C-H Activation

Tandem C–H Activation/Arylation Catalyzed by Low-Valent Iron **Complexes with Bisiminopyridine Ligands**

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Dedicated to Professor Max Malacria on the occasion of his 65th birthday

Abstract: Tandem C-H activation/arylation between unactivated arenes and aryl halides catalyzed by iron complexes that bear redox-active non-innocent bisiminopyridine ligands is reported. Similar reactions catalyzed by first-row transition metals have been shown to involve substratebased aryl radicals, whereas our catalytic system likely involves ligand-centered radicals. Preliminary mechanistic in-

Introduction

Noble metals reign in the realm of catalysis and their ability to sustain two-electron redox events that occur at the metal center plays a large part in this success. However, growing concerns with regards to the foreseeable stock depletion of noble metals and inherent cost-related issues are driving chemists to revisit the chemistry of their more modest cousins: the first-row transition metals. Among these, the well-established contribution of iron to organometallic chemistry^[1] has resulted in a significant number of synthetic applications and helped deem this metal a potential alternative to noble metals hegemony. More specifically, well-defined low-valent iron species have lately elicited great excitement over their ability to participate in useful catalytic endeavors and shed light on the benefits obtained through more precise control of the coordination sphere.^[2] These species show promise in terms of reactivity, however, such low-valent complexes are still only marginally used and synthetic efforts towards their development are of prime interest.

One of the strategies to enlarge the applicability of these low-valent iron species lies in the use of redox-active non-inno-

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ļ http://dx.doi.org/10.1002/chem.201304459 vestigations based on spectroscopic and reactivity studies, in conjunction with DFT calculations, led us to propose that the reaction could proceed through an inner-sphere C-H activation pathway, which is rarely observed in the case of iron complexes. This bielectronic noble-metal-like behavior could be sustained by the redox-active non-innocent bisiminopyridine ligands.

cent ligands, $^{\!\!\![3]}$ which can act as electronic reservoirs, and thus provide the metal with the additional electron(s) needed to perform bielectronic redox elementary steps, such as oxidative addition and reductive elimination.^[4] Indeed, rationalization of the mechanisms involved in iron catalysis often involves substrate-centered radical pathways, which tend to impair both scope and selectivity. In this prospect, the use of non-innocent ligands to promote two-electron redox events could bypass these limitations.^[5] Among non-innocent redox ligands, bisiminopyridines have been shown to participate in redox changes that occur in the complex through stabilization of one or more electrons on the ligand core, and thus engage in ligand-based redox behavior.^[6] These bisiminopyridine^[7] ligands have been popularized through their successful use with iron in polymerization,^[7b-d] cycloisomerization,^[7e] cycloaddition,^[7f,g] hydrosilylation,^[7h] and hydroboration reactions.^[7i]

Iron-based reactions overall dubbed C-H activation are being reported at great pace^[8] and stoichiometric inner-sphere C-H activations that involve iron cyclometalated species have been reported.^[9] However, apart from a few notable exceptions,^[10] strictly speaking, metal-catalyzed inner-sphere catalytic C-H activation pathways have so far been the private preserve of the noble metals. Among these transformations, one of the trademark reactions of noble metals is the highly studied carbon-carbon bond formation. Reliable iron-catalyzed crosscoupling alternatives have now been widely developed with a variety of functionalized partners^[1d,11] but the specific case of tandem C-H activation/C-C cross-coupling has been put under scrutiny by recent studies. Tandem iron-catalyzed directed C-H activation/arylation^[12] has been achieved by Nakamura by using diarylzinc or Grignard reagents as the coupling partner,^[10c, 13] and reports of related iron-catalyzed direct arylation of unactivated arenes with aryl halides have been simulta-

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neously disclosed by the groups of Charette^[14] and Lei^[15] in 2010. Although synthetically useful, these reactions do not seem to proceed by genuine inner-sphere C–H activation and the mechanisms proposed involve substrate-centered radicals. Although such catalytic developments of C–H activation strategies with iron-based systems are being reported, well-defined iron complexes with bisiminopyridine ligands have not been tested yet in C–H activation strategies or cross-coupling reactions. A recent report based on DFT calculations suggests that benzylic C–H activation with a diazocarbene coupling partner should be possible.^[16] Mindful of these challenges, we decided to investigate this transformation and report the first tandem C–H activation/arylation of unactivated benzene with aryl bromides catalyzed by iron complexes that bear bisiminopyridine ligands.

Results and Discussion

Initial studies were focused on arylation with bromoanisole by using benzene as the solvent (100 equiv) and potassium hexamethyl disilazide (KHMDS; 2 equiv) as the base at 80 °C for 18 h. Under these conditions, low amounts of the desired product, 4-phenylanisole, and degradation products were obtained when using FeBr₂ alone, and the use of NaBEt₃H to generate a reduced iron catalyst^[17] did not yield any of the expected product (Table 1, entries 1 and 2).



In the presence of NaBEt₃H and base, the bisiminopyridine complex [1·FeBr₂] gave the coupling product in 38% yield, whereas the same amount of free ligand mixed in situ with FeBr₂ provided a lower yield of 21% (Table 1, entries 3 and 4). The yield could be further improved to 56% by omission of NaBEt₃H, which also gave a cleaner reaction (Table 1, entry 5). Catalyst [1·FeCl₂] gave a slightly lower yield (Table 1, entry 6), and premixing the ligand with the iron source for in situ for-

mation of the catalyst did not provide significantly different results (Table 1, entry 7). Therefore, we selected complex [1-FeBr₂] as the catalyst for the rest of our study. X-ray diffraction studies performed on a single crystal of deep-blue [1-FeBr₂], grown by slow evaporation from a solution in CD₂Cl₂, confirmed a geometry (see the Supporting Information) very close to that of previously described [1-FeCl₂].^[18]

A subsequent base screen showed that KHMDS allowed for complete conversion (Table 2, entry 1) and use of 1.5 equivalents gave comparable results (Table 2, entry 2). However, use

Table 2.	Screening of bases.		
(100 Entry	equiv) (1 equiv) Base ([equiv])	(1-FeBr ₂) (15 mol%) base (x equiv) 80 °C, 18 h Conversion [%]	GC yield [%]
1	KHMDS (2)	100	56
2	KHMDS (1.5)	100	53
3	KHMDS (1.3)	92	42 (35) ^[a]
4	KHMDS (0.5)	56	7 ^[a]
5	LiHMDS (1.5)	100	11
6	NaHMDS (1.5)	100	30
7	Cs_2CO_3 (1.5)	0	0
8	tBuOK (1.5)	49	10
9	DBU (1.5)	52	0
10	DABCO (1.5)	43	0
11	Ph ₂ NPh-4-OMe (1.5)	52	14
12	LDA (1.5)	40	7
13	LiTMP (1.5)	100	19
[a] Isolated yield.			

of less than 1.5 equivalents resulted in incomplete conversion and lower yields (Table 2, entries 3 and 4). The influence of the counterion was found to be critical; LiHMDS and NaHMDS provided lower yields (Table 2, entries 5 and 6). Cesium carbonate proved completely ineffective (Table 2, entry 7) and bulky tertiary nitrogen bases (1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), and Ph₂N(4-MeO)Ph; Table 2, entries 9-11) gave similarly disappointing results, with lower conversions and little or no expected product. Interestingly, though often used successfully in arylation reactions, tBuOK provided the expected product in only 10% yield (Table 2, entry 8). Stronger bases such as lithium diisopropylamide (LDA) and lithium 2,2,6,6-tetramethylpiperidide (LiTMP; Table 2, entries 12 and 13) were also far less efficient than KHMDS, which suggested that the chemical structure of the base, rather than high pKa values, was crucial for the reaction.

The influence of the metal source was also evaluated and it was observed that, when combined with ligand **1**, $Fe(OAc)_2$ performed similarly to FeBr₂, whereas FeCl₂ afforded a slightly lower yield (Table 3, entries 4–6). Furthermore, copper salts (Table 3, entries 7 and 8) were found to be completely inefficient and resulted in complex mixtures of degradation products, which suggested that the catalytic activity was indeed iron based.^[19]

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Table 3. Influence of the metal source.			
(100 eq	H + OMe Br (1 equiv)	catalyst (15 mol%) KHMDS (1.5 equiv) 80 °C, 18 h	OMe
Entry	Catalyst	Conversion [%] ^[c]	GC yield [%]
1	[1·FeBr ₂]	100	53
2 ^[a]	[1·FeBr ₂]	100	54
3 ^[b, c]	[1·FeCl ₂]	100	45
4 ^[c]	1+FeBr₂	96	53
5 ^[c]	$1 + FeCl_2$	90	42
6 ^[c]	1+Fe(OAc)₂	93	52
7 ^[c]	1+CuCl ₂	80	0
8 ^[c]	1+Cu(OAc) ₂	81	0
[a] Iron-sou	urce purity $=$ 99.995	% (Alfa Aesar). [b] K	HMDS (2 equiv). [c] Pre-

Table 4. Screening of the ligand structure.^[a] Entry Ligand Conversion [%] GC yield [%] 1 $R = CH_3$, R' = iPr, R'' = H; 1 96 53 $R = R' = CH_3, R'' = H; 2$ 100 40 2 41^[b] 3 $R = H, R' = R'' = CH_3; 3$ 93 17^[e] 4 98 $R = CH_3, R' = iPr, R'' = H; 4$ 5^[c] 22^[e] >95 6 >95 17^[e] $R = R'' = H, R' = CH_3; 5$ 7^[c] 28^[e] >95 8^[d] terpyridine 100 18 [a] Reaction conditions: bromoanisole (1 equiv), benzene (100 equiv), KHMDS (1.5 equiv), FeBr₂ (15 mol%), ligand (15 mol%), 80 °C, 18 h. [b] Yield determined by GC analysis with trimethylbenzene as an internal standard. [c] Ligand (30 mol%). [d] FeCl₂ used instead of FeBr₂, KHMDS (2 equiv). [e] Isolated yield.

With optimal conditions in hand, we aimed to explore the effect of the ligand structure. The best results were obtained with the sterically hindered ligand **1** and reduction of the steric bulk—either at the aryl ring by replacement of the diisopropylphenyl moiety with *o*,*o*'-dimethylphenyl (ligand **2**) or at the imine sp² carbon (ligand **3**)—resulted in slightly decreased yields (Table 4, entries 2 and 3). Monoiminopyridine ligands, used in iron-catalyzed dimerization of 1,3-dienes,^[20] 1,4-addition of olefins to dienes,^[21] hydroboration,^[22] and hydrosilylation reactions,^[23] were also tested and a sharp decrease in yield was observed, regardless of the substitution pattern and the amount used (metal/ligand ratio of 1:2 and 1:1; Table 4, entries 4–7). Terpyridine gave similarly low conversions (Table 4, entry 8).

Investigation of the substrate scope revealed two interesting features (Table 5). First, the reaction exhibits a strong bias towards electron-rich scaffolds and all electron-deficient aromatic or heteroaromatic compounds that were tested gave very

Table 5. Substrate scope.				
	H + Ar-Br	[1•FeBr ₂] (15 mol%) KHMDS (1.5 equiv.) 80 °C, 18 h	Ar + Ar-Ar	
Entry	ArBr	Conversion [%]	Ar—Ph [%]	Ar—Ar [%]
1	MeO	100	53	23
2	MeO	100	35	-
3	Br	100	20	-
4	EtO	100	63	10
5	(Me) ₂ tBuSiO	Br 100	35	3
6	MeO	100 le	26	-
7	O Br	100	7	-
8	BnO	100	16	trace
9	Me ₃ Si	r 100	50	-
10	Br	100	55	-
11	Me ₂ N Br	92	20	trace
12		75	-	-
13	F	100	41	-
14	F ₃ C	100	7	-
15	N Br	100	trace	-
16	Br Br	100	-	-
17	S Br	100	-	-
18	O ₂ N	100	-	-

poor, if any, conversion. Second, homocoupling products, which can arise from the aryl halide, were only detected alongside the expected product, suggesting that these two products might share a common intermediate in the catalytic cycle. However, the coupling product can be observed in the absence of the homocoupling adduct.

The influence of the halogen in the halide partner was evaluated and similar yields were obtained with iodides and bro-

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mides (Table 6, entries 1 and 2), whereas aryl chlorides were much less reactive towards coupling; only 15% yield was obtained (Table 6, entry 3). This reactivity trend was confirmed when an equimolar mixture of bromoanisole (1 equiv) and chloroanisole (1 equiv) was used (Table 6, entry 4); almost all of the bromoanisole reacted, whereas only 22% of the chloroanisole was converted, which confirmed that aryl bromides were preferentially converted over aryl chlorides.

Complete conversion of the aryl bromide is always observed, but the comparatively modest yields (\approx 50%) obtained with our system led us to investigate the reaction mixture for potential byproducts (Scheme 1). It was found that the expected



Scheme 1. Product distribution for the C–H arylation.

biaryl product is usually formed along with varying amounts of the biaryl product from homocoupling of the aryl bromide. In contrast with previously reported studies^[14, 15] of iron-catalyzed C–H arylation, in which biphenyl (a result of benzene homocoupling) was isolated as a byproduct, the only homocoupling product we observe arises, instead, from the aryl bromide. With a 100:1 ratio of benzene/bromoanisole in the reaction mixture, this unusual observation could imply that different mechanistic pathways operate in these reactions.

The procedures reported by the groups of Charette and Lei call for catalytic amounts of iron salts $(Fe(OAc)_2 \text{ and } FeCl_3, \text{ respectively})$ and no directing or activating group is required. Preliminary mechanistic studies, which included kinetic isotope effect (KIE) measurements and the introduction of radical scavengers, such as 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO), suggested that a radical pathway was at work in both systems. Interestingly, similar coupling reactions have been reported with other first-row transition metals,^[24] such as nickel,^[25]

copper,^[26] and cobalt.^[27] For the vast majority of reaction conditions, the use of a base (such as *t*BuOK or LiHMDS) and a bidentate nitrogen-based ligand (such as *N,N'*-dimethylethylenediamine (DMEDA) or bathophenanthroline) along with the metal source was mandatory. Concomitant reports by Shi,^[28] Lei,^[29] and Hayashi^[30] even indicated that the metal source was superfluous; the coupling reactions occurred in the sole presence of base and ligand, which tipped the scale towards a seemingly organocatalytic approach. However, later comments by Studer and Curran^[31] suggested that HAS (homolytic aromatic substitution) was most likely to be involved and that these results might not indicate organocatalytic or metal-catalyzed reactions, but rather HAS or metal-initiated base-promoted HAS reactions.

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Addition of radical scavengers, such as TEMPO or galvinoxyl (1 equiv), to our reaction conditions was found to induce complete inhibition of the reaction. Though indicative of the formation of radicals in the catalytic pathway, these experiments cannot distinguish between ligand- versus substrate-based radicals. Further studies were conducted to determine whether the radical(s) involved were substrate- or ligand-centered. Substitution of benzene with toluene afforded the expected coupling products in 46% overall yield and a relative o/m/p distribution of 2.2:1.95:1 (see the Supporting Information). Relative to the ratios reported by Charette (3.1:1.9:1) and Lei (2.47:1.9:1) for the same reaction, the observed pattern was found to be closer to a statistical distribution and, therefore, less in favor of an ortho effect, usually consistent with the presence of aryl radicals. Furthermore, this distribution does not correlate with the regioselectivities observed in radical aromatic substitutions on related systems.^[32] Also noteworthy is the fact that poor yield (10%; Table 2, entry 8) was obtained when potassium tert-butoxide was used, which is usually very efficient in HAS reactions. A KIE of 1.23 was measured (see the Supporting Information), which indicated that breaking of the C-H bond might not be the rate-limiting step.^[33]

Furthermore, reaction with a dihalide probe (4-chloro-bromobenzene; Scheme 2 a) for radical-anion mechanisms, described by Bunnett and Creary,^[34] provides a mixture of 4chlorobiphenyl (**6**; 15%), the result of monocoupling at the bromo-substituted carbon atom, and *para*-terphenyl (**7**; 15%), the result of biscoupling at both the bromo- and chloro-substituted carbon atoms. In radical-type mechanisms that involve substrate-based radicals, the intramolecular electron-transfer step that occurs on such dihalide probes would generate mainly terphenyl **7**, as observed by Kwong and Lei.^[29] Consequently, the significant amounts of **6** obtained do not fit well with a substrate-based radical mechanism, nor does the presence of trace amounts of dichlorobiphenyl **8** that arise from homocoupling at the bromo-substituted carbon atom, which is totally unprecendented in such reactions.

To confirm this hypothesis, subsequent radical-trap experiments were carried out on substrates **9** and **10** (Scheme 3). Under conditions that involve substrate-based radicals, these compounds are known to undergo intramolecular 6-*endo*-trig cyclization to yield compound **12** as the major product.^[24a,27a,35] However, upon reaction with our catalytic system, the iodinat-

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Scheme 2. Dihalide probe for the C–H arylation: results with a) our system and b) under HAS conditions.



Scheme 3. Intramolecular radical-trap experiments.

ed substrate **9** did not provide any cyclized adduct **12** but rather the reduced product **11**, albeit in modest yield (28%). The brominated substrate **10** provided reduced product **11** (10%), along with the cyclized adduct **12** (27%). Both substrates **9** and **10** are known to favor cyclization in good yield under conditions that involve substrate-based radicals, through a mechanism via the same aryl-radical intermediate. However, in our case, the low yield and discrepancy observed between the iodo- and bromo-substrates under our conditions does not support this pathway and these results suggest that substratebased radicals are probably not operative in this system.

In situ IR experiments performed on a solution of catalyst [1-FeBr₂] in benzene, to which increasing amounts of KHMDS were introduced, showed complete consumption of up to two equivalents of KHMDS before a stationary point was reached (Figure 1 a and b). Addition of more KHMDS (up to 15 equiv; a similar ratio to the catalytic reaction conditions) only resulted in the appearance and growth of the bands from KHMDS (in particular, $\tilde{\nu} = 1110$ and 1080 cm^{-1}), up to the maximum solubility of KHMDS in benzene. Heating this solution to $80 \,^{\circ}\text{C}$ did not lead to changes in the IR spectrum (except for very slight intensity variations), which attests to the stability of the mixture in the absence of substrate. Addition of bromoanisole (10 equiv) to the mixture under catalytic conditions induces



Figure 1. 3D evolution profile of the in situ IR spectrum of $[1 \cdot \text{FeBr}_2]$ upon portionwise addition of KHMDS (0.1 equiv increments) up to 2 equiv, then at 3 equiv a) $\tilde{v} = 1300-1100 \text{ cm}^{-1}$, b) $\tilde{v} = 960-790 \text{ cm}^{-1}$. c) In situ IR bands upon catalysis: consumption of KHMDS (decrease at $\tilde{v} = 1110$ and 1080 cm^{-1}), formation of the coupling product (increase at $\tilde{v} = 1180 \text{ cm}^{-1}$). Substrate was added at t = 05:10:00.

immediate consumption of KHMDS, attested to by a decrease of the bands at $\tilde{v} = 1110$ and 1080 cm⁻¹ (Figure 1 c). Concomitant growth of a band at $\tilde{v} = 1180$ cm⁻¹ is observed, related to the formation of the cross- and homo-coupling products, which both display such a band.

The complete consumption of the catalyst under portionwise addition of KHMDS in benzene was accompanied by a color change of the reaction mixture from dark blue to deep green. The paramagnetic NMR spectrum of a solution of $[1-FeBr_2]$ with KHMDS (2 equiv) in C_6D_6 was recorded and

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Figure 2. a) Spin density calculated for the reagent in the quintet spin state. b) Energy profiles for C–H activation with an Fe^{\parallel} catalyst. Values are in kcalmol⁻¹ and the ground state of the reagent was taken as a reference. Values in plain text correspond to enthalpy, values in italics to Gibbs free energy. c) Possible transition state.

showed a shift of the peaks in the paramagnetic region, which suggested modifications of the complex structure. The spectrum was rather complicated and could only confirm the formation of new unidentified paramagnetic species in solution. However, full interpretation is difficult due to the instability of the system under the NMR conditions. Attempts to record a clean X-band EPR spectrum of this solution ([1·FeBr₂] and KHMDS (2 equiv) in benzene) only led to reproducible complex spectra that precluded straightforward interpretation. However, the fact that this solution displays EPR activity is noteworthy because the starting complex [1·FeBr₂] is X-band EPR silent. These results collectively suggest that single-electron transfer could have occurred between the starting complex and KHMDS.

DFT calculations were conducted to rationalize the C-H activation step. The C-H activation on the iron(II) complex in presence of benzene and KHMDS (1 equiv) was scrutinized by using a classical DFT functional (UB3LYP) in conjunction with a double-dzeta polarized basis set (Figure 2). Several spin states (triplet, quintet, and septet) were tested for reagents, transition states, and products. It appears that the quintet spin state is the ground state for the starting complex [LFeBr₂], which is not surprising for this family of d⁶ complexes. We assumed that, upon interaction with KHMDS, loss of KBr would result in a [LFe^{II}Br]⁺/HMDS⁻ ion pair. When this ion pair is formed, the calculations showed that four unpaired electrons remain localized in the d orbitals of iron. At the same time, electron transfer occurs from HMDS⁻ to the ligand, which results in a single electron localized on the nitrogen of the former HMDS⁻ unit antiferromagnetically coupled to another radical localized inside the aromatic ring of the ligand. Thus, even in the presence of the reactants, the ground state is still a quintet. The corresponding quintet spin density is shown in Figure 2. Moreover, a triplet state is close in energy, around 3 kcal mol⁻¹ above this quintet state in ΔH and more stable by 0.5 kcal mol⁻¹ in ΔG , with two alpha unpaired electrons on iron, one beta unpaired electron on the ligand, and one alpha unpaired electron on the base (HMDS). Thus, triplet or quintet spin states both emerge from a formal reduction of the ligand by the base, which could be expected with regards to the well-known redox properties of this ligand–iron complex. Sensibly, higher in energy is a septet state; its electronic picture is basically identical to that of the triplet or quintet state, except that all the unpaired electrons are of alpha spin.

The transition state that corresponds to the C-H activation involves the three components (catalyst, benzene, base) in a concerted fashion. This could formally be regarded as an acid-base reaction, in which the base abstracts the proton and the iron-phenyl bond is created simultaneously (Figure 2C). However, because the HMDS⁻ base also has strong radical character, one could also consider the transformation as a hydrogen atom abstraction concomitant with a radical ironcarbon coupling. With regards to the energetics, the barrier in the quintet state is slightly below 20 kcal mol⁻¹, which is compatible with the experimental conditions. The septet spin state gives a rather high barrier of 38 kcal mol⁻¹, which is related to the fact that all the unpaired electrons are of alpha spin and, thus, cannot rearrange to create bonds. Finally, the reaction is clearly favorable for the products, with an exothermic $\Delta H =$ $-16 \text{ kcal mol}^{-1}$ for the quintet ground state. It could be expected that the second equivalent of KHMDS could reduce the Fe^{II} complex obtained after the C-H activation step. Furthermore, the KIE of this step was calculated and a theoretical value of 1.37 was found, which is a close match to the experimental value of 1.23 and provides good theoretical support for the proposed model for the C–H activation step.

Conclusion

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We have developed a tandem C–H activation/arylation of unactivated arenes with aryl bromides catalyzed by iron complexes with bisiminopyridine ligands. Experimental data are

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clearly in favor of a mechanism distinct to that previously reported for iron-based catalytic systems and, especially, not compatible with homolytic aromatic substitution. Based on preliminary theoretical studies, we propose that the system operates through a metal-based inner-sphere C–H activation that involves concomitant electron transfer from the ligand and the substrate, Further investigation of the mechanism is currently underway. This strategy expands the scope of first-row base metal catalysis and should undoubtedly promote their chemistry into exciting new venues.

Experimental Section

General procedure for aryl coupling

Complex [1·FeBr₂] (78.4 mg, 0.1125 mmol, 0.15 equiv) and benzene (2 mL) were added to a flame-dried Schlenk flask that had been previously evacuated and backfilled with nitrogen (×3). KHMDS (236 mg, 1.125 mmol, 1.5 equiv) was added under a N₂ stream, then the aryl bromide (0.75 mmol, 1 equiv) and benzene (4 mL) were added. The resulting brownish solution was stirred for 18 h at 80 °C under nitrogen. After cooling to room emperature, the mixture was filtered through a plug of silica gel and eluted with Et₂O or AcOEt. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (pentane/CH₂Cl₂ or cyclohexane/AcOEt) to afford the desired coupling product and, in some cases, the homocoupling product. The yields were determined by GC analysis with 1,3,5-trimethylbenzene as an internal standard.

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A radical choice! A low-valent iron complex with non-innocent bisiminopyridine ligands performs C–H activation/arylation of unactivated aryl compounds (see figure). The reaction likely involves ligand-based radicals, whereas previously reported iron-based systems imply substrate-based radicals.

C-H Activation

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Tandem C–H Activation/Arylation Catalyzed by Low-Valent Iron Complexes with Bisiminopyridine Ligands