α-Diimine-Mediated C-H Functionalization of Arenes for Aryl-Aryl Cross-Coupling Reactions

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α-Diimine-Mediated C-H Functionalization of Arenes for Aryl-Aryl Cross-Coupling Reactions

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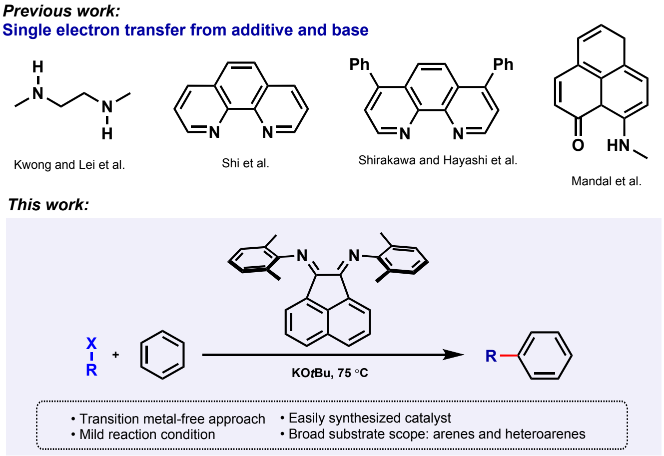
Easily accessible methods for direct C-H arylation of arenes have been explored in the presence of transition metal catalysts to facilitate C-C bond formation; however, the absence of transition-metal impurities is a significant concern in the preparation of active pharmaceutical ingredients (APIs). Herein, we examine the use of bis(imino)acenaphthene (BIAN) as a potential single-electron transfer initiator in transition metal-free C-C bond-forming reactions. Using this approach, arenes are coupled to several aryl and heteroaryl halides. Based upon preliminary mechanistic evidence and crystallographic probation of an active initiator species, we tentatively propose a potassium-stabilized 'metal-free' radical pathway is in operation.

Introduction

The formation of aryl-aryl bonds is of great significance in synthetic chemistry. The biaryl motif is often encountered in natural products and has been incorporated as an integral component in important pharmaceutical, medicinal, and agricultural chemicals.[1, 2] Hence, there is an ongoing interest in the generation of C_{Ar}-C_{Ar} bonds by easily accessible and robust routes. While there are several methods available to create an aryl-aryl bond, the most well-established techniques exploit transition metals (TMs) such as palladium-, rhodium-, and ruthenium-based catalysts.[3] Although high yields and selectivity can be obtained by these methods, recent (and growing) demand for transition metal-free transformations has emerged. Precious metal impurities in active pharmaceutical ingredients (APIs), which run afoul of regulatory agencies, can be avoided in TM-free strategies and is an important driving force for the development of such approaches. Recently, single-electron transfer reactions have emerged as one TM-free alternative to traditional, heavy metal-mediated, two-electron chemistry.[4-7]

The use of an organic additive in concert with a base can generate an effective system for electron transfer in single-electron transfer (SET) reactions.[8] The role of organic electron donors in the initiation of base-promoted homolytic aromatic substitution (BHAS) is crucial in coupling reactions between haloarenes and arenes.[9] Such a combination may lead to BHAS reactions to deliver C-C bond formation, thus avoiding C_{arene}-H activation via oxidative addition, eschewing the need for transition metal centers to regulate such activation modes.[10] This transformation has been developed using a variety of amino- and phenanthroline-based initiators including DMEDA,[4] 1,10-phenanthroline,[5] 2,9-diphenyl-1,10-phenanthroline,[6] and phenylhydrazine[11] in combination with bases such as KO*t*Bu (Scheme 1). These reports have demonstrated that simple organic molecules can serve as efficient electron donors that facilitate C-C bond-forming reactions through a single-electron pathway. Despite this success, from a practical perspective these transformations suffer from the requirements of either high temperatures or high initiator loadings.



Scheme 1 Examples of initiators employed in direct C-H arylation reactions and the current work using ^{Ar}BIAN.

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Our group has been active in the exploration of the use of the redox non-innocent bis(arylimino)acenaphthene (BIAN) ligand to support transition metals (M = Fe,[16] Ni,[17] Co[18]) in catalytic hydrofunctionalization chemistry.[12] A recent report from Adhikari and co-workers disclosed the use of a simple pyrazole system capable of effecting C_{Ar}-C_{Ar} bond formation under mild reaction conditions.[10] Intrigued by this report, we wondered if a similar approach could be adapted to employ the BIAN motif as the initiator in the absence of any transition metals. The core structural features of the BIAN ligand, generically a diimine ligand, can be thought of as arising from the fusion between a 1,4-diaza-1,3-butadiene (DAB) and naphthalene unit. The rigid naphthalene backbone in aryl BIAN (Ar-BIAN) ligands prevents free-rotation around the diimine C-C bond, thus locking them in *s-cis* conformations.[13] One of the important features of BIAN ligands is their ability to accept electrons, and consequently stabilize a variety of complexes photochemically[14] and electrochemically.[15] This redox behavior prompted us to explore its ability to promote SET chemistry.

Results and Discussion

Ligand Effects. Initially, we chose the formation of C_{Ar}-C_{Ar} bonds between iodoanisole (**1a**) and benzene as a model reaction system. We examined a mixture comprising **1a**, Ar-BIAN (**L$_1$**-**L$_8$**; 10 mol%), and KO*t*Bu (2 equiv.) in benzene, and the reaction mixture was heated at 75 °C (Scheme 2). The impact of electron donating/withdrawing substituents in the aryl component of the BIAN ligand on reaction efficiency was explored. Analysis of the reaction mixture by GC-MS after 4h showed that the reaction proceeded in good to excellent yields (71-99 %) when electron-releasing substituents were present on the BIAN ligand. The performance of the 2,6-dimethyl-BIAN (**L$_1$**) is noteworthy, surprisingly the 3,5-dimethyl-BIAN (**L$_3$**) exhibited a distinct drop in product formation, 99 and 71 %, respectively. Addition of a third methyl group (**L$_2$**) had essentially no impact on the observed reactivity. Thus, we conclude that some steric impact arising from 2,6-disubstitution is responsible for the superior performance of **L$_1$**. Introduction of either a bromine atom or a methoxy group at the 4-position (**L$_4$** and **L$_5$**) afforded conversions of 98% and 95%, respectively. Significantly, the presence of a strongly electron-withdrawing fluorine atom at the 4-position (**L$_6$**), a bulky isopropyl group at the 2- and 6- positions (**L$_7$**), or the absence of the naphthalene scaffold (**L$_8$**) in the initiator essentially shut down the transformation. From these results, it appears that electronic influences and steric effects can influence the reaction efficiency. Moreover, the lack of extended π-conjugation has a deleterious impact on reaction yield.

Initiator Loading. Initial screening of the transformation of **1a** in the presence of benzene was performed using 10 mol% **L$_1$** and 2 equiv. KO*t*Bu; 99% conversion of **1a** was observed when the reaction mixture was analyzed by GC-MS after 4 h (Table 1, entry 1). Lowering the initiator loading to 5 mol% afforded 84% conversion of **1a** to the desired product (**2a**) under otherwise identical reaction conditions (Table 1, entry 2). Gratifyingly, 99% conversion of **1a** employing 5 mol% **L$_1$** could be achieved with longer reaction times (15 h, Table 1, entry 3). A control reaction revealed that no desired product forms in the absence of **L$_1$** (Table 1, entry 5).

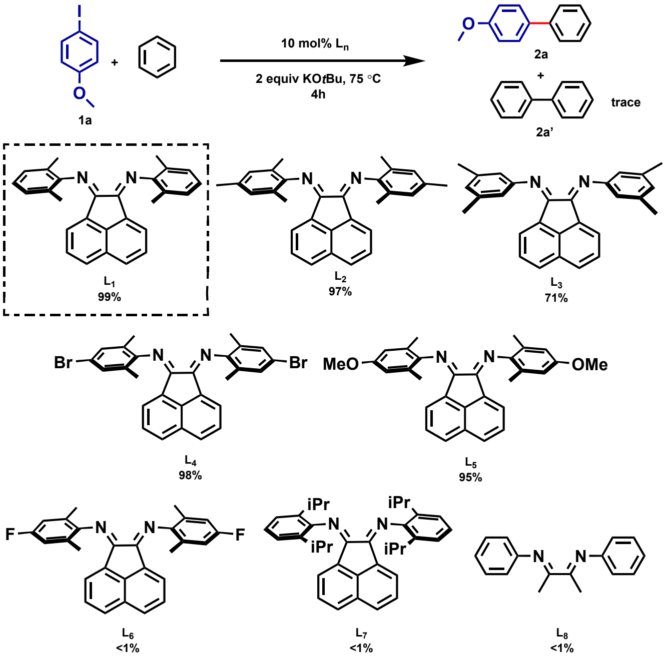
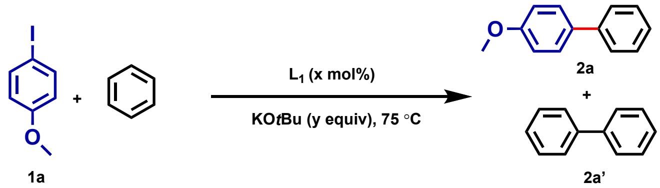


Table 1 Optimization of ligand and base loading.



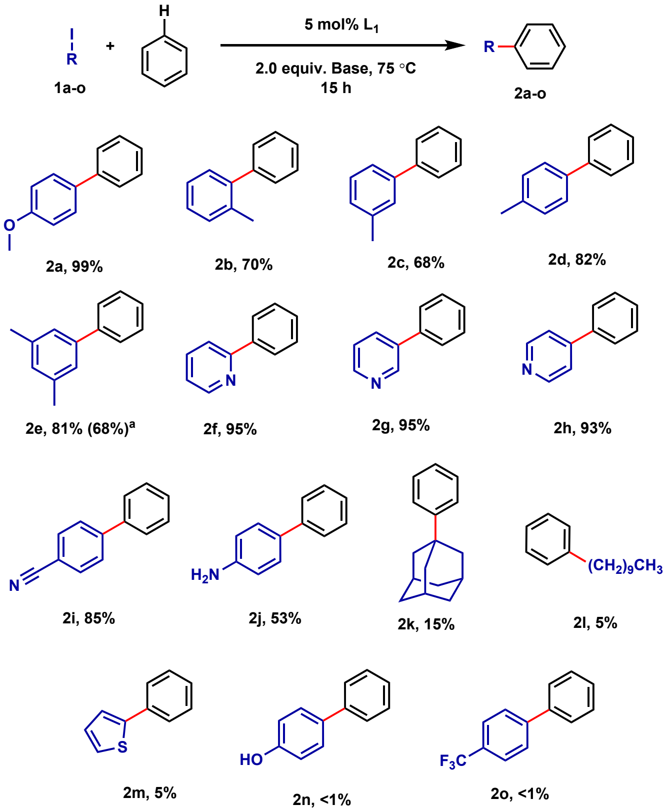
Entry	L$_1$ (mol%)	KO*t*Bu (equiv)	Time (h)	Conversion (%)	2a'
1	10	2	4	99	trace
2	5	2	4	84	trace
3	5	2	15	99	trace
4	5	1.5	15	>99	-
5	-	2	15	<1	-
6	5	-	15	<1	-
7[b]	5	2	15	82	trace
8[c]	5	2	15	<1	-

[a]Reaction conditions: **1** (1 mmol), Benzene (2mL); Yields determined by GC-MS. [b]Reaction under dark. [c]Reaction in air.

Scheme 2 Ligand effects on reactivity. Yields determined by GC-MS.

Loading of Base. Subsequently, we decided to explore the use of different bases and were initially surprised to learn that only KO*t*Bu was effective in facilitating product formation (Supporting Information, Table S1).[16] Since the only difference amongst the bases examined was the counter cation (NaO*t*Bu, KO*t*Bu, Mg(O*t*Bu)$_2$, and Be(O*t*Bu)$_2$), we further investigated the role of the base. A control reaction conducted in the absence of base afforded no conversion (Table 1, entry 6). This result suggested that the alkali metal cation possibly played a role in this transformation. It is noteworthy that trace quantities of biphenyl by-product **2a'** were formed in each case. A series of reactions revealed that 1.5 equiv of the base is required to reach the optimum product yield and suppress formation of **2a'** (Table 1, entry 4).

To examine whether the reaction is light-initiated, we performed a control reaction in complete darkness, where the yield was undiminished (Table 1, entry 7). To assess the robustness of the reaction, an experiment was conducted in air and no product could be detected (Table 1, entry 8). With these optimization results in hand, we explored a small scope of substrates amenable to these reaction conditions with a variety of aryl iodides (Scheme 3).

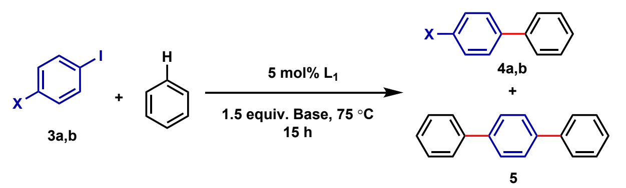


Scheme 3 Substrate scope. NMR yield analyzed with hexamethylbenzene or trimethoxybenzene standards. [a]Isolated yield.

Aryl iodides with electron donating and withdrawing groups were compatible with our reaction system. Substrates with methyl or methoxy groups (**1a**-**e**) on the backbone reached good to excellent yields (68-99%) in most cases; in the case of substrates **1b** and **1c**, in which a methyl group is located at the ortho and meta position, respectively, diminished yields were observed. The impact of electron-withdrawing substituents was more difficult to assess as a range of yields were obtained. For example, with - CF_3 in the para position (**2o**), no appreciable yield was observed. However, in the case of a cyano group **2i**, an 85% yield was obtained. In the case of heteroatom containing iodides, iodopyridines were highly effective substrates and yields reached >93% while 2-iodothiophene (**1m**) proved an ineffective substrate. In the case of iodo-C(sp3) substrates such as **1k** and **1l**, only low yields were observed. Finally, we tested amino- and alcohol-containing substrates and discovered that although amines were tolerated, 53% yield of **2j**, in contrast, phenol--containing species were not competent substrates (**2n**). As phenols possess low pKa value, the substituent may react with an equivalent of base instead of formation of the active species.

To assess the relative reactivity of dihaloarene substrates, (*p*-iodo)halobenzene was employed as a substrate (Table 2). In the case of fluoro-iodo-substrate (**3a**) 82% conversion to monocoupled product (**4a**) was observed with no evidence for the formation of terphenyl (**5**). When the chloro-iodo-substrate (**3b**) was employed, a ~2:1 ratio of mono-coupling product (**4b**) to terphenyl (**5**) was obtained. Finally, 1,4-diiodobenzene (**3c**) afforded almost 1:1 mixtures of mono- (**4c**) and diarylation (**5**) products. In prior studies, Studer and co-workers previously reported related reactions of dihaloarene substrates which also displayed competing pathways to afford either disubstituted or monosubstituted products.[17] In this report, as the halide leaving group changes from -F, to -Br and -I, the difunctionalization pathway becomes increasingly competitive with the monofunctionalization pathway.

Table 2 Competition experiment employing dihalogenated aryl substrates. Yields were measured by NMR using standard, trimethoxybenzene.

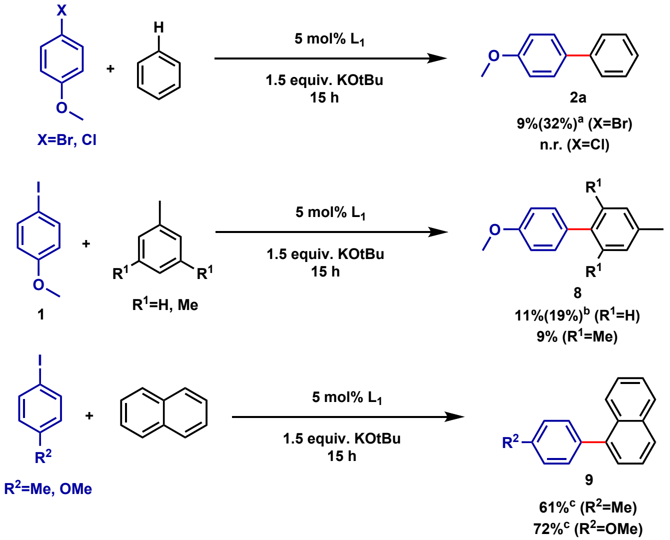


	X group	4:5 (%)
a	F	82 (66)[a]:0
b	Cl	67:33
c	I	45 (30)[a]:52(44)[a]

[a]Isolated yield.

Previously reported mechanisms which invoke aryl radical generation through SET, predict that more electron-deficient aryl halides have higher reactivities.[18] A qualitative competition reaction between aryl iodides (Supporting information, Scheme S1) did not conclusively reveal that more electron-deficient aryl iodides react faster with benzene than electron-rich aryl iodides.

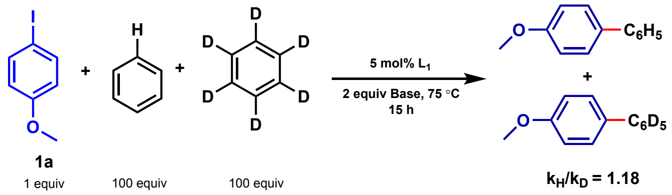
Upon changing the non-activated arene coupling partner from benzene to toluene and mesitylene, the biaryl coupling products were obtained in lower yields (Scheme 4). It is noteworthy that no reactions were observed where aryl chlorides were employed as the electrophiles, and less than 10% direct arylation with bromoanisole was observed. When both toluene and bromoanisole, are employed, minor increases in product yield can be obtained using higher temperatures and longer reaction times. When the arene coupling partner was switched to naphthalene higher yields were obtained, 61% and 72% for methyl and methoxy groups in the para position, respectively (**9a** and **9b**).



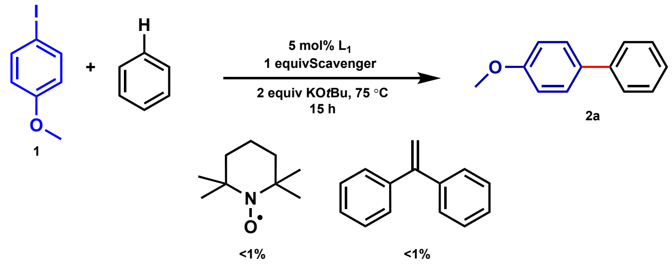
Scheme 4 Different aryl coupling partners. Yields measured by NMR using standards, hexamethylbenzene. ᵃ100 °C for 24h. ᵇ120 °C for 48h. ᶜIsolated yield.

Metal-Free Chemistry? Recent cautionary tales of 'metal-free' alternatives to traditional transition metal-catalysed transformations[19] demand chemists to tread lightly when evaluating such claims.[20, 21] This motivated us to investigate and identify any possible sources of 'catalytic' metals present in the reaction mixture. Initially, we had prepared BIAN using a previously reported strategy which employs a Zn templating strategy.[12] An ICP-MS analysis of the BIAN prepared in this fashion revealed the presence of small traces of Zn (2.55 ppm; Supplementary Information) carried over from BIAN synthesis. Recognizing that Zn has seen application as a catalyst in C-C bond forming reactions,[22, 23] we investigated the possible role of Zn in our catalytic transformation. A stoichiometric amount of TMEDA was added to trap the Zn cation during the reaction;[24] however, no significant effect upon reactionperformance was observed (95% NMR yield of 4-methoxybiphenyl, **2a**) under otherwise identical reaction conditions. Subsequently, we introduced a stoichiometric amount of $ZnCl_2$ as a possible source of catalyst; similarly, no enhancement of reaction performance was observed.

We also explored alternative reaction conditions to synthesize the BIAN in the absence of metals. We adapted a condensation procedure for the reaction between 2,6-dimethylaniline and acenaphthenequinone in the presence of an acid catalyst instead of $ZnCl_2$ (Supporting Information, Scheme S2).[25] Using these reaction conditions, we successfully isolated the BIAN product in 63% yield after crystallization. We then carried out the same catalytic transformations using this 'metal-free' BIAN also using new glassware and equipment (Supplementary Information, Figures S1 and S2). These reactions afforded an excellent and highly reproducible yield (94% NMR yield) of the desired C-C coupled product. Finally, to eliminate the possibility of any unintended transition-metal contamination arising from the presence of the KO*t*Bu base, which could plausibly promote the biaryl coupling reaction, we purchased and employed "99.99% pure" base from a commercial vendor, and again the reaction proceeded smoothly. When taken together, we believe this strongly argues against the presence of 'hidden' transition metal-catalysed processes.



Scheme 5 KIE Experiments employing H_6- and D_6-benzene.



Scheme 6 Radical Experiments employing TEMPO and 1,1-diphenylethylene, based on GC-MS analysis.

Preliminary Mechanistic Investigation. We have also carried out preliminary investigations to gain insight into the reaction mechanism by using iodoanisole (**1a**) as a model substrate in a series of experiments described below. A competition experiment was carried out in which equimolar amounts of benzene and benzene-d_6 were employed as coupling partners with **1a** under otherwise standard reaction conditions (Scheme 5). The ratio of products formed after the overnight reaction was calculated using GC-MS analysis. The ratio of incorporation of non-deuterated vs. deuterated benzene (k_H/k_D) was found to be 1.18/1 (Supplementary information, Figure S3). This indicates the absence of a primary kinetic isotope effect in (or before) the rate-determining step; hence we propose that C-H(D) bond-breaking is not involved in the rate-determining step. This conclusion correlates with previously reported KIE study[6] which proposed similar k_H/k_D value.

Based on literature precedent,[6] we believed that the involvement of radical species as reactive intermediates was highly likely. Thus, we repeated our catalytic transformations in the presence of commonly employed free-radical traps: TEMPO and 1,1-diphenylethylene. In both cases, the reaction was completely inhibited and afforded <1% of desired product (**2a**). This strongly suggests the involvement of free radical species in the reaction pathway (Scheme 6).

In the majority of previous reports the initiators of SET are generated *in situ*,[10] we were interested in investigating the nature of the promoter in our system. $\mathbf{L_1}$ is bright orange, and treatment of 1 equiv of KO*t*Bu darkens its color to brown, likely suggesting the coordination of K^+ with the BIAN $\mathbf{L_1}$. Upon recrystallization, we were able to isolate a BIAN-supported potassium cation in the presence of 18-Crown-6. Dark brown crystals suitable for study employing single crystal X-ray diffraction experiments were harvested from a mixture of diethyl ether and 1,2-dimethoxyethane solution of $\mathbf{L_1}$ and KO*t*Bu (in the presence of 18-Crown-6) at -30 °C for several days. Further scrutiny of the molecular structure reveals that the potassium is encapsulated in the crown cavity and is in close proximity to both nitrogens of $\mathbf{L_1}$. The K–N distances for both nitrogen atoms are 2.852(2) and 2.907(2) Å. It is likely that the presence of such chelating nitrogens is required for K–N interaction, which is also indirectly supported by the failure of BIAN $\mathbf{L_7}$ in initiation, where steric impacts likely retard coordination.

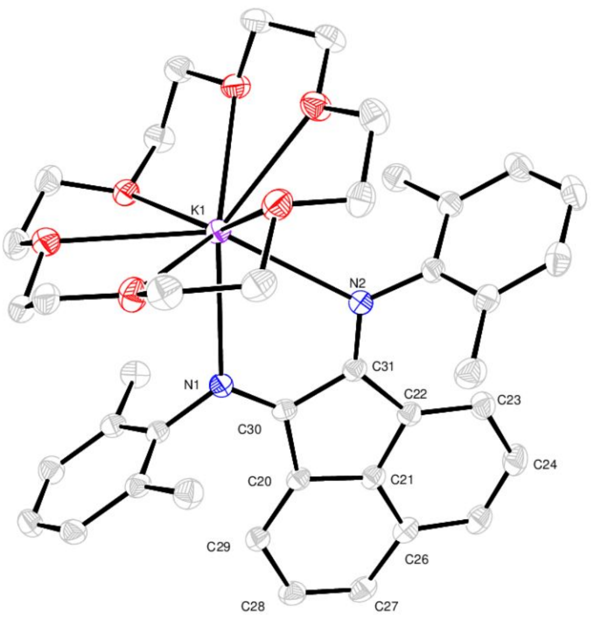
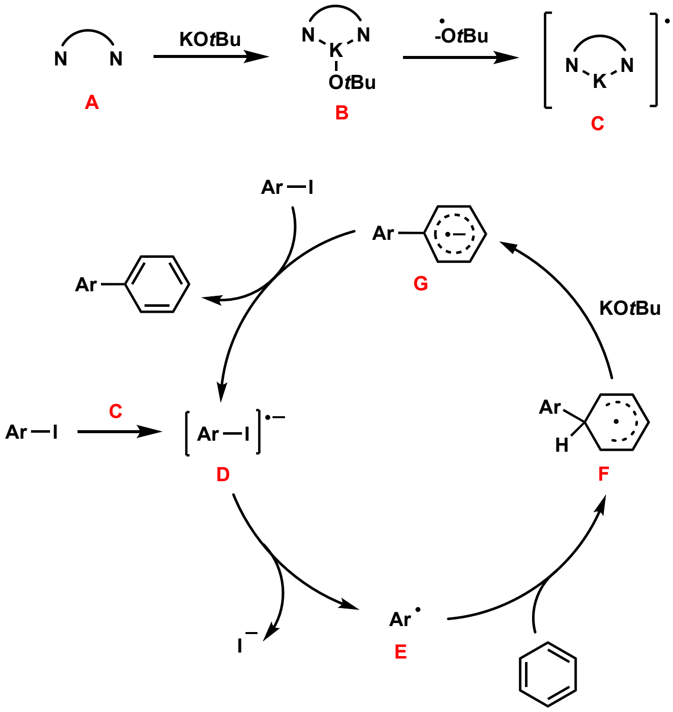


Figure 1 ORTEP representation of [$^{2,6\text{-Me}}$BIAN][K-C18-Crown-6]. Thermal ellipsoids are drawn at the 30% probability level. Selected bond length [Å] and angles [°] for complex: K1–N1 2.852(2), K1–N2 2.907(2), N1–C30 1.320(9), N2–C31 1.325(9), C30–C31 1.454(13), N1–K1–N2 59.8 (6), K1–N1–C30 117.0 (6), N1–C30–C31 122.8(4), C30–C31–N2 122.0(3), and C31–N2–K1 116.3(6). Hydrogen atoms were omitted for clarity.

BIANs are widely studied and find application as a redox non-innocent ligand in coordination chemistry arising from their ability to support multiple formal metal oxidation states. The reduction of BIAN by one-electron produces a radical anion that is delocalized between the diimine scaffold.[12] This stabilization is enabled via delocalization of the electron density into ligand-based antibonding orbitals. The N1–C30 and N2–C31 bond lengths of the imine residues (1.320(9) and 1.326(9) Å, respectively) are slightly elongated from typical C=N bond values and the C30-C31 distance is shortened compared to a typical C-C bond.[26] These bond lengths are typically interpreted as the outcome of a single reduction event occurring within the BIAN ($\mathbf{L_1}$) framework.

It is conceivable that the potassium-bound BIAN can facilitate SET to break the aryl iodide bond, generating an aryl radical. To support this hypothesis, we conducted a reaction with isolated crystals of **[L$_1$][K(crown)]** . Consistent with our assertion, the reaction initiated by **[L$_1$][K(crown)]** proceeded smoothly and afforded the biphenyl product in 96% yield.

A plausible reaction mechanism for the BHAS,[11] specifically arylation of benzene using the BIAN as initiator is shown in Scheme 7. BIAN (A) coordinates with KO*t*Bu to form complex B followed by formation of reduced 'active' species C. In the initiation step, a single electron transfer (SET) from K-BIAN complex C takes place to the aryliodide substrate to afford an intermediate radical anion D. The radical anion D delivers aryl radical E upon loss of iodide anion. The aryl radical is quickly converted to a cyclohexadienyl radical F upon reaction with benzene, followed by deprotonation to give G. Electron transfer to the starting material aryl halide eventually delivers the coupling product and close the catalytic cycle.



Scheme 7. A plausible reaction mechanism based upon experimental observations.

Conclusions

In a similar fashion to other nitrogen-based systems, BIAN can act as an initiator for C-C bond-forming reactions in the absence of a transition metal center. Based upon preliminary mechanistic investigations, we propose a potassium-BIAN complex forms which is capable of effecting single-electron transfer to an aryl-halide substrate followed by radical addition to an arene to form a new C-C bond. A small scope of substrate study was also carried out. Further studies towards the application of this approach in more functionally dense substrates is underway.

Author Contributions

DB, KB and MF conceived the project and subsequent experimental studies. DB and KB carried out the experiments while MCT provided mechanistic interpretations and performed crystallography. KB and MF wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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