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A simple N-heterocyclic carbene for the catalytic up-conversion of aldehydes into stoichiometric super electron donors†

Nadhrata Assani,^a Ludivine Delfau,^b Preslav Smits,^b Sébastien Redon,^a Youssef Kabri,^a Eder Tomás-Mendivil,^b Patrice Vanelle,^a David Martin^{b*} and Julie Broggi^{a*}

Catalytic amounts of 1,3-di(methyl)imidazole-2-ylidene, one of the simplest and most prototypical N-heterocyclic carbenes, can up-convert aldehydes into powerful stoichiometric sources of electrons (Super Electron Donors) for reductive transformations of iodoaryls ($E_{\text{red}} < -2$ V). In particular, the hydroarylation of 1,1'-diarylethylenes, which may require high temperatures and inherently generate stoichiometric amounts of oxidized waste, was performed at room temperature, with the concomitant formation of esters as oxidized co-products.

Introduction

The development of Organic Electron Donors (OEDs) has allowed for a broad range of selective metal-free reductive transformations.¹ The design of compounds with increasingly reducing power, termed Super Electron Donors (SEDs), has culminated so far in the report of tetra(iminophosphorano)-substituted bispyridinylidene **A**, which can undergo reversible oxidation at $E_{1/2}(\text{A}/\text{A}^{2+}) = -1.7$ V versus SCE and perform the challenging reduction of iodoarenes (Fig. 1a).²

Note that, similarly to other OEDs with dimeric patterns,³ **A** can be generated *in situ* by the deprotonation of precursor **B**, which is air-stable and easier to handle. More generally, a variety of reductant up-conversions^{4,5} of weak reagents into various SEDs have been considered, ranging from *in situ* stoichiometric chemical reactions³ to photoactivation.⁶ Several groups described reactions involving catalytic amounts of chemically upconverted SEDs, such as benzimidazole radical **C**⁷ ($E_{\text{P}}^{\text{ox}} = -2.1$ V),⁸ dioxane-derived radical anion **D**,⁹ diketopiperazine bis-enolate **E**,¹⁰ or phenanthroline-based anion **F**,¹¹ which promote the reductive transformations of halogenoaryls at high temperatures (Fig. 1b–d). In these processes, the stoichiometric sacrificial electron donors are solvents or metallic hydrides. They are required for feeding electrons into the catalytic cycle, but yield wasteful oxidized co-products and can cause side reactions.

On the other hand, aldehydes are ubiquitous synthons in organic synthesis, some of which are available from biomass resources, and they represent a valuable source of electrons. They are up-converted by N-heterocyclic carbenes (NHCs) into Breslow intermediates **G·H** (Fig. 2a).^{12,13} The oxidation of the latter into acyliums **G⁺** yields numerous valuable products upon reaction with nucleophiles.¹⁴ Yet, very few studies have considered the fate of the oxidative partner. In 1980, Inoue and Higashiuba showed that phenazine ($E_{\text{red}} = -0.6$ V)¹⁵ and azobenzene ($E_{\text{red}} = -1.3$ V)¹⁶ are reduced in the presence of aldehydes under NHC catalysis, yielding dihydrophenazine and benzidine, respectively.¹⁷ The group of Chi also designed a few

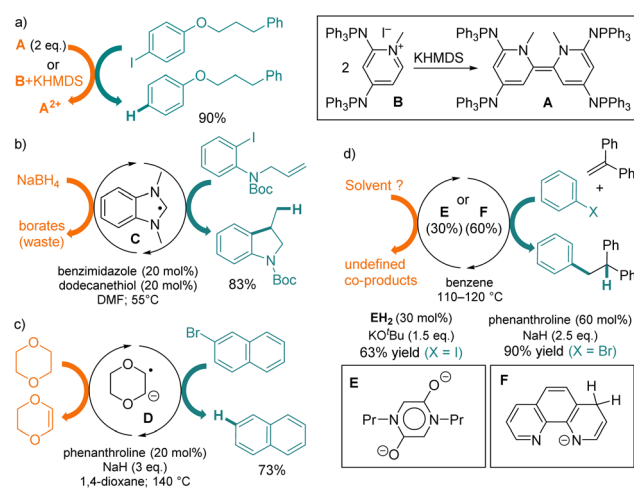


Fig. 1 (a) Reduction of aryl halides with a stoichiometric organic Super Electron Donor (SED, 2 equiv.) **A** or (b–d) with catalytically up-converted SEDs **C–F**.

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4sc04011b>



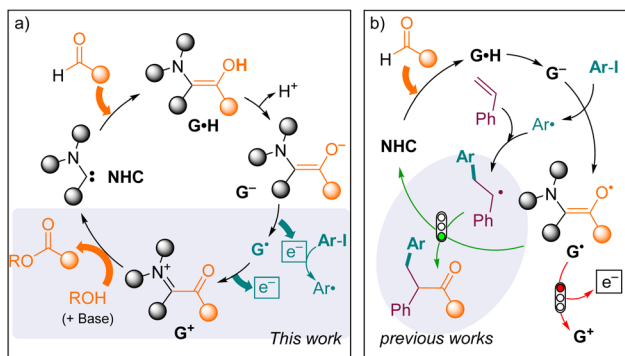


Fig. 2 (a) Reductant up-conversion of aldehydes under NHC catalysis. (b) Interception of G[•] by transient radicals in the redox-neutral NHC-catalysed acylarylation of styrenes.

NHC-catalysed reductive functionalization reactions of activated nitrobenzyl bromides ($E_{\text{red}} < -0.8$ V) or nitroalkenes ($E_{\text{red}} < -0.6$ V)¹⁸ in the presence of methanol, with the concomitant formation of a methyl ester.¹⁹ More recently, NHC-catalysed radical transformations of aldehydes²⁰ have advanced to include the activation of more challenging substrates, such as iodoaryls ($E_{\text{red}} < -2$ V),²¹ via single electron transfer (SET) from Breslow-type enolates G⁻ stemming from thiazol-2-ylidenes (Ohmiya group),²³ 1,3,4-triazol-2-ylidenes (Chi group)²⁴ or meso-ionic 1,4,5-triazol-2-ylidenes (Bertrand and Yan groups).²⁵ However, so far, these radical reactions have remained redox-neutral overall, because the transient radicals are intercepted by persistent Breslow-type radicals G[•], affording ketone derivatives (Fig. 2b).

Herein, we show that catalytic amounts of 1,3-di(methyl)imidazole-2-ylidene, one of the simplest and most prototypical N-heterocyclic carbenes (NHCs), can up-convert aldehydes into strong SED reagents for the light-free reductive transformations of iodoaryls ($E_{\text{red}} < -2$ V) at room temperature, with the concomitant formation of esters as oxidized co-products.

Results and discussion

We were intrigued by electrochemical²⁶ and computational²⁷ studies, indicating that imidazole-2-ylidene NHCs should provide some of the strongest electron-donor enolates G⁻ with oxidation potentials (*ca.* -2.1 V) lower than those of enolates stemming from thiazolylidenes (-1.4 V) or mesoionic carbenes (-1.8 V), which are known to perform the reductive radical activation of iodoaryls. Thus, although imidazolylidenes have been disregarded as mediocre catalysts for the radical transformations of aldehydes,^{19b,28} we attempted the reductive addition of iodobenzene **2a** to 1,1'-diphenylethylene **3a**, in the presence of benzaldehyde **1a**, potassium *tert*-butoxide and a catalytic amount of the imidazolium precursor of NHC **C2**, featuring bulky 1,3-di(isopropyl)phenyl *N*-substituents (Fig. 3a). After one day at room temperature, NMR monitoring of the crude mixture indicated the presence of 1,1,2-triphenylethane **5aa** with a low, but encouraging, 11% conversion, and the concomitant formation of *tert*-butyl benzoate ester **4a**.

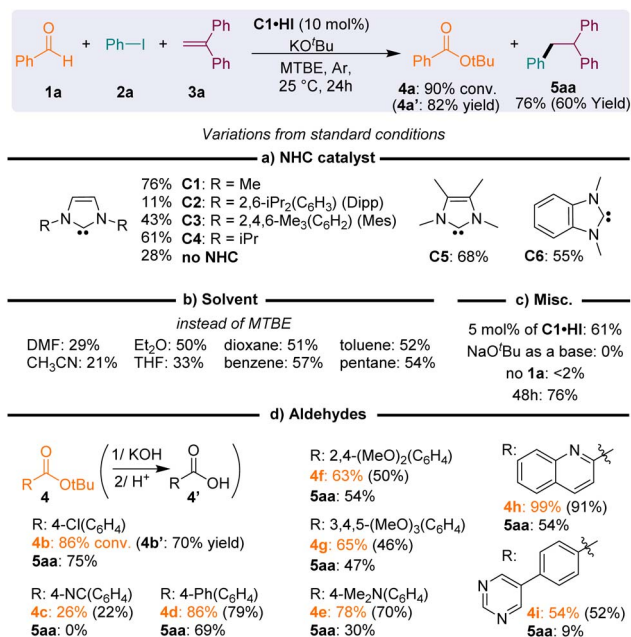


Fig. 3 Optimization of NHC-catalysed reductive anti-Markovnikov hydroarylation of 1,2-diphenylethylene with phenyl iodide; standard reaction conditions were: **1a** (0.3 mmol), **2a** (0.36 mmol), **3a** (0.20 mmol), C1•HI (10 mol%), and KO^tBu (0.3 mmol) in dry MTBE (0.6 mL) under an argon atmosphere for 24 h at 25 °C. Percentages are for the conversion of **3a** into product **5aa**, unless otherwise noted. Values in brackets are yields.

The use of NHCs **C1–6** with decreasing steric bulk increased the conversion of **5aa**, up to 76% with 1,3-di(methyl)imidazolylidene **C1**. The reaction also worked with *N*-methyl substituted NHCs **C5** and **C6** (with 3,4-dimethylimidazole and benzimidazole backbones, respectively), though with slightly lower conversions. The clear reactivity difference of NHCs **C1–6** could not be attributed to the similar reducing power of their Breslow derivative ($E_p \approx -1.1, -1.8$ V vs. SCE, see the ESI†). The deleterious effect of steric hindrance at the *N*-substituents of the NHC catalyst was interpreted as resulting from a significant decrease of the nucleophilicity of the NHC, therefore precluding the fast formation of the Breslow intermediate G⁻H. The steric hindrance of G⁻H itself could also impede the formation of a tight charge transfer complex (CTC) with the substrate, leading to slow electron transfers. Interestingly, 28% conversion was observed in the absence of the NHC, indicating the existence of some background reactions, likely promoted by stoichiometric potassium *tert*-butoxide.²⁹ In the absence of aldehyde **1a**, starting iodobenzene **2a** was recovered (<2% **5aa**).

Further optimization established *tert*-butyl methyl ether (MTBE) as the solvent and the reaction performed better at room temperature (25 °C) with a 10 mol% catalyst loading (Fig. 3b and c). The best conversion rates were obtained with non-polar solvents. Note that the conversion rate was not influenced by their C–H bond dissociation energy (BDE_{C–H}). Solvents with high BDE_{C–H} (benzene: 113 kcal mol⁻¹ and pentane: 100 kcal mol⁻¹) exhibited the same reactivity as solvents with lower BDE_{C–H} (diethyl ether: 93 kcal mol⁻¹ and



toluene: 89 kcal mol⁻¹). No conversion was observed with sodium *tert*-butoxide as a base, likely due to its poor solubility in MTBE.

Other aryl aldehyde partners were tolerated, provided that they were neither too electron-rich nor too electron-poor (Fig. 3d). This balance is in line with the expected necessity for the aldehyde to be both electrophilic enough for fast addition of the NHC and electron-rich enough to yield a highly reducing Breslow enolate. Satisfyingly, the ester co-product was easily removed from the crude reaction and recovered in good yields by saponification, followed by acidic precipitation of the corresponding carboxylic acid **4'** from the aqueous solution.

Next, we considered various substrates under these optimized conditions (Fig. 4). Aryl iodides bearing electron-donating or electron-withdrawing groups reacted well,

affording the corresponding arylation products **5aa–5ma** in moderate to good yields. Sterically hindered aryl iodides (**2f**, **2h**, and **2j–l**) were also tolerated. Substrate **2m**, featuring both iodoaryl and alkene moieties, underwent intramolecular cyclisation to afford dihydro-benzofuran **5ma**, which was isolated in a modest 30% yield.

A limitation was reached with heterocycles: 2-iodo thiophene **2n** and 4-iodopyridine **2o** were reduced, but less than 10% of the desired addition products **5na** and **5oa** was observed. Indeed, the 1,1'-diphenylethylene **3a** was not sufficiently electron-rich to trap these electrophilic pyridyl and thienyl radicals under our mild room-temperature conditions.³⁰ On the other hand, the reduction of the more challenging iodoester **2p** failed and the starting materials were mainly recovered.

The reductive coupling of iodobenzene also performed well with geminal diaryl- and heteroaryl-ethylenes **3a–g**. Addition to trisubstituted ethylene **3e** was also possible, albeit sluggish (**5ae** conv. 15%). However, neither *trans*-stilbene **3h** nor aliphatic counterparts **3i–k** could trap the phenyl radical, as the formation of the corresponding products **5ah–5ak** was not observed. Note that in the case of the electron poor α -(trifluoromethyl) styrene **3k**, broad band shapes in the ¹H NMR spectra of the crude mixture suggested the formation of oligomers.

Importantly, when styrene was introduced as a radical trap, aryl-acylation products **6** were obtained, indicating the interception of the persistent Breslow-type radical **G'** (Fig. 5a). Although the conditions have not been optimized for this specific reaction, compounds **6** were isolated in 26–45% yields, which compared well with the results of the previously reported

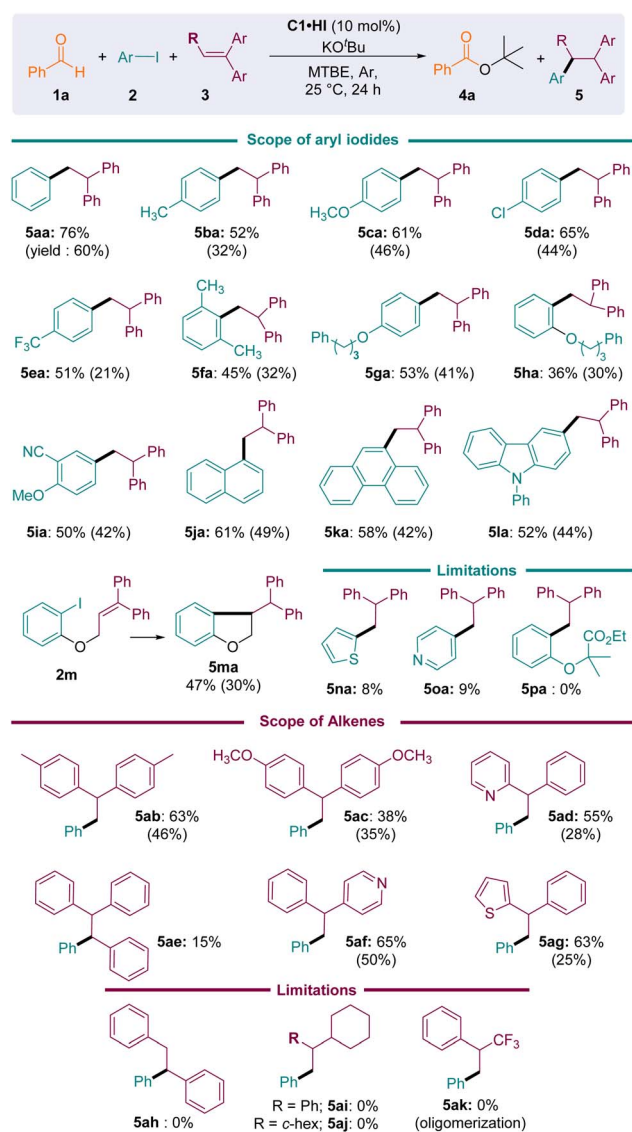


Fig. 4 Substrate scope of the NHC-catalysed hydroarylation of 1,1'-diarylethylenes with aryl iodides under pre-optimized conditions. Conversions were evaluated from the ¹H NMR spectra of the crude reaction. Values in brackets are yields.

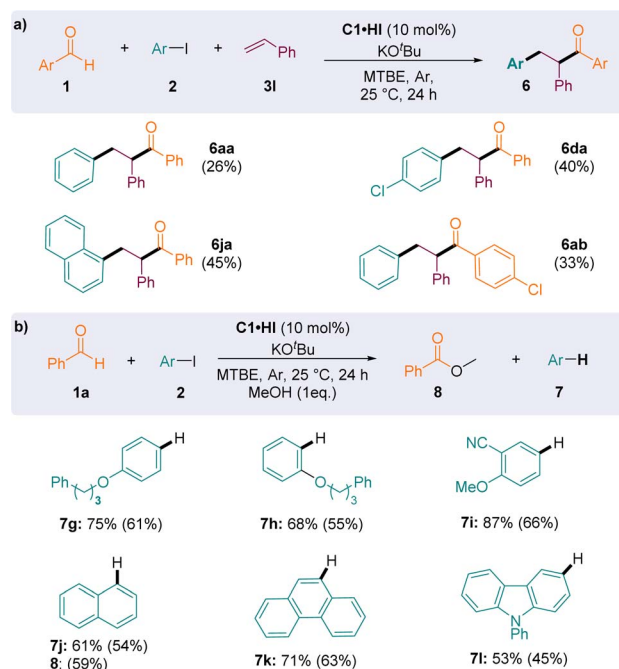


Fig. 5 (a) NHC-catalysed (redox-neutral) aryl-acylation of styrene. (b) NHC-catalysed reduction of iodoaryls to arenes with benzaldehyde as a source of electron. Values in brackets are yields.



In particular, this mechanistic proposition accounts for the formation of aryl-acylation products **6** when styrene is the co-reactant, with **Y'** being then a more difficult-to-reduce benzylic radical.

Prior to our investigations, imidazole-2-ylidenes had been unsuccessfully tested and considered unfit for the promotion of radical transformations of aldehydes. In contrast, this work reveals the unforeseen potential of these NHCs for the generation of strong SED enolates. We are currently reinvestigating the use and scope of this family of organic catalysts for the reductive activation of challenging substrates.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

J. B. and D. M. conceived the project and acquired funding. J. B., D. M., E. T.-M. and P. V. provided resources and supervised the project. N. A., L. D., E. T.-M. and P. S. conducted the investigation and formal analysis of the methodology. All authors contributed to the reviewing and editing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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