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From 2- to 3-Substituted Ferrocene Carboxamides or How to Apply Halogen "Dance" to the Ferrocene Series

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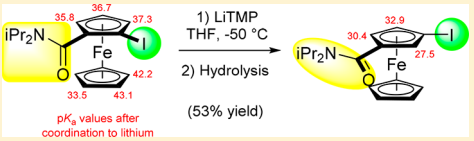
Supporting Information

ABSTRACT: Two methods were compared to convert ferrocene into *N*,*N*-diisopropylferrocenecarboxamide, *N*,*N*-diethylferrocenecarboxamide, *N*,*N*-dimethylferrocenecarboxamide, and (4-morpholinocarbonyl)ferrocene, namely, deprotometalation followed by trapping using dialkylcarbamoyl chlorides and amide formation from the intermediate carboxylic acid. The four ferrocenecarboxamides were functionalized at C^2; in the case of the less hindered and more sensitive amides, recourse to a mixed lithium−zinc 2,2,6,6-tetramethylpiperidino-based base allowed us to achieve the reactions. Halogen migration using lithium amides was next optimized. Whereas it appeared impossible to isolate the less hindered 3-iodoferrocenecarboxamides, 3-iodo-*N*,*N*-diisopropylferrocenecarboxamide proved stable and was converted to new 1,3-disubstituted ferrocenes by Suzuki coupling or amide reduction. DFT calculations were used to rationalize the results obtained.



INTRODUCTION

Polysubstituted ferrocenes are much appreciated scaffolds for various applications including catalysis, fuel additives, material sciences, and medicinal chemistry.[1]

Methods to access 1,2-disubstituted ferrocenes have been largely developed from monosubstituted ferrocenes.[2] Among the methods used, deprotonative lithiations directed at neighboring sites by coordinating or acidifying groups are of crucial importance. Ferrocenecarboxylic acid derivatives such as hindered *N*,*N*-dialkylcarboxamides[3] and oxazolines[2b,4] have been often employed for this purpose, with stereoselective reactions being possible by using chiral ligands or chiral directing groups, respectively.

In sharp contrast, if 1,3-disubstituted ferrocenes appear as promising for different applications,[5] their synthesis is far less developed. Obtaining such structures by building the ferrocene core[6] is possible but subject to tedious preparation of the required substrates. Thus, access by functionalization of ferrocene is an attractive approach. From monosubstituted ferrocenes, direct electrophilic substitutions are hardly regioselective.[7] Stoichiometric and catalytic CH-functionalizations can take place at positions remote from substituents, but these reactions are limited to specific groups[8] or bases,[9] and can hardly be made stereoselective. Alternative ways to access 1,3-disubstituted ferrocenes consist in using retractable directing groups. Chlorine,[10] bromine,[11] and sulfoxide[12] have been successfully used for this purpose, and enantiopure derivatives could be obtained.[12,11e]

Base-catalyzed aromatic *halogen "dance"* is an elegant way to convert 2-halogeno substituted benzenes (I > Br) into the corresponding 3-substituted derivatives.[13] Relatively well-developed in the benzene series, the reaction has been subjected to very few studies for ferrocenes. In 2010, we reported the competitive formation of 1-bromo-3-iodoferrocene in the course of the deprotometalation−iodolysis of bromoferrocene using the base *in situ* prepared from $ZnCl_2$·TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and LiTMP (TMP = 2,2,6,6-tetramethylpiperidino) in a 1:3 ratio[14] and supposed to be a 1:1 mixture of LiTMP and $Zn(TMP)_2$.[15] More recently, Wang, Weissensteiner, and co-workers showed that the reactions performed on ferrocenyl 1,2-dihalides (1-chloro-2-iodo-, 1-bromo-2-iodo-, 1,2-dibromo-, and 1,2-diiodoferrocene) using LiTMP look more like a "scrambling" than a "dance", with complex mixtures obtained.[16]

We thought a way to reduce this complexity was to involve in such reactions 1,2-disubstituted ferrocenes bearing only one halogen and a fixed *N*,*N*-dialkylcarboxamide directing group. We thus chose 2-iodoferrocenecarboxamides to attempt base-catalyzed halogen migration. Herein, we describe our efforts to efficiently synthesize the required substrates and to convert

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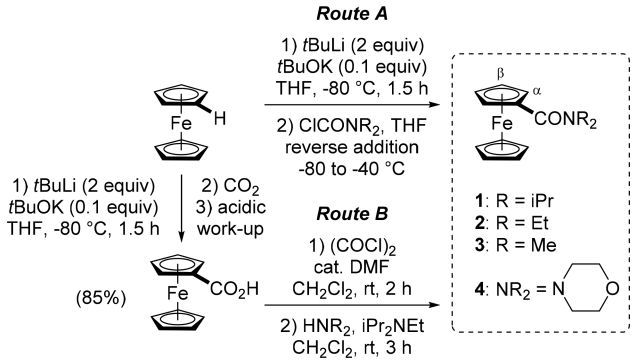
them into the corresponding 3-iodoferrocenecarboxamides. The molecular structure of the above-mentioned ferrocenes was studied by ^{1}H and ^{13}C NMR spectroscopy, and DFT calculations were used to rationalize the results.

RESULTS AND DISCUSSION

Compared Methods to Access *N,N*-Dialkyl Ferrocenecarboxamides. *N,N*-dialkyl ferrocenecarboxamides are important substrates for subsequent elaboration. Therefore, we planned the synthesis of four ferrocenecarboxamides, namely, the *N,N*-diisopropyl, *N,N*-diethyl, *N,N*-dimethyl, and morpholino. Direct reaction of ferrocene with dialkylcarbamoyl chlorides was reported to give the corresponding carboxamides in moderate yields.[17] In our hands, reacting ferrocene with diethylcarbamoyl chloride in the presence of $AlCl_3$ (1.1 equiv) at dichloromethane reflux provided *N,N*-diethylferrocenecarboxamide in 33% yield (5% yield by using 2 equiv of $AlCl_3$; no product and 66% recovered ferrocene by employing 1.1 equiv of $SnCl_4$). This disappointing yield led us to consider alternative syntheses.

We considered and evaluated two routes toward these substrates: ferrocene deprotometalation followed by trapping using dialkylcarbamoyl chlorides (route A)[18] and amide formation from ferrocenecarboxylic acid[19] (route B).[20] As shown in Table 1, the two routes work in similar yields

Table 1. Formation of the *N,N*-Dialkyl Ferrocenecarboxamides 1−4 Using Route A and Route B



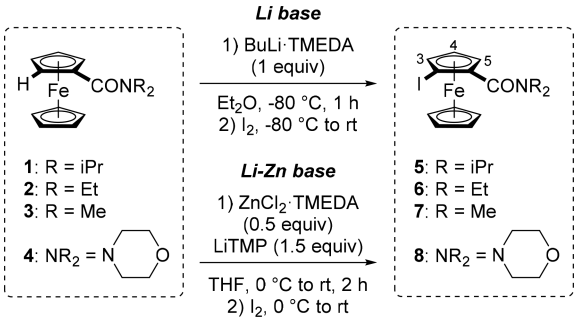
entry	product	route	yield[a] (%)
1	**1**	A	71
2	**1**	B	94 (80)
3	**2**	A	86.5
4	**2**	B	95 (81)
5	**3**	A	77
6	**3**	B	82 (70)
7	**4**	A	76
8	**4**	B	83 (71)

[a]The yields (after purification by column chromatography over silica gel) for Routes A and B were calculated from ferrocene and ferrocenecarboxylic acid, respectively. The yields in parentheses are calculated from ferrocene.

although route A provides the ferrocenecarboxamides **1**−**4** in only one step from cheap ferrocene. All the products obtained were fully characterized, and their main spectroscopic and X-ray diffraction data are furnished in Supporting Information.

Deprotometalation to Afford *N,N*-Dialkyl 2-Iodoferrocenecarboxamides (Table 2). *N,N*-Diisopropyl- and *N,N*-diethylferrocenecarboxamide (**1** and **2**) can be depro-

Table 2. Formation of the *N,N*-Dialkyl 2-Iodoferrocenecarboxamides 5−8



entry	product	base	yield[a] (%)
1	**5**	Li	88
2	**5**	Li−Zn	84
3	**6**	Li−Zn	88
4	**7**	Li−Zn	78
5	**8**	Li−Zn	84

[a]Yields after purification by column chromatography over silica gel.

tolithiated by butyllithium in Et_2O at −80 °C.[3a,b] From **1**, using the chelate BuLi·TMEDA followed by iodolysis led to the expected iodide **5**[21] in 88% yield. Alternatively, employing at room temperature the base *in situ* prepared from $ZnCl_2$·TMEDA (0.5 equiv) and LiTMP (1.5 equiv)[14] (supposed to be a 1:1 mixture of LiTMP and $Zn(TMP)_2$)[15] furnished **5** in 84% yield. From **2**, we preferred the latter method, and we isolated the 2-iodo derivative **6** in 88% yield.

When compared to **1** and **2**, *N,N*-dimethylferrocenecarboxamide (**3**) and morpholinoferrocenecarboxamide (**4**) are more sensitive to nucleophilic attacks. Consequently, ketones are concomitantly formed upon their treatment by organolithiums, and lower yields of 2-substituted derivatives are noticed after subsequent quenching. Recourse to LiTMP with *in situ* trapping (e.g., $ClSiMe_3$) makes functionalization of such substrates possible.[22] Although iodine cannot be used as *in situ* trap, the zinc species formed next to the directing group by deprotolithiation−"trans-metal trapping"[23] using the combination of LiTMP (0.5 equiv) and $Zn(TMP)_2$ (0.5 equiv) can be converted to the corresponding iodides **7** and **8**, which were isolated in 78% and 84% yield, respectively. The main spectroscopic and X-ray diffraction data are given in Supporting Information or Figure 1.

Halogen Dance to Afford *N,N*-Dialkyl 3-Iodoferrocenecarboxamides. Deprotonation-triggered heavy halogen migration[13] appeared to be a suitable approach for the conversion of 1-substituted 2-iodoferrocenes into their 1-substituted 3-iodo isomers.[14,16] A *N,N*-dialkylcarboxamide being capable of coordinating lithium when located at a neighboring position on a ring, it can contribute to the stabilization of a lithio compound and thus direct halogen migration. To the best of our knowledge, such a group has only been used to direct halogen migration in the case of 3-iodo-*N,N*-diisopropyl-2-pyridinecarboxamide (Chart 1, left).[24] According to the generally accepted mechanism,[13] the reaction promoted by a lithium amide (LiDA = lithium diisopropylamide) proceeds through deprotonation at the 4 position and repetitive halogen/metal exchanges.

Besides different electronic and geometrical features (e.g., angles), the position next to the carboxamide is locked by the pyridine nitrogen in the reported example, whereas it can be

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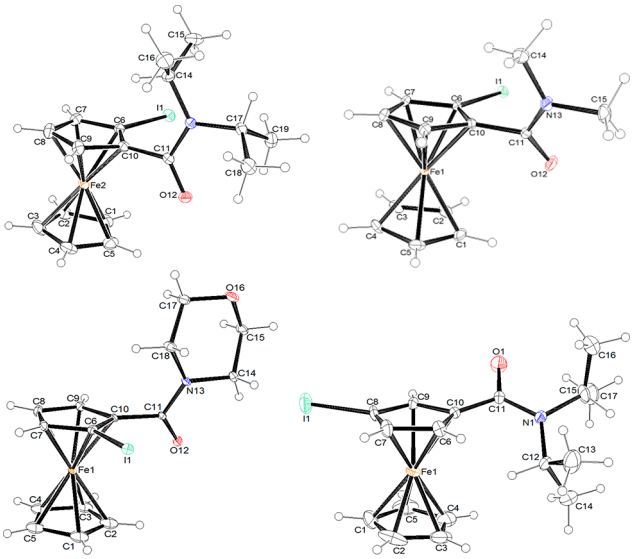
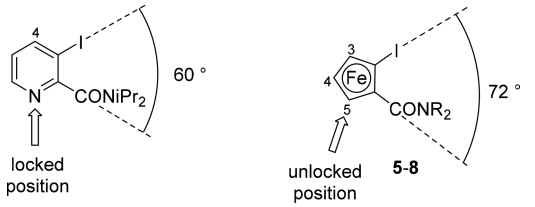


Figure 1. ORTEP diagrams (30% probability level) of the ferrocenecarboxamides **5** (C^9–C^{10}–C^{11}–O^{12} torsion angle 94.36°), **7** (C^9–C^{10}–C^{11}–O^{12} 121.02°), **8** (C^9–C^{10}–C^{11}–O^{12} −70.86°), and **9** (C^9–C^{10}–C^{11}–O^1 27.01°).

Chart 1. Substrate on Which a Carboxamide Has Been Used to Direct Halogen Migration (left) and Planned Substrates to Attempt Ferrocene Halogen "Dance" (right)



attacked by a base in the case of the ferrocenecarboxamides **5**–**8** (Chart 1). Although silyl protection is possible, we did not consider this strategy as studies showed that hindered ferrocene carboxamides[22] bearing such silanes at C^2 can hardly be deprotonated at C^5, but rather on the unsubstituted Cp ring. Carboxamide orientation seems to impact the metalation efficiency, the reaction being favored when the C═O group is in the plane of the substituted Cp ring.[25]

Different aspects of the molecular structure of ferrocenes and their derived properties were studied by quantum chemical calculations.[26] It is established that ferrocenes can exist as eclipsed and staggered conformations with a low internal rotation barrier.[27] In our case (see Supporting Information), the investigated ferrocenes are predominantly in an eclipsed form with hydrogens slightly bent inward. We considered the carboxamide conformation space next.

Due to the presence of the heavy halogen at C^2 in **5**, as in the case of silyl-protected carboxamide, the favored conformation seems to have the carboxamide C═O out of the Cp plane (even nearly perpendicular, see Figure 1) and thus is not suitable to induce metalation at C.[5] We thus tried to assess, for **1** and **5**, the energy difference between the most stable conformation and the conformation with coplanar C═O and Cp ring. Because we could not get this information by using dynamic NMR studies (see Supporting Information), we calculated their energy profiles upon rotation around their C^1–C═O bond (Figure 2). It was found earlier[28] that for

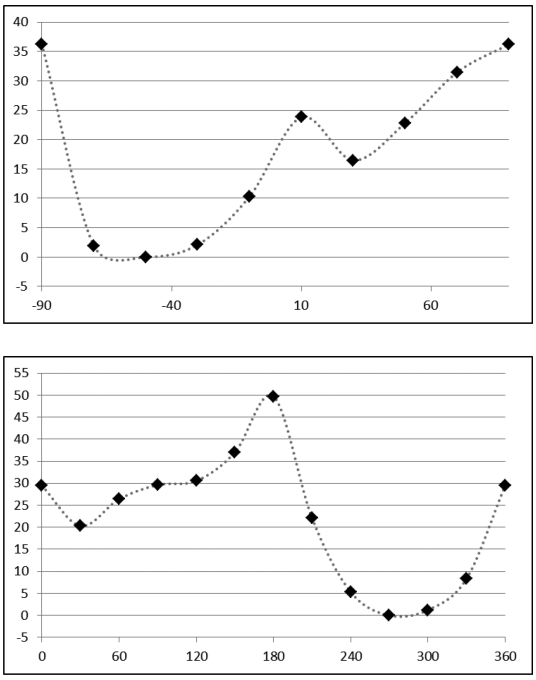
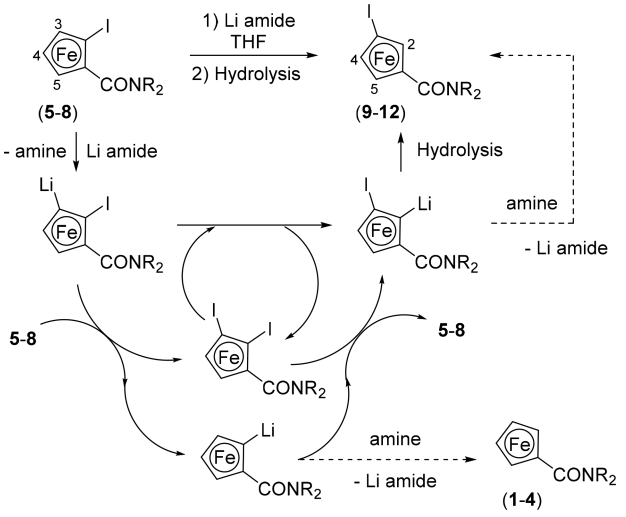


Figure 2. Energy profiles (kJ/mol) of **1** (top) and **5** (bottom) upon torsion angle (deg) C^2–C^1–C═O change.

Scheme 1. Proposed Mechanism for Halogen Dance on 2-Iodoferrocenecarboxamides



ferrocenecarboxamides the bulkier the substituent is, the greater the value of the angle between the Cp and amide planes is.

Whereas the computed conformations of lowest energy are very close to the structures obtained by X-ray diffraction, a local maximum (+24 kJ/mol) is noticed for the conformation of **1** with the C═O group in the plane of the Cp (Figure 2, top), and two maxima (local at +30 and global at +50 kJ/mol) were recorded for the two "in-plane" conformers of **5** (Figure 2, bottom; respectively, 0° in the case of the C═O group on the iodine side (syn) and 180° for the C═O group on the opposite side (anti)).[28] This large value led us to suppose that the C═O group can hardly stabilize a 2-iodo-5-lithioferrocenecarboxamide by lithium coordination, and we were confident that halogen migration will take place without a protective group.

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We decided to optimize the reaction on 2-iodo-*N*,*N*-diisopropylferrocenecarboxamide (**5**) and to next apply the best conditions to the other *N*,*N*-dialkyl-2-iodoferrocenecarboxamides **6**, **7** and **8**. On the basis of the mechanism proposed in Scheme 1, we considered LiTMP as a better lithium amide than LiDA.[29] Indeed, 2,2,6,6-tetramethylpiperidine (H-TMP; pK_a = 37.3)[30] is less prone to protonate 2-lithio-*N*,*N*-diisopropylferrocenecarboxamide than diisopropylamine (pK_a = 35.7).[30]

Thus, we treated the 2-iodoferrocenecarboxamide **5** by LiTMP (1.1 equiv) in THF (THF = tetrahydrofuran) for 2 h at different reaction temperatures (from −30 to −80 °C) before subsequent hydrolysis. In all these experiments, we observed (gas chromatography (GC) mass spectrometry) the formation of 3-iodo-*N*,*N*-diisopropylferrocenecarboxamide (**9**) as well as the deiodinated compound **1** in addition to the recovered starting material **5**. Whereas −30 °C favored deiodination (**1** formed in ∼40% estimated yield), starting material **5** was importantly recovered at −80 °C (∼55% estimated yield). Regarding the expected isomerized iodide **9**, its formation was favored at −50 °C. Other mono- and diiodides were formed, but in general as minority products.

Consequently, we kept −50 °C and checked different reaction times (5 min, 15 min, 30 min, 6 h, 14 h and 20 h; see Supporting Information). The results show that the 2-lithioferrocenecarboxamide is rapidly formed (giving **1** by hydrolysis), but the conversion to the 3-iodo-2-lithio derivative (affording **9** by hydrolysis) takes more time. Once the starting **5** exhausted (∼14 h), there is no benefit to use longer reaction times.

Under the optimized reaction conditions, LiTMP proved superior to LiDA, often employed as halogen dance mediator.[13] With LiDA, extending the reaction time favored the deiodinated product **1** to the detriment of the expected 3-iodoferrocenecarboxamide **9** (see Supporting Information). These results, which could be due to the higher propensity of diisopropylamine to protonate the 2-lithioferrocenecarboxamide when compared with LiTMP, led us to abandon LiDA.

These optimized conditions (1.1 equiv of LiTMP, THF, −50 °C, 14 h) in hand, we studied the behavior of the less hindered 2-iodoferrocenecarboxamides **6**−**8** in the reaction. For more sensitive 2-iodo-*N*,*N*-dimethylferrocenecarboxamide (**7**), the estimated yield of the 3-iodo product **11** was improved at a lower temperature. From *N*,*N*-diethyl-2-iodoferrocenecarboxamide (**6**) and 1-iodo-2-(4-morpholinocarbonyl)ferrocene (**8**), conducting the reaction at a larger scale (4.0 mmol instead of 1.0) provided the respective 3-iodo derivatives **10** and **12** more efficiently (see Supporting Information).

One main issue of the approach is to isolate the isomerized products **9**−**12**. Unlike the *N*,*N*-diisopropylferrocenecarboxamide **9**, separable from the deiodinated compound **1** and the other iodides by column chromatography over silica gel (36% yield at a 1.0 mmol scale; 53% yield at a 4.0 mmol scale), the less hindered *N*,*N*-dialkyl ferrocenecarboxamides **10**−**12** proved much less stable. The *N*,*N*-diethylcarboxamide **10** could be purified by column chromatography over silica gel (32% yield at a 1.0 mmol scale), but in a nonreproducible way. Even worse, the *N*,*N*-dimethylcarboxamide **11** and the morpholino-based carboxamide **12** were never isolated. As a consequence, crystals suitable for X-ray diffraction were only obtained for the 3-iodo derivative **9** (Figure 1).

To understand why deiodination competes, we treated the ferrocenecarboxamide **1** with LiTMP (1.1 equiv) in THF at −50 °C for 6 h. After subsequent iodolysis, we isolated the 2-iodo derivative **5** in a low 7% yield. Similarly, iodolysis of the halogen dance reaction mixture after 6 h at −50 °C produces much more **1** (∼ 60% yield) than 2-lithioferrocenecarboxamide (∼ 10%). That the latter easily reacts with H-TMP could explain why **1** first and easily accumulates in the reaction mixture before disappearing. In order to reduce such a protonation, we tried to use 2 equiv of LiTMP. Unfortunately, the formation of **9** is not favored under these conditions. By decreasing the amount of lithium amide to 0.5 equiv, the halogen dance is considerably prevented with **5** remaining present in ∼30% yield and deiodination similarly taking place (see Supporting Information).

Last but not least, as *N*,*N*-diisopropyl-2-lithioferrocenecarboxamide, 3-iodo-*N*,*N*-diisopropyl-2-lithioferrocenecarboxamide is prone to *in situ* protonation by H-TMP. Indeed, trapping the halogen dance reaction mixture with electrophiles (PhCHO, PhSSPh, $ClPPh_2$) led to complex mixtures, while using DCl−D_2O only allowed 2-deuterio-3-iodo-*N*,*N*-diisopropylferrocenecarboxamide to be isolated as a 1:1 mixture (∼30% yield) with **9**.

In most cases, the deiodination is accompanied by formation of unwanted unstable mono- and diiodides. Because we could not isolate any of the side products, we tried to get information from the NMR spectra of fractions containing them. First, we completely assigned the ^1H and ^{13}C NMR signals of **1**, **5**, and **9** and deduced the NMR increments of both the $CONiPr_2$ and iodo substituents (see Supporting Information).

In several experiments (notably by using an excess of base to attempt the reaction), we observed the formation (<10% yield estimated by GC mass spectrometry) of an isomer of **5** and **9**. This compound was identified as being 1′-iodo-*N*,*N*-diisopropylferrocenecarboxamide by NMR and GC comparison with the product resulting from silyl deprotection of 1′-iodo-*N*,*N*-diisopropyl-2-(trimethylsilyl)ferrocenecarboxamide.

Concerning the diiodides, we could get information from the ^{13}C NMR spectra of fractions containing them. In particular, the chemical shift of the C^1 carbon (connected to C═O) largely depends on the presence of iodine atoms at C^2 and C^5. Indeed, at 81.3 ppm in the absence of neighboring iodine (compound **1**), this signal moves to 92.6 ppm in the presence of iodine at C^2 (compound **5**), but is not modified significantly with iodine at C^3 (82.8 ppm, compound **9**). Thus, with a C^1 at 97.2 ppm, we are inclined to think that the diiodide most often formed in our halogen dance−hydrolysis sequences is the 2,5-diiodocarboxamide. After halogen dance−iodolysis, a new diiodide is formed (longer retention time on GC mass spectrometry); we supposed it is the 2,3-diiodocarboxamide shown in Scheme 1, formed by iodolysis of the 3-iodo-2-lithioferrocenecarboxamide. Nevertheless, this second diiodide is rarely observed in our halogen dance-hydrolysis reactions; instead, in addition to the 2,5-diiodocarboxamide, a third diiodide is often noticed. We have no clue to identify it, but the 2,4-diiodo derivative could be a possible candidate. This NMR study at least seems to show that deprotometalation of **5** lacks regioselectivity (next to iodine vs carboxamide).

To get more information on these diiodides, we attempted the use of the base *in situ* prepared from $ZnCl_2$·TMEDA (0.5 equiv) and LiTMP (1.5 equiv)[14] to prepare diiodides from the iodocarboxamide **5**. Under the conditions used in Table 2, the preponderant formation of 2,5-diiodinated ferrocene-

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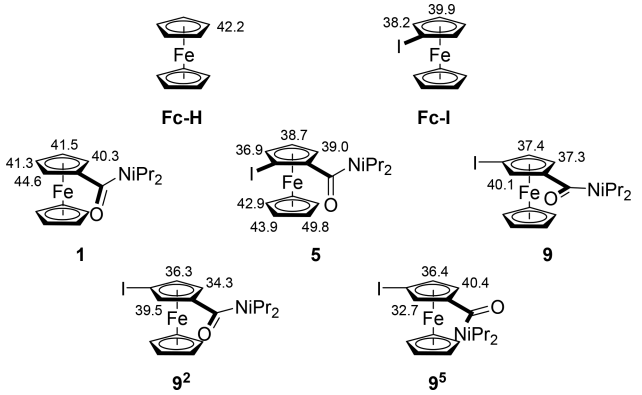
carboxamides was suspected on the basis of the ^{13}C NMR data of the mixture obtained (peaks at 97.2 and 98.1 ppm for the main polyiodides formed). This evidenced a favored kinetic deprotometalation of **5** next to the carboxamide function.

All these observations led us to consider the results in the light of the pK_a values of key ferrocene derivatives. In 1973, Denisovich and Gubin described ferrocene as being more acidic than benzene, with a pK_a value of 39 ± 3 on the MSAD scale (polarography).[31] To our knowledge, this represents the only ferrocene pK_a determination. Thus, we calculated the CH acidity (pK_a values) in THF solution of **Fc-H**, **Fc-I**, **1**, **5**, and **9** within the DFT framework by using the approach elaborated earlier[32] (Chart 2). Whereas iodine exerts its known short- and

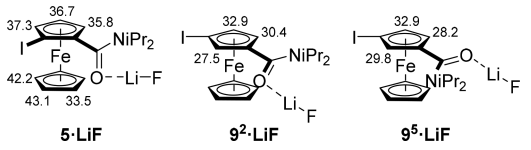
Chart 2. Selected Calculated pK_a Values in THF Solution for Fc−H, Fc−I, 1, 5, and 9[a]



[a]Top and middle, most stable conformation; bottom, Cp and C═O coplanar 9^2 and 9^5 with the C═O group, respectively, pointing toward C^2 and C^5.

long-range acidifying effects, the carboxamide function as such acidifies more moderately. When coordinated to lithium (calculations performed by using LiF), the carboxamide becomes a stronger directing group, as shown in Chart 3.

Chart 3. Selected Calculated pK_a Values in THF Solution for 5·LiF (Most Stable Conformation of 5) and 9·LiF (Cp and C═O Coplanar)



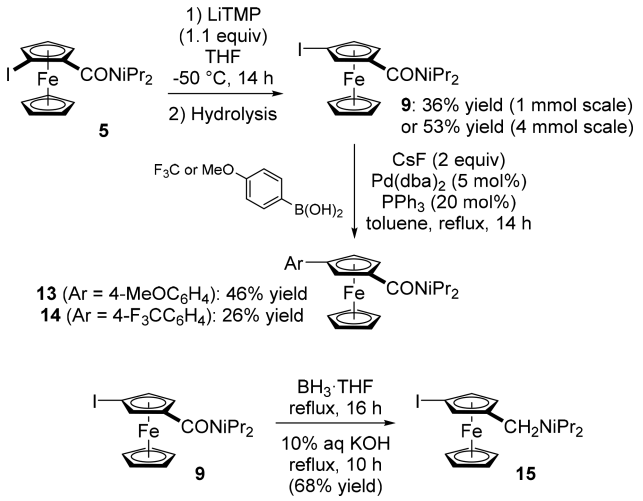
Upon carboxamide coordination to lithium, the 1′ position of ferrocene **5** is greatly acidified and amenable to deprotonation; this might explain why 1′-iodo-*N*,*N*-diisopropylferrocenecarboxamide is observed in experiments. Besides, when compared to the site next to iodine, the position adjacent to the carboxamide is somewhat more activated; this could explain why deprotonation competitively takes place at C^5, as demonstrated by 2,5-diiodocarboxamide formation.

Once coordinated to the metal, the C^2 position of the 3-iodoferrocenecarboxamide **9** is highly activated; this allows us to explain why the equilibria between the different lithioferrocenes are shifted toward the expected 3-iodo-2-lithioferrocenecarboxamide.

The reason why reaction times exceeding 14 h are not suitable to reach high yields could be due to LiTMP destruction,[33] favoring 2-lithioferrocenecarboxamide reprotonation. Competitive iodine/lithium exchange by LiTMP[34] could also be advanced to rationalize the iodine loss observed all along the reaction.

In order to obtain new kinds of ferrocenes, we made derivatives from the 3-iodoferrocenecarboxamide **9** (Scheme 2). Using 4-methoxyphenyl- and 4-(trifluoromethyl)phenyl-

Scheme 2. Conversion of 9 by Suzuki Coupling and Carboxamide Reduction



boronic acid in the presence of cesium fluoride,[35] and catalytic amounts of Pd(dba)$_2$ (dba = dibenzylideneacetone) and triphenylphosphine, at the reflux temperature of toluene,[36] afforded the Suzuki coupling products **13** and **14**, respectively, in moderate yields. The *N*,*N*-diisopropylaminomethylferrocene **15** was in turn prepared by reduction of the carboxamide function using BH_3·THF, as documented previously.[3a]

We have thus shown that it is possible to access 1,3-disubstituted ferrocenes, which are promising substrates for different applications,[5] with recourse to halogen dance.

CONCLUSION

We studied the halogen dance reaction from different *N*,*N*-dialkyl 2-iodoferrocenecarboxamides. In spite of the low stability of the less hindered 3-iodoferrocenecarboxamides, we could optimize the reaction giving 3-iodo-*N*,*N*-diisopropylferrocenecarboxamide (**9**) and identify possible reasons for the origin of the side product formation.

One limit encountered in this halogen dance is the formation of undesirable diiodides, notably due to the relatively high acidity found at C^5 on 2-iodo-*N*,*N*-diisopropylferrocenecarboxamide (**5**). By using deuterium to protect this position toward deprotonation,[4b] one could favor the formation of the expected 3-iodo-2-lithioferrocenecarboxamide.

Competitive deiodination and lithioferrocene reprotonation proved to be main issues of the reaction. We will devote efforts in order to identify ferrocene substituents capable of making the generated ferrocenyllithiums more stable toward H-TMP.

EXPERIMENTAL SECTION

General Details. All the reactions were performed under an argon atmosphere using standard Schlenk techniques. THF was distilled over

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sodium/benzophenone. Column chromatography separations were achieved on silica gel (40−63 μm). Melting points were measured on a Kofler apparatus. IR spectra were taken on a PerkinElmer Spectrum 100 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded either (i) on a Bruker Avance III spectrometer at 300 and 75 MHz, respectively, or (ii) on a Bruker Avance III HD at 500 and 126 MHz, respectively. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak, and ^{13}C chemical shifts are relative to the central peak of the solvent signal.[37] Ferrocenecarboxylic acid is commercially available but can be easily prepared according to a previously reported procedure.[19]

For **2**−**4**, **6**−**9**, and **13**, the X-ray diffraction data were collected using D8 VENTURE Bruker AXS diffractometer at the temperature given in the crystal data. The samples were studied with monochromatized Mo Kα radiation (λ = 0.71073 Å). The structure was solved by dual-space algorithm using the *SHELXT* program[38] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[39] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. The molecular diagrams were generated by ORTEP-3 (version 2.02).[40]

General Procedure 1 (Route A). The protocol was adapted from a previously reported procedure.[41] To a stirred mixture of ferrocene (0.93 g, 5.0 mmol) and ^{t}BuOK (56 mg, 0.5 mmol) in THF (45 mL) at −80 °C was added dropwise ^{t}BuLi (∼1.9 M in pentane, 10 mmol). After 1.5 h at this temperature, the mixture was rapidly transferred dropwise through a cannula to a solution of the required dialkyl carbamoyl chloride (the amount is given in the product description) in THF (15 mL) at −80 °C, and the resulting mixture was allowed to warm to −40 °C before quenching by an aqueous saturated solution of NH_4Cl (50 mL). Extraction with AcOEt (3 × 20 mL), washing with brine (20 mL), drying over $MgSO_4$, removal of the solvents, and purification by chromatography on silica gel (the eluent is given in the product description) led to the expected compound (see Supporting Information for experimental data on the compounds **2**−**4**).

General Procedure 2 (Route B).[20] To a stirred mixture of ferrocenecarboxylic acid (4.6 g, 20 mmol) in CH_2Cl_2 (50 mL) containing DMF (5 drops) was added dropwise oxalyl chloride (3.5 mL, 40 mmol). After 2 h at room temperature, the solvent and excess oxalyl chloride were removed under vacuum. The crude ferrocenoyl chloride was next dissolved in CH_2Cl_2 (65 mL) before dropwise addition of the required amine (60 mmol) at 0 °C. After stirring for 3 h, 1 M aqueous HCl (30 mL) was added. Extraction with Et_2O (20 mL) and AcOEt (2 × 20 mL), washing with brine (20 mL), drying over $MgSO_4$, removal of the solvents, and purification by chromatography on silica gel (the eluent is given in the product description) led to the expected compound (see Supporting Information for experimental data on the compound **1**).

2-Iodo-*N*,*N*-diisopropylferrocenecarboxamide (5, Racemic Mixture). To Et_2O (15 mL) containing TMEDA (1.6 g, 2.1 mL, 13 mmol), BuLi (∼1.6 M in hexanes, 13 mmol) was added dropwise at −80 °C, under stirring. After 15 min at this temperature, a solution of *N*,*N*-diisopropylferrocenecarboxamide (**1**, 3.6 g, 11.5 mmol) in Et_2O (20 mL) was added, and the mixture was stirred for 1 h before addition of a solution of I_2 (5.8 g, 23 mmol) in Et_2O (15 mL) and THF (8 mL). After 30 min stirring, the cooling bath was removed, and the mixture was allowed to reach room temperature. Addition of an aqueous saturated solution of $Na_2S_2O_3$ (75 mL), extraction with Et_2O (3 × 20 mL), drying over $MgSO_4$, removal of the solvents, and purification by chromatography on silica gel (eluent, heptane−AcOEt 95:5; R_f = 0.65) gave **5** in 88% yield as an orange powder: mp 138 °C; IR (ATR) 686, 811, 1002, 1024, 1036, 1315, 1368, 1455, 1620, 2970, 3094 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 0.99 (br s, 3H, CH_3), 1.11 (br s, 3H, CH_3), 1.51 (br s, 6H, $2CH_3$), 3.41 (br s, 1H, C*H*Me$_2$), 3.62 (br s, 1H, C*H*Me$_2$), 4.17 (s, 1H, Cp-H), 4.28 (s, 1H, Cp-H), 4.34 (s, 5H, Cp-H), 4.42 (s, 1H, Cp-H); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 0.94 (d, 3H, J = 6.7 Hz, CH_3), 1.05 (d, 3H, J = 6.8 Hz, CH_3), 1.47 (t, 6H, J = 6.2 Hz, CH_3), 3.36 (t, 1H, J = 7.1 Hz, C*H*Me$_2$), 3.57 (t, 1H, J = 7.1 Hz, C*H*Me$_2$), 4.13 (t, 1H, J = 2.4 Hz, H4), 4.24 (dd, 1H, J = 2.6 and 1.3 Hz, H5), 4.30 (s, 5H, Cp-H), 4.38 (dd, 1H, J = 2.4 and 1.3 Hz, H3); ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 298 K) δ 0.95 (br s, 3H, CH_3), 1.04 (br s, 3H, CH_3), 1.41 (br s, 6H, $2CH_3$), 3.44 (br s, 1H, C*H*Me$_2$), 3.50 (br s, 1H, C*H*Me$_2$), 4.27 (t, 1H, J = 2.4 Hz), 4.28 (s, 5H, Cp-*H*), 4.41 (dd, 1H, J = 2.5 and 1.3 Hz), 4.50 (dd, 1H, J = 2.4 and 1.3 Hz); ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 383 K) δ 1.21 (d, 6H, J = 6.7 Hz, CH_3), 1.26 (d, 6H, J = 6.5 Hz, CH_3), 3.56 (sept, 2H, J = 6.7 Hz, 2C*H*Me$_2$), 4.27 (t, 1H, J = 2.5 Hz), 4.29 (s, 5H, Cp), 4.38 (br s, 1H, Cp-H), 4.48 (br s, 1H, Cp-H); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 21.0 ($4CH_3$), 40.6 (C−I), 46.0 (*C*HMe$_2$), 50.9 (*C*HMe$_2$), 66.9 (*C*H), 67.7 (CH), 72.9 (5CH, Cp), 73.7 (CH), 92.8 (*C*−C═O), 166.4 (C═O); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 20.7 (CH_3), 20.8 (CH_3), 21.0 (CH_3), 21.0 (CH_3), 40.5 (C−I), 45.9 (*C*HMe$_2$), 50.8 (*C*HMe$_2$), 66.8 (CH, C5), 67.7 (CH, C4), 72.7 (5CH, Cp), 73.6 (CH, C3), 92.6 (*C*−C═O), 166.3 (C═O). These data are similar to those reported previously.[3a] The obtained crystal structure was found to be similar to that described (CCDC 170421; NEMLAS).[21]

General Procedure 3. To a stirred, cooled (0 °C) solution of H-TMP (0.85 mL, 5.0 mmol) in THF (4 mL) were successively added BuLi (∼1.6 M in hexanes, 4.5 mmol) and, 5 min later, $ZnCl_2$·TMEDA[42] (0.38 g, 1.5 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the required ferrocene (3.0 mmol) at 0−10 °C. After 2 h at room temperature, a solution of I_2 (0.75 g, 3.0 mmol) in THF (4 mL) was added. The mixture was stirred overnight before addition of an aqueous saturated solution of $Na_2S_2O_3$ (10 mL) and extraction with AcOEt (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by chromatography over silica gel (the eluent is given in the product description; see Supporting Information for experimental data on the compound **6**).

*2-Iodo-N,N-dimethylferrocenecarboxamide (**7**, Racemic Mixture).* The general procedure 3 using *N*,*N*-dimethylferrocenecarboxamide (**3**, 0.77 g) gave **7** (eluent, heptane−AcOEt 70:30; R_f = 0.28) in 78% yield as an orange powder: mp 58 °C; IR (ATR) 689, 816, 872, 961, 999, 1008, 1106, 1117, 1224, 1262, 1360, 1379, 1418, 1453, 1496, 1631, 2926 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 2.71 (br s, 3H, CH_3), 2.92 (br s, 3H, CH_3), 4.13 (t, 1H, J = 2.5 Hz, Cp-H), 4.21 (s, 5H, Cp), 4.26 (dd, 1H, J = 2.6 and 1.3 Hz, Cp-H), 4.37 (dd, 1H, J = 2.4 and 1.3 Hz, Cp-H); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 35.3 (CH_3), 38.8 (CH_3), 40.3 (C−I), 68.3 (CH), 68.4 (CH), 72.7 (5CH, Cp), 74.4 (CH), 87.7 (*C*−C═O), 167.8 (C═O). Anal. Calcd for $C_{13}H_{14}FeINO$: C, 40.77; H, 3.68; N, 3.66. Found: C, 40.84; H, 3.71; N, 3.69. Crystal data for **7**. $C_{13}H_{14}FeINO$, M = 383.00, T = 150(2) K, orthorhombic, $P2_12_12_1$, a = 7.3581(8), b = 9.0317(11), c = 19.773(3) Å, V = 1314.0(3) Å^3, Z = 4, d = 1.936 g cm^{-3}, μ = 3.480 mm^{-1}. A final refinement on F^2 with 2939 unique intensities and 157 parameters converged at $\omega R(F^2)$ = 0.0398 ($R(F)$ = 0.0162) for 2914 observed reflections with $I > 2\sigma(I)$. CCDC 1565040.

*1-Iodo-2-(4-morpholinocarbonyl)ferrocene (**8**, Racemic Mixture).* The general procedure 3 using (4-morpholinocarbonyl)-ferrocene (**4**, 0.90 g) gave **8** (eluent, heptane−AcOEt 80:20; R_f = 0.18) in 84% yield as a yellowish powder: mp 135−136 °C; IR (ATR) 687, 810, 866, 959, 1001, 1021, 1062, 1111, 1186, 1250, 1273, 1404, 1437, 1466, 2363, 2856, 2971, 3081 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 3.45 (br s, 3H, CH_2), 3.66 (br s, 5H, CH_2), 4.25 (br s, 1H, Cp-H), 4.34 (s, 5H, Cp), 4.36 (br s, 1H, Cp-H), 4.49 (br s, 1H, Cp-H); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 40.2 (C−I), 43.1 ($2CH_2$), 47.8 ($2CH_2$), 67.0 (CH), 68.8 (CH), 73.1 (5CH, Cp), 74.8 (CH), 87.6 (*C*−C═O), 167.1 (C═O). Anal. Calcd for $C_{15}H_{16}FeINO$: C, 42.39; H, 3.79; N, 3.30. Found: C, 42.45; H, 3.86; N, 3.33. Crystal data for **8**. $C_{15}H_{16}FeINO_2$, M = 425.04, T = 150(2) K, monoclinic, $P2_1/c$, a = 10.3514(15), b = 7.2576(10), c = 20.081(3) Å, β = 101.480(4)°, V = 1478.5(3) Å^3, Z = 4, d = 1.910 g cm^{-3}, μ = 3.108 mm^{-1}. A final refinement on F^2 with 3368 unique intensities and 148 parameters converged at $\omega R(F^2)$ = 0.0859 ($R(F)$ = 0.0351) for 3211 observed reflections with $I > 2\sigma(I)$. CCDC 1565041.

General Procedure 4. To a stirred, cooled (0 °C) solution of H-TMP (0.19 mL, 1.1 mmol) in THF (2 mL) was added BuLi (∼1.6 M in hexane, 1.1 mmol). The mixture was stirred for 5 min at 0 °C before introduction of the required iodoferrocene (1.0 mmol) at −50 °C. After 14 h at −50 °C, MeOH (2.0 mL) and aqueous 1 M HCl (10

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mL) were successively added. Extraction with AcOEt (3 × 15 mL), drying over $MgSO_4$, concentration under reduced pressure, and purification by azeotropic reflux chromatography[43] over silica gel (eluent, cyclohexane−AcOiPr 78:22) led to the expected product.

*3-Iodo-N,N-diisopropylferrocenecarboxamide (**9**, Racemic Mixture).* The general procedure 4 using 2-iodo-*N*,*N*-diisopropylferrocenecarboxamide (**5**, 0.44 g) gave **9** (R_f = 0.32) in 36% yield (53% yield on a 4.0 mmol scale) as an orange powder: mp 112 °C; IR (ATR) 763, 803, 825, 1007, 1033, 1324, 1368, 1457, 1602, 2959, 3005 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 291 K) δ 1.25−1.40 (br s, 12H, $4CH_3$), 3.44 (br s, 1H, C*H*Me_2), 4.25 (s, 5H, Cp), 4.40 (br s, 1H, C*H*Me_2), 4.50 (dd, 1H, J = 2.5 and 1.2 Hz, Cp-H), 4.57 (dd, 1H, J = 2.5 and 1.4 Hz, Cp-H), 4.73 (t, 1H, J = 1.3 Hz, Cp-H); ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 1.20 (br s, 6H, $2CH_3$), 1.45 (br s, 6H, $2CH_3$), 3.42 (br s, 1H, C*H*Me_2), 4.30 (s, 5H, Cp), 4.45 (br s, 1H, C*H*Me_2), 4.51 (s, 1H, H4), 4.58 (s, 1H, H5), 4.73 (s, 1H, H2); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 21.2 ($4CH_3$), 39.6 (C−I), 46.6 (*C*HMe_2), 49.5 (*C*HMe_2), 71.1 (CH), 73.0 (5CH, Cp), 75.2 (CH), 75.6 (CH), 82.9 (*C*−C═O), 167.8 (C═O);^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 21.2 ($4CH_3$), 39.6 (C−I), 46.5 (*C*HMe_2), 49.9 (*C*HMe_2), 71.1 (CH, C5), 73.0 (5CH, Cp), 75.2 (CH, C4), 75.6 (CH, C2), 82.8 (*C*−C═O), 167.8 (C═O). Anal. Calcd for $C_{17}H_{22}FeINO$: C, 46.50; H, 5.05; N, 3.19. Found: C, 46.61; H, 5.10; N, 3.29. Crystal data for **9**. $C_{17}H_{22}FeINO$, M = 439.10, T = 293(2) K, monoclinic, $P2_1/n$, a = 7.5144(6), b = 10.3128(8), c = 22.4379(17) Å, β = 91.475(3)°, V = 1738.2(2) Å^3, Z = 4, d = 1.678 g cm^{-3}, μ = 2.642 mm^{-1}. A final refinement on F^2 with 3955 unique intensities and 194 parameters converged at $\omega R(F^2)$ = 0.3102 ($R(F)$ = 0.1108) for 3229 observed reflections with $I > 2\sigma(I)$. CCDC 1565042.

*N,N-Diethyl-3-iodoferrocenecarboxamide (**10**, Racemic Mixture).* The general procedure 4 using 2-iodo-*N*,*N*-diethylferrocenecarboxamide (**6**, 0.41 g, 1.0 mmol) gave **10** (R_f = 0.10) in 32% yield as an orange powder: mp 86−87 °C; IR (ATR) 668, 823, 1001, 1209, 1449, 1474, 1604, 2967 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 1.16 (t, 6H, J = 6.9 Hz, $2CH_3$), 3.42 (br s, 4H, $2CH_2$), 4.21 (s, 5H, Cp), 4.51 (dd, 1H, J = 2.5 and 1.3 Hz, H4), 4.60 (dd, 1H, J = 2.6 and 1.4 Hz, H5), 4.77 (t, 1H, J = 1.4 Hz, H2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 12.9 (CH_3), 14.8 (CH_3), 39.6 (C−I), 40.9 (CH_2), 42.7 (CH_2), 71.2 (CH, C5), 72.9 (5CH, Cp), 75.5 (CH, C4), 75.9 (CH, C2), 80.3 (*C*−C═O), 168.1 (C═O).

General Procedure 5 (Suzuki Coupling). The protocol was adapted from a previously reported procedure.[36] A solution of CsF (0.30 g, 2.0 mmol), 3-iodo-*N*,*N*-diisopropylferrocenecarboxamide (**9**, 0.44 g, 1.0 mmol), and boronic acid (4.0 mmol) in toluene (10 mL) was degassed with Ar before addition of $Pd(dba)_2$ (28 mg, 50 μmol) and PPh_3 (52 mg, 0.20 mmol). The resulting mixture was heated for 14 h under reflux before cooling and dilution with Et_2O (60 mL), washing with H_2O, and extraction with CH_2Cl_2 (3 × 20 mL). After drying over anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure, and the coupled product was isolated by purification by flash chromatography on silica gel.

*N,N-Diisopropyl-3-(4-methoxyphenyl)ferrocenecarboxamide (**13**, Racemic Mixture).* The general procedure 5 using 4-methoxyphenylboronic acid (0.61 g) gave **13** (eluent, heptane−AcOEt 80:20; R_f = 0.43) in 46% yield as an orange powder (slow crystallization): mp 134−136 °C; IR (ATR) 791, 807, 831, 1024, 1036, 1158, 1178, 1246, 1272, 1321, 1342, 1372, 1437, 1452, 1467, 1525, 1609, 2929, 2965, 3001 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 1.15−1.36 (br s, 6H, $2CH_3$), 1.40−1.58 (br s, 6H, $2CH_3$), 3.45 (br s, 1H, C*H*Me_2), 3.82 (s, 3H, OCH_3), 4.10 (s, 5H, Cp), 4.56 (br s, 1H, C*H*Me_2), 4.64 (dd, 1H, J = 2.5 and 1.4 Hz, Cp-H, H5), 4.67 (dd, 1H, J = 2.4 and 1.5 Hz, Cp-H, H4), 5.01 (t, 1H, J = 1.4 Hz, Cp-H, H2), 6.85−6.89 (m, 2H, H3′), 7.41−7.43 (m, 2H, H2′); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 21.3 ($4CH_3$), 46.5 (*C*HMe_2), 49.6 (*C*HMe_2), 55.4 (OCH_3), 66.9 (CH, C4), 68.3 (CH, C2), 70.1 (CH, C5), 71.4 (5CH, Cp), 81.7 (*C*−C═O), 86.8 (C, C3), 114.1 (2CH, C3′), 127.3 (2CH, C2′), 130.3 (C, C1′), 158.5 (C, C4′), 169.5 (C═O). Anal. Calcd for $C_{24}H_{29}FeNO_2$: C, 68.74; H, 6.97; N, 3.34. Found: C, 68.70; H, 6.88; N, 3.31. Crystal data for **13**. $C_{24}H_{29}FeNO_2$, M = 419.33, T = 150(2) K, orthorhombic, $P2_1cn$, a = 6.0222(2), b = 13.0671(5), c = 26.0685(8) Å, V = 2051.40(12) Å^3, Z = 4, d = 1.358 g cm^{-3}, μ = 0.754 mm^{-1}. A final refinement on F^2 with 4632 unique intensities and 225 parameters converged at $\omega R(F^2)$ = 0.0998 ($R(F)$ = 0.0440) for 4212 observed reflections with $I > 2\sigma(I)$. CCDC 1565043.

*N,N-Diisopropyl-3-(4-(trifluoromethylphenyl))ferrocenecarboxamide (**14**, Racemic Mixture).* The general procedure 5 using 4-(trifluoromethyl)phenylboronic acid (0.76 g) gave **14** (eluent, heptane−AcOEt 85:15; R_f = 0.23) in 26% yield as an orange oil: IR (ATR) 690, 729, 807, 822, 842, 908, 1040, 1068, 1106, 1121, 1162, 1285, 1321, 1371, 1446, 1468, 1615, 2241, 2933, 2969 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 1.15−1.35 (br s, 6H, $2CH_3$), 1.40−1.60 (br s, 6H, $2CH_3$), 3.47 (br s, 1H, C*H*Me_2), 4.12 (s, 5H, Cp), 4.62 (br s, 1H, C*H*Me_2), 4.72 (dd, 1H, J = 2.6 and 1.4 Hz, Cp-H, H5), 4.77 (dd, 1H, J = 2.6 and 1.5 Hz, Cp-H, H4), 5.12 (t, 1H, J = 1.8 Hz, Cp-H, H2), 7.54 (d, 2H, J = 8.6 Hz, H2′), 7.57 (d, 2H, J = 8.5 Hz, H3′); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 21.3 ($4CH_3$), 46.5 (*C*HMe_2), 49.9 (*C*HMe_2), 67.3 (CH, C4), 69.1 (CH, C2), 70.9 (CH, C5), 71.7 (5CH, Cp), 83.4 (*C*−C═O), 84.0 (C, C3), 125.6 (q, 2CH, J = 3.8 Hz, C3′), 126.2 (2CH, C2′), 128.3 (C, J = 32.5 Hz, C4′), 124.5 (q, C, J = 272 Hz, CF_3), 142.8 (C1′), 168.7 (C═O); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ −62.5. Anal. Calcd for $C_{24}H_{26}F_3FeNO$: C, 63.03; H, 5.73; N, 3.06. Found: C, 63.12; H, 5.75; N, 2.98.

1-(*N*,*N*-Diisopropylaminomethyl)-3-iodoferrocene (15, Racemic Mixture). The protocol was adapted from a previously reported procedure.[3a] To a stirred solution of 3-iodo-*N*,*N*-diisopropylferrocenecarboxamide (**9**, 1.0 mmol, 0.44 g) in THF (10 mL) under argon was added BH_3·THF (5.0 mmol, 5.0 mL of a 1.0 M solution). The mixture was refluxed for 16 h, cooled to room temperature, quenched with 10% aqueous KOH (35 mL) and refluxed for 10 h. The resulting solution was cooled to room temperature. Brine (50 mL) was added before extraction with Et_2O (3 × 20 mL), drying over $MgSO_4$, concentration under reduced pressure, and purification by chromatography over silica gel (eluent, heptane−AcOEt 60:40 to 0:100). The compound **15** was isolated in 68% yield: yellow oil; IR (ATR) 748, 818, 871, 933, 1001, 1031, 1106, 1137, 1160, 1202, 1362, 1463, 1673, 2926, 2961, 3096 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 0.98−1.01 (m, 12H, $4CH_3$), 3.03 (sept, 2H, J = 6.6 Hz, 2C*H*Me_2), 3.34 (d, 1H, J = 14.4 Hz, CH_2N), 3.40 (d, 1H, J = 14.5 Hz, CH_2N), 4.13 (s, 5H, Cp), 4.20 (s, 1H, H5), 4.31 (s, 1H, H4), 4.46 (s, 1H, H2); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 20.9 ($4CH_3$), 39.8 (C−I), 43.8 (CH_2N), 47.6 ($2CHMe_2$), 70.1 (CH, C5), 71.7 (5CH, Cp), 73.7 (CH, C4), 75.9 (CH, C2), 89.9 (*C*-CH_2). Anal. Calcd for $C_{17}H_{24}FeIN$: C, 48.03; H, 5.69; N, 3.29. Found: C, 48.11; H, 5.73; N, 3.12.

Density Functional Theory (DFT) Calculation Details. All the DFT calculations were performed by using the Gaussian 09 software package.[44] The structures from the X-ray diffraction analysis were used as starting guess. All the molecular geometries were completely optimized with no constraints. We used the B3LYP hybrid functional[45] together with the LANL2DZ basis set for both Fe and I and the 6-31G(d) basis set for the other atoms to calculate the optimized geometries and vibrational frequencies. Relaxed PES scans for **1** and **5** were obtained at the same level of theory. The solvent influence was treated by using the polarized continuum model (IEF PCM)[46] with the default parameters for THF. The pK_a values were calculated from the Gibbs energy of the homodesmic reaction between the studied and probe aromatic substrates.[47] The single point energies were obtained at the CAM-B3LYP/LANL2DZ + 6-31+G(d,p) level of theory.[48]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00659.

Optimization of halogen dance reaction, experimental data for compounds **1**−**4** and **6**, X-ray diffraction data for compounds **1**−**4**, **6**, and **13**, and NMR spectra (PDF)

DFT structural data (XYZ)

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Accession Codes

CCDC 1565036−1565043 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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