR of the crude mixture, probably due to various side reactions with the nitro group. Good compatibility was found for naphthalene and pyridine motifs, with 70% and 62% yields, respectively.

Once the scope was well-established, we turned to the mechanistic studies of the transformation. We started to identify the main intermediate of the catalytic cycle. To this end, the cyclization was attempted with the aniline **7**, prepared from the nitro derivative **1a** by Béchamp reduction, in our standard conditions defined previously (Table 1). However, the dihydrobenzo[*c*]carbazole **2a** was only obtained in a 5% yield, and the starting material **7** was recovered simultaneously (Scheme 4a). This result indicated that

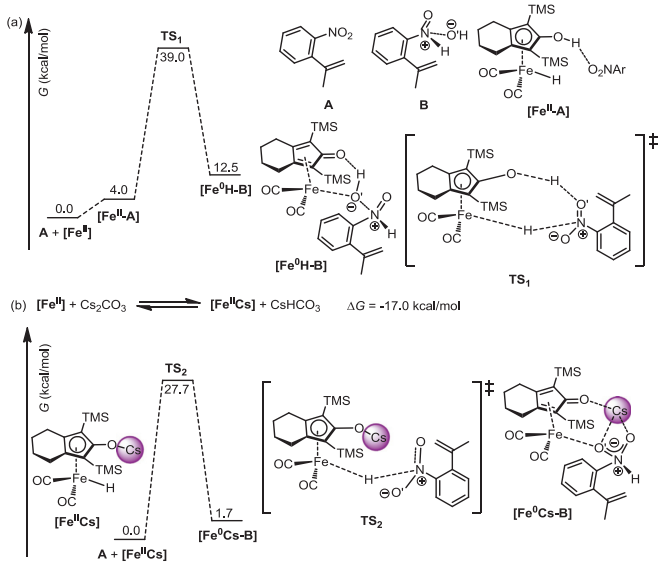
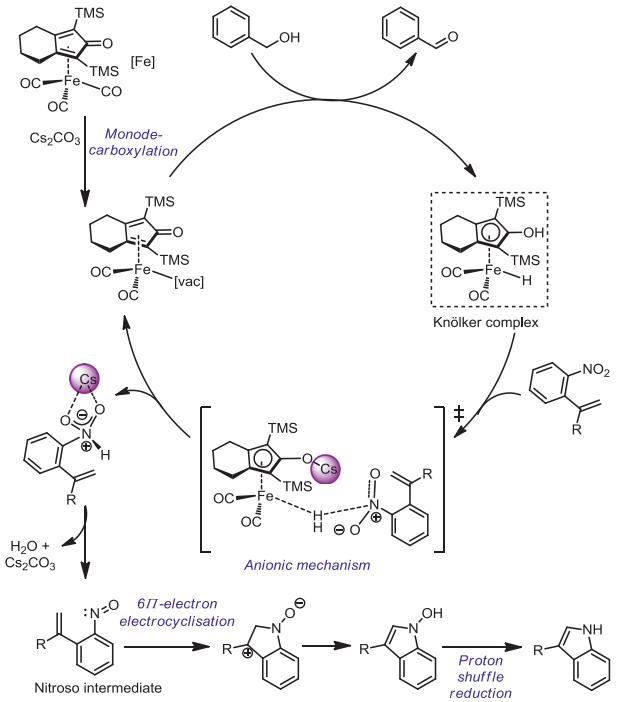


Fig. 2. DFT-computed surface for A reduction by (a) direct hydrogen transfer mechanism (**TS$_1$**) or (b) stepwise reduction mediated by deprotonated Knölker's complex (**TS$_2$**); see Supporting information for computational details.



Scheme 5. Suggested pathway for the iron-catalyzed reductive cyclization of nitroarenes.

the cyclization step would not occur through an amine intermediate. Second, we investigated whether the pathway would follow a radical or two-electron process.

By adding 2 equiv. of TEMPO or 1,1-diphenylethylene as radical traps to the reaction mixture, a yield decrease was noticed (Schemes 4b and c). Further LC-MS analyses of the crude product with TEMPO were achieved at different reaction times (45 min, 2, 7, 18 h), but no adducts with the radical trap were detected. This observation would hint that free radical reactive species were not involved in the reductive cyclization. According to Shevlin *et al.* [56], the mechanism would imply an *N*-hydroxyindole as a reactive intermediate. To verify this hypothesis, we synthesized *N*-hydroxyindole **8** from the nitroalkene **3a** *via* partial pallado- and tin-catalyzed reduction of the nitro group (Scheme 4d). The elaboration of *N*-hydroxyindole derived from nitro derivative **1a** following the same procedure was also envisioned, but the corresponding formed *N*-hydroxyindole was highly unstable (data not shown). *N*-Hydroxyindole **8** was submitted to our cyclization conditions. To our delight, the desired indole was isolated with a 74% yield, confirming the crucial role of the *N*-hydroxyindole in the catalytic cycle.

Besides, DFT calculations were performed. The reduction of nitroalkene **A** has been used as a model reaction for DFT calculations (Fig. 2). Computational work was carried out using the Gaussian09 code at a PBE0 level. Dispersion effects were considered using Grimme's D3 correction (see Supporting information for references and computational details).

In the first time, the reactivity of **A** with Knölker's complex [Cp(OH)Fe^{II}(CO)$_2$(H)] (**[Fe^{II}]**) was investigated. The reaction of the aforementioned reagents (Table 1) can afford a hydrogen-bonded adduct (**[Fe^{II}-A]**, requiring a 4.0 kcal/mol barrier (Fig. 2a). The evolution of **[Fe^{II}-A]** following the classic hydrogen transfer path (HT) proved to be highly endergonic, with a 39.0 kcal/mol computed free energy span (**TS$_1$**). Reduced product **B** can be obtained as an adduct to the Fe^0 complex, **[Fe^{0}H-B]**, located 12.5 kcal/mol above the reactants. Reduction of **A** following the classic HT path is thus difficultly compatible with the experimental conditions developed herein. Moreover, the reduction of **A** by direct HT is much more energy-demanding than the reduction of more classic substrates such as benzaldehyde. Reduction of the latter indeed requires a smaller 11.9 kcal/mol span (Supporting information). Such a discrepancy originates in the structural properties of **B**, which show that the N–O'H bond is particularly long (1.51 Å *vs.* 1.28 Å for the N–O bond, Fig. 2a). In other words, the O'H group in **B** is almost a free HO$^-$ anion, meaning that **B** can be described as a high-energy adduct between a protonated nitroso species and a HO$^-$ anion, such as [ArNH(O)–O'H]. Consequently, we sought an alternative mechanism allowing a formal stabilization of **A**'s reduction product.

In the basic medium provided by the reaction conditions developed herein (Table 1), deprotonation of **[Fe^{II}]** by Cs_2CO_3 was found to be thermally favored, leading to formation of [Cp(OCs)Fe^{II}(CO)$_2$(H)] (**[Fe^{II}Cs]**) with a stabilization of 17.0 kcal/mol (Fig. 2b). This stabilization is however probably overestimated, since Cs_2CO_3 exists in the reaction medium as insoluble oligomers, which is not taken into account in those calculations. Reduction of **A** by complex **[Fe^{II}Cs]**, involving a formal Fe-to-N hydride transfer, can proceed with a 27.7 kcal/mol computed barrier (**TS$_2$**, Fig. 2b), in line with the reaction conditions used herein (24 h, 100 °C).

Reduced product **B** is obtained as an 18-electron adduct to the Fe^0 complex, **[Fe^{0}Cs-B]**. The negative charge developed at the O and O' atoms of the starting nitro reagent is stabilized by close interaction with the bridging Cs$^+$ cation ($d_{O'\text{-}Cs} = 3.07$ Å and $d_{O\text{-}Cs} = 3.04$ Å). It is of note that the N–O'Cs and N–OCs bonds are shorter in **[Fe^{0}Cs-B]** (resp. 1.39 Å and 1.34 Å) than the N–O'H bond in **[Fe^{0}H-B]** (1.56 Å). In other words, those N–O bonds are much stronger in **[Fe^{0}Cs-B]** than in **[Fe^{0}H-B]**, making the adduct **[Fe^{0}Cs-B]** more easily reachable. The latter has been indeed located at 1.7 kcal/mol above the reactants (for further details of the suggested pathway see Supporting information).

Considering all these conclusions, we thus propose the following pathway (Scheme 5). First, the Knölker-type catalyst ([Fe]) is converted into a metallated complex with a vacant site through a monodecarboxylation induced by Cs_2CO_3. This latter iron species undergoes a heterolytic addition of a hydrogen donor (BnOH), leading to the Knölker complex, with oxidation of Fe(0) to Fe(II) and the aromatization of the η^5-hydroxycyclopentadiene cycle. This "hydrogen borrowing" process was firstly described by the Feringa

group [59,60]. It should be highlighted that benzyl alcohol was converted into benzaldehyde, which could be noticed in the crude ^{1}H NMR of all our cyclization reactions. The nitro derivative would then react with the active iron complex by an anionic mechanism (interaction of the nitro compound with the hydride bearing by the iron complex, triggering the hydrogen transfer) to form the nitroso reactive intermediate. The 6π-electrocyclization of the nitroso derivative followed by the iron-catalyzed proton shuffle reduction of the *N*-hydroxyindole furnishes the corresponding *N*-heterocyclic molecule [61,62].

In summary, we have established a new synthetic strategy for constructing the dihydrobenzo[*c*]carbazole and the indole scaffolds. This methodology was based on an iron-mediated reductive cyclization of nitroarenes, substrates easily accessible through Barluenga-Valdés couplings. Our approach requires an iron catalyst derived from the Knölker complex, air-stable and easy-handling, and benzyl alcohol as the non-expensive and low volatile hydrogen donor. The versatility of the method permitted a wide range of dihydrobenzo[*c*]carbazoles (18 examples) and indoles (12 compounds) with moderate to excellent yields. We also confirmed the applicability of our methodology with a gram-scale synthesis of dihydrobenzo[*c*]carbazole **2a** and the preparation of biologically active indole **4d**. DFT modelings show that the reduction mechanism of nitroalkenes reported in this work is in stark contrast with the usual, single-step HT mechanism involving Knölker's complex and more classic substrates such as carbonyls. Indeed, reducing nitroalkenes likely requires the involvement of the conjugate base of Knölker's complex, the counter-cation of the latter playing a crucial role in the stabilization of the reduced intermediate.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.107758.

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