Dual Roles for Potassium Hydride in Haloarene Reduction: CSNAr and Single Electron Transfer Reduction via Organic Electron Donors Formed in Benzene

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Supporting Information

ABSTRACT: Potassium hydride behaves uniquely and differently than sodium hydride toward aryl halides. Its reactions with a range of haloarenes, including designed 2,6-dialkylhaloarenes, were studied in THF and in benzene. In THF, evidence supports concerted nucleophilic aromatic substitution, CSNAr, and the mechanism originally proposed by Pierre et al. is now validated through DFT studies. In benzene, besides this pathway, strong evidence for single electron transfer chemistry is reported. Experimental observations and DFT studies lead us to propose organic super electron donor generation to initiate BHAS (base-promoted homolytic aromatic substitution) cycles. Organic donor formation originates from deprotonation of benzene by KH; attack on benzene by the resulting phenylpotassium generates phenylcyclohexadienylpotassium that can undergo (i) deprotonation to form an organic super electron donor or (ii) hydride loss to afford biphenyl. Until now, BHAS reactions have been triggered by reaction of a base, MOtBu (M = K, Na), with many different types of organic additive, all containing heteroatoms (N or O or S) that enhance their acidity and place them within range of MOtBu as a base. This paper shows that with the stronger base, KH, even a hydrocarbon (benzene) can be converted into an electron-donating initiator.

INTRODUCTION

The transition metal-free dehalogenative coupling reaction between haloarenes and arenes, mediated by a base (typically KOtBu) and an organic additive is now well established in the chemical literature.1–16 The propagation cycle of this radical chain reaction is well characterized by the base-promoted homolytic aromatic substitution (BHAS)17 mechanism. An aryl radical 2 adds to the arene partner to yield an intermediate radical, 3, and deprotonation yields radical anion 4. Electron transfer from 4 to aryl halide 1 propagates the radical chain reaction, simultaneously releasing biaryl product 5 (Scheme 1). The initiation step generating the aryl radical 2 in the first instance has been a topic of much debate. Some authors have proposed single electron transfer (SET) to the haloarene from the tert-butoxide anion of KOtBu alone, or as a complex with the organic additive. However, computational studies found these proposals to be untenable.18,19 Our recent study critically examined the evidence presented for KOtBu as a single electron donor to haloarenes in a number of different reports and found that, in each case, organic additives initiate the BHAS reaction by forming organic electron donors in situ,20 for example, electron donor 9 from phenanthroline 6 (Scheme 2A).18 While organic additives are not absolutely required for most substrates in this transformation,9,10,15 they significantly enhance the yield of the coupled products, simultaneously

Scheme 1. Radical Chain Mechanism Depicting BHAS

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allowing reactions to be conducted at lower temperatures and for a shorter duration.\textsuperscript{18,21–23} In the absence of suitable organic additives,\textsuperscript{15} BHAS reactions can be initiated by arynes (benzynes), formed by base-induced elimination of HX from substrate haloarenes ArX such as

This a

add to benzene, taking the role of radical

13

Our original goal was to explore coupling of

RESULTS AND DISCUSSION

Our original goal was to explore coupling of 10 with benzene using phenanthroline 6 as an additive with KH as a base (instead of KOtBu). Successful coupling would support the idea that an alkoxide is not a necessary component of the coupling reactions and would further challenge KOtBu’s privileged status\textsuperscript{20} in these reactions. Subjecting 10a) and additive 6 to the reaction conditions using KOtBu or KH as a base (Table 1, entries 2 and 3) afforded coupling in both cases, to give the characteristic ratio of 12:11 between 3:1 and 4:1. For steric reasons, the yields from substrate 10 are always lower than for substrates like iodobenzene or p-iodotoluene, but the mechanistic information provided by 10 is invaluable.

\section*{RESULTS AND DISCUSSION}

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We have investigated this with a range of haloarene substrates, and present experimental and computational evidence in relation to the mechanistic pathways.

The generation of biaryls 11 and 12 in the KH control reaction reveals that SET reduction occurred. However, the high conversion of 10a observed indicates additional pathway(s) for reaction of the substrate, and the change of ratio of 12:11 to \( \sim 7:1 \) indicates an additional route for formation of biphenyl. The corresponding bromide 10b (entry 6) and chloride 10c (entry 7) showed similar results and almost identical 12:11 ratios. NaN gave no reaction under the same conditions (entry 5).

The high conversion of 10 in the reactions using KH can be explained by reductive dehalogenation. Dehalogenation of iodo-, bromo- and chlorobenzene with KH in THF under mild conditions was reported by Pierre et al.,\textsuperscript{24} who found that treating iodobenzene 16 with KH (5.0 equiv)\textsuperscript{25} in THF for 3 h at rt gave quantitative conversion to volatile benzene as product. Pierre found the order of reactivity ArI > ArBr > ArCl, in contrast to the normal order of reactivity for SNAr reactions, and so a traditional SNAr-type mechanism was ruled out. Benzyne formation was excluded in THF as solvent due to the absence of evolved hydrogen gas.\textsuperscript{24} Although Pierre had no access to computational chemistry, he proposed a concerted displacement from an aryl halide through a 4-centered TS; the reaction type would now be termed a CSNAr and more examples of such reactions have recently become evident.\textsuperscript{25a,26}

Using DFT methods, we now computed an energy pro

Table 1. Coupling Reactions of 2,6-Dimethylhalobenzenes with Benzene

<table>
<thead>
<tr>
<th>entry</th>
<th>additive/base</th>
<th>ratio 12:11</th>
<th>11 + 12 yield\textsuperscript{a}</th>
<th>recovered 10 (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KOtBu</td>
<td>–</td>
<td>&lt;0.5</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>KOtBu</td>
<td>3.7:1</td>
<td>18.2</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>KH</td>
<td>3.9:1</td>
<td>16.3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4\textsuperscript{a}</td>
<td>KH</td>
<td>7.7:1</td>
<td>5.5</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>NaN</td>
<td>–</td>
<td>no reaction detected</td>
<td>3</td>
</tr>
<tr>
<td>6\textsuperscript{b}</td>
<td>KH</td>
<td>7.4:1</td>
<td>3.9</td>
<td>3</td>
</tr>
<tr>
<td>7\textsuperscript{c}</td>
<td>KH</td>
<td>7.0:1</td>
<td>1.5</td>
<td>9</td>
</tr>
</tbody>
</table>

\textsuperscript{a}2,6-Dimethyliodobenzene 10a was used as a substrate unless otherwise stated. Ratios are determined by \(^1\)H NMR of the crude reaction mixture (see Supporting Information). \textsuperscript{b}Yield (% of combined biaryls (11 and 12), or yield (%) of returned 10 determined by \(^1\)H NMR. \textsuperscript{c}Average of two runs. \textsuperscript{d}10b was used as a substrate. 10c was used as a substrate.
On the other hand, product 18 arises from BHAS chemistry, where biphenyl radicals 19 are also intermediates. The interesting comparison in Table 3 is between entries 3 and 4. The only difference between these experiments lies in the choice of solvent—benzene in entry 3 and deuterated benzene in entry 4. Of the two mechanisms in operation, the Pierre reaction should not be affected by the change in solvent, while the BHAS mechanism will likely be significantly affected. Entry 4 shows a lower yield of terphenyl 18 and, particularly, of biphenyl 12, compared with entry 3. The established routes to radicals in these BHAS reactions either involve the presence of an electron donor as in Scheme 2(b) or of a benzene intermediate, generated from the haloarene substrate. As there is no apparent electron donor (but see below for the presence of electron donors), the benzene route is shown in Scheme 4, and features benzene 20.

Addition of the benzyne, as a biradical, to benzene affords biradical 21. This biradical has one very reactive radical, the aryl radical, and one highly delocalized radical (the cyclohexadienyl radical). Of these, the reactive aryl radical should undergo rapid reaction (addition to, or hydrogen atom abstraction from, a molecule of benzene are likely reactions), affording 22, followed by deprotonation to afford radical anion 23, which can then transfer an electron to substrate 17 to begin a BHAS cycle by generating biphenyl radical 19. This radical can then add to the solvent, benzene, as in Scheme 1, ultimately to afford terphenyl 18, or can abstract a hydrogen atom from benzene to afford biphenyl 12. In deuterated benzene, the conversion of 22-d to electron donor 23-d would require that a C–D bond be broken (Scheme 4, inset). But this step of BHAS reactions is routinely not the rate-determining step, and so no isotope effect is likely to be seen in this step. However, the conversion of biphenyl radical 19 to biphenyl 12 involves a hydrogen atom transfer from solvent benzene in the unlabeled case, and from deuterated benzene when that is used as the solvent, and these reactions may show a substantial kinetic isotope effect. This is reflected in the significant drop in yield for biphenyl 12 on going from entry 3 to entry 4.

To find out more information about these electron transfer reactions, we turned to 2,6-disubstituted haloarene probes, in mechanism via direct displacement of iodide by hydride described above.

In benzene at rt, no reaction occurred with KH (Table 3, entry 1). At 130 °C in benzene as solvent, reactions gave biphenyl 12 and terphenyl 18 in a ~3:1 12:18 ratio. Studies using D2O quench and C6D6 as solvent (Table 3, entries 3 and 4) confirmed that any deuterated biphenyl (12-d1) arose by deuterium abstraction from the solvent, rather than from the quench with D2O, ruling out formation of aryl anions. In entry 4, the level of labeling with deuterium was not high (12-d1, 8:1). Product 12 can arise either from a Pierre reaction (with KH, affording unlabeled 12) or from quenching of biphenyl radical 19 (affording 12-d1 when C6D6 is solvent).

Table 3. Coupling Reactions of 4-Iodobiphenyl with Benzene

<table>
<thead>
<tr>
<th>entry</th>
<th>base</th>
<th>solvent/quench</th>
<th>12 yield (%)</th>
<th>18</th>
<th>17 yield (%)</th>
<th>D-incorp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>KH</td>
<td>C6H6/H2O</td>
<td></td>
<td></td>
<td></td>
<td>no reaction detected</td>
</tr>
<tr>
<td>2d</td>
<td>KH</td>
<td>C6H6/H2O</td>
<td>54</td>
<td>16</td>
<td>3</td>
<td>N/A</td>
</tr>
<tr>
<td>3e</td>
<td>KH</td>
<td>C6H6/D2O</td>
<td>58</td>
<td>24</td>
<td>4</td>
<td>no</td>
</tr>
<tr>
<td>4</td>
<td>KH</td>
<td>C6D6/D2O</td>
<td>18</td>
<td>15</td>
<td>34</td>
<td>yesd</td>
</tr>
<tr>
<td>5h</td>
<td>KOtBu</td>
<td>C6H6/H2O</td>
<td>11</td>
<td>76</td>
<td>7</td>
<td>N/A</td>
</tr>
<tr>
<td>6t</td>
<td>KOtBu (+6)</td>
<td>C6H6/H2O</td>
<td>9</td>
<td>87</td>
<td>&lt;1</td>
<td>N/A</td>
</tr>
</tbody>
</table>

D-incorp = Deuterium incorporation, N/A (not applicable). a Yields determined by 1H NMR of the crude reaction mixture. b Reaction conducted at rt with KH (5 eq.). c Average of three replicates. d Average of two replicates. e No D-incorporation detected by GC–MS. f D-incorporated: 18-d1 and 12-d1 detected by GC–MS but not 12-d2. Here, a 2% yield of 12-d1 is observed. g tert-Butoxide adducts to the aryne were observed to give a 1:1 ratio of regioisomers in 6% combined yield. h 20 mol % of phenanthroline 6 was used as an additive.
Scheme 4. In Substrates That Can Form Benzynes, e.g., Iodobiphenyl 17, an Alternative and Slower Initiation Route for BHAS Cycles from the Benzyne (in this case, 20′), Can Occur

Table 4. KH-Mediated Reactions of 2,4,6-Tri-tert-butyl-bromobenzene

<table>
<thead>
<tr>
<th>entry</th>
<th>base</th>
<th>solvent/quench</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>D-incorp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>–</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>no reaction detected</td>
<td>N/A</td>
</tr>
<tr>
<td>2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>KO(tBu)</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>no reaction detected</td>
<td>N/A</td>
</tr>
<tr>
<td>3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>KH</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>28  5  6  56</td>
<td>no&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>KH</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;6&lt;/sub&gt;/D&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>18  11  3  66</td>
<td>yes&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>5&lt;sup&gt;h&lt;/sup&gt;</td>
<td>KH</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>31  1  13  29</td>
<td>N/A</td>
</tr>
<tr>
<td>6&lt;sup&gt;h&lt;/sup&gt;</td>
<td>NaH</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4  &lt;1  1  95</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td>KO(tBu)/NaH (1:1)</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>75  &lt;1  10  &lt;1</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<sup>a</sup>D-incorp = Deuterium incorporation. N/A (not applicable). Unless otherwise stated, conditions A were used. <sup>b</sup>Yields determined by <sup>1</sup>H NMR of the crude reaction mixture. <sup>c</sup>No products were observed, 25 was recovered in quantitative (ca. 100%) yield. <sup>d</sup>Average of eight replicates. <sup>e</sup>After quenching with D<sub>2</sub>O, D-incorporation was not detected. <sup>f</sup>D-incorporated was detected by <sup>2</sup>H NMR and/or GC–MS analysis of the reaction mixture (see Supporting Information). <sup>g</sup>After quenching with H<sub>2</sub>O, D-incorporation was still detected. <sup>h</sup>Reaction conducted under conditions B.
DFT calculations were performed with details as in SI.
cannot form a benzyne, caused us to examine the reaction in depth. We first considered whether traces of residual potassium metal that might be present in the KH sample could trigger formation of biphenyl. However, ICP-OES analysis and control reactions with K metal ruled against this (see Supporting Information).

In our previous investigations of BHAS reactions, performing blank reactions (in the absence of substrate) led to helpful information, and the same was true here. Notably, treatment of benzene with KH in a control reaction led to small amounts of biphenyl, characterized by NMR (see SI), whereas reaction with NaH (or KO-tBu) afforded no biphenyl.

In a manner reminiscent of other BHAS reactions, a strong organic electron donor could be formed if KH deprotonates benzene to form PhK (Scheme 6). Here, PhK would attack benzene to form phenylcyclohexadienyl potassium. Whereas this anion might function as a mild electron donor, more likely it could be deprotonated again to form the disalt, a biphenyl dianion and a known class of strong electron donors. This could initiate electron transfer to haloarenes to trigger radical chemistry. Indeed, sequential transfer of two electrons would form biphenyl. Alternatively, biphenyl could also be formed by expelling KH from anion 35. Indeed, it is known that phenylpotassium attacks benzene to form biphenyl and an insoluble polybenzene. From our previous work on initiation of BHAS reactions, we know that the amount of initiator that needs to be present is vanishingly small, and that evidence of the electron donating initiator is generally not found in the products of these reactions.

Using DFT methods, we have modeled the first step of the reaction, i.e., the formation of phenylpotassium which has a very achievable reaction barrier of 23.8 kcal/mol, under the conditions of the reaction. The formation of 47 is endergonic by 13.6 kcal/mol, but the reaction is irreversible due to release of hydrogen. The following two steps, 47 → 35 and 35 → 48 are also accomplished easily, and feature low kinetic barriers.

Returning to Table 4, an important comparison is between entries 3, 4, and 5. In deuterated benzene, the amount of 26 is decreased relative to the reaction in C6H6. This can arise because less electron donor is present in the reaction with the labeled solvent. Formation of electron donor, 48-d10 (Scheme 6B) would require a difficult deprotonation from 35-d11 that could be subject to an isotope effect. In C6D6, (compared to C6H6) that would lead to a lower concentration of electron donor, and so the reaction would be more sluggish. When an electron transfer occurs, bromide loss is followed by intra-molecular HAT to afford 30. This radical can then easily abstract a bromine atom from another molecule of substrate to form 27 in an atom transfer chain, or radical 30 can enter a neophyl rearrangement to a radical 32. Bromide 27 can react with another molecule of electron donor to a disalt 32. The aliphatic radicals on this pathway may afford hydrocarbon, together with 34, by disproportionation. An alternative possibility is that an intermediate like 35, which would have a weakened C(sp3)–H bond, would surrender a hydrogen atom to radical 32. This may be particularly difficult in the deuterated analogues.

Under the harsher conditions B, NaH gave only traces of dehalogenated product (Table 4, entry 6).

Interestingly, while KO-tBu and NaH gave no reaction by themselves, the combination gave full conversion, a high yield of 26 (75%) and some hydrocarbon 28 (10%) as the main product. The DFT calculations were performed with details as in SI.
byproduct (Table 4, entry 7); we have not investigated this in detail, but the high yield of 26 may indicate the empowerment of NaH as a nucleophile.** Formation of 28 indicates that some radical chemistry also occurs under those conditions.

In view of the D-incorporation detected in the reaction of 25 in C₆D₆ (Table 4, entry 4) we wished to gain more information about the roles of HAT as a pathway for aromatic dehalogenation vs H-incorporation from KH. Halide 25 is a most interesting substrate because its derived aryl radical undergoes intramolecular HAT reaction. We were interested to find out whether its deuterated counterpart would behave analogously. To do so, substrate 25-d₁₅ was synthesized (with 99% atomic % D and 95% aliphatic atom % D) and treated with KH in C₆D₆ quenching with D₂O. Recovered bromide starting material was the main component at the end of the reaction (65%), with hydrocarbons 26-d₁₉ (5%) and 26-d₁₀ (trace) as the new products; no products of side-chain rearrangement were detected (Scheme 7).

Product 26-d₁₉ can arise directly by the Pierre mechanism, while 26-d₁₀ would either require deuterium atom abstraction from benzene-d₆ or could arise through the Pierre mechanism through reaction with KD, generated during the reaction (Scheme 6B); (for spectra and D-incorporation calculations, see Supporting Information).** We compared the outcome of this experiment with that of entry 4 in Table 4. Both return similar amounts of residual starting substrate, 25 and 25-d₁₅ respectively. The Pierre reaction proceeds more easily for the unlabeled substrate. This may reflect that less steric compression of the Br atom is present in the deuterated substrate, as the C–D bonds in 25-d₁₅ are shorter than the C–H bonds in 25.** With the deuterated substrate, the observation of less evidence of radicals on the side-chain is as would be expected, as this would now involve breaking a higher energy C–D bond.

Comparison between H-incorporation from KH vs HAT from solvent was emphasized when 2,4,6-tri-isopropylbromobenzene 50 was employed. Given that the 2,6-dimethyl-substituted aryl radical 13 adds to benzene 4 times more slowly than it undergoes HAT with benzene, due to steric hindrance, then the aryl radical 49 derived from 50 (Table S) should add to benzene even more slowly and HAT with benzene should also be slow. Subjecting 50 to KH under conditions A (Table S, entry 1) gave dehalogenated product 51 and biphenyl 12 in a 3:1 ratio. Notably, the reactivity of 50 was significantly lower than that of 25. This can be rationalized by the greater release of steric strain in reactions of 25.** When the reaction was conducted in C₆D₆ 51-d₁₁ and 12-d₁₀ were now detected (Table S, entry 2), but in very low yield. No arylation product from coupling of ary radical 49 to benzene was observed.

Under conditions A, it is clear that the reaction of 50 is slow to initiate. Comparison of entries 1 and 2 shows that deuterated solvent does suppress products from the BHAS process. It is clear that the extent of the Pierre mechanism with this substrate is very small. Harsher conditions B (Table S, entry 3) gave higher yields of 51 and 12; curiously, when the reaction was repeated in C₆D₆ (Table S, entry 4) high conversions to 51 (51 + 51-d₁₁, 55%) were observed, together with some recovered 50 (14%). Only traces of product 51 and biphenyl 12 were observed when NaH was used (conditions B; Table S, entry 5).

Looking at the higher yield of product 51 in C₆D₆ (entry 4) at these higher temperatures (150 °C), the spectra reveal that there is substantial monolabeling in the aromatic ring. Formation of anion 35-d₁₁ (Scheme 6B) takes place analogously to Scheme 6A; if isotope effects for conversion of 35-d₁₁ to 48-d₁₀ are large, then the concentration of 35-d₁₁ may build up in solution to a level greater than for the nondeuterated counterpart that is present when benzene is the solvent. This means that if a molecule of 48-d₁₀ forms and executes SET to the haloarene substrate to form an aryl radical, that radical can abstract D from 35-d₁₁, thereby forming 36-d₁₀ which in turn can donate an electron to another molecule of haloarene to initiate another cycle. The comparison between conditions A (entries 1 and 2) and conditions B (entries 3 and 4) reflects that the higher temperature selectively helps the reaction in C₆D₆, possibly either by creating a greater concentration of 35-d₁₁, or by facilitating the conversion to 48-d₁₀.

In summary, unlike sodium hydride, KH undergoes substitution of haloarenes in THF or benzene as proposed.

**Note:** Detailed tables and figures are omitted for brevity, but are available in the Supporting Information.
by Pierre. DFT studies support a concerted 4-centered transition state for these substitution reactions. In benzene as solvent, 2,6-dialkyl substituted halobenzenes show clear evidence of electron transfer chemistry when KH is used, and studies with deuterated versus unlabeled benzene show a clear dependence on the solvent. Isolation of small quantities of biphenyl on reaction of KH with benzene supports the formation of phenylpotassium by deprotonation of benzene, and generation of an organic electron donor 48 in trace amounts as an initiator for BHAS cycles to rationalize the observed chemistry. 2,6-Dialklyhalobenzenes 10a–c, 25 and 50 are particularly helpful reporters of the mechanisms of the reactions. The intramolecular hydrogen abstracting behavior of aryl radicals derived from unusual substrate 25 has previously been demonstrated. Further unusual reactivity of 25 is reported here, as the first haloarene to undergo exergonic halogen atom abstraction by alkyl radicals, including tertiary alkyl radicals.

## CONCLUSION

Placing this work in context, BHAS reactions mediated by KOtBu are now widely recognized in dehalogenation and in coupling chemistry, where electron transfer reactions arise from organic donors formed in situ. The diversity of structures that have been shown to act as precursors of organic electron donors is quite revealing. This paper extends that range, and shows that in the presence of an appropriately strong base, organic electron donors can arise even by deprotonation of benzene. Minute amounts of donors can set up desired chain reactions, or can create undesired byproducts, and so, awareness of this chemistry is important in strategic planning of synthetic chemistry. Having demonstrated that the strong base, KH, can trigger formation of organic electron donors, a challenge for the immediate future is the generation of strong organic electron donors either under nonbasic conditions or with bases that are significantly milder than either KH or KOtBu.

## ASSOCIATED CONTENT

1. Supporting Information
   The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07632.
   Experimental procedures, key NMR spectra, ICP-OES data, characterization data of novel compounds, computational studies and computational coordinates (PDF)

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### Notes
The authors declare no competing financial interest.

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## REFERENCES

(24) Handel, H.; Pasquini, M. A.; Pierre, J. L. *Tetrahedron* **1980**, *36*, 3205–3208. The possibility of a single electron transfer process was described by Pierre, but no evidence for radical intermediates could be found by EPR spectroscopy in that study.


(31) In reactions that are initiated by benzenes, products 24 derived from benzenes are not detected; this is because the rate of the propagating cycle in Scheme 1 is so much faster than the rate of generation of initiating species via benzyne.


(33) (a) Brunton, G.; Tejo, C.; Chiba, S.; Ritter, T.
