Halide-Mediated Ortho-Deprotonation Reactions Applied to the Synthesis of 1,2- and 1,3-Disubstituted Ferrocene Derivatives

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ABSTRACT: The ortho-deprotonation of halide-substituted ferrocenes by treatment with lithium tetramethylpiperidide (LiTMP) has been investigated. Iodo-, bromo-, and chloro-substituted ferrocenes were easily deprotonated adjacent to the halide substituents. The synthetic applicability of this reaction was, however, limited by the fact that, depending on the temperature and the degree of halide substitution, scrambling of both iodo and bromo substituents at the ferrocene core took place. Iodoferrocenes could not be transformed selectively into ortho-substituted iodoferrocenes since, in the presence of LiTMP, the iodo substituents scrambled efficiently even at −78 °C, and this process had occurred before electrophiles had been added. Bromoferrocene and certain monobromo-substituted derivatives, however, could be efficiently ortho-deprotonated at low temperature and reacted with a number of electrophiles to afford 1,2- and 1,2,3-substituted ferrocene derivatives. For example, 2-bromo-1-iodoferrocene was synthesized by ortho-deprotonation of bromoferrocene and reaction with the electrophiles diiodoethane and diiodotetrafluoroethane, respectively. In this and related cases the iodide scrambling process and further product deprotonation due to the excess LiTMP could be suppressed efficiently by running the reaction at low temperature and in inverse mode. In contrast to the low-temperature process, at room temperature bromo substituents in bromoferrocenes scrambled in the presence of LiTMP. Chloro- and 1,2-dichloroferrocene could be ortho-deprotonated selectively, but in neither case was scrambling of a chloro substituent observed. As a further application of this ortho-deprotonation reaction, a route for the synthesis of 1,3-disubstituted ferrocenes was developed. 1,3-Diiodoferrocene was accessible from bromoferrocene in four steps. On a multigram scale an overall yield of 41% was achieved. 1,3-Diiodoferrocene was further transformed into symmetrically 1,3-disubstituted ferrocenes (1,3-R₂Fc; R = CHO, COOEt, CN, CH=CH₂).

INTRODUCTION

Ferrocene derivatives have found broad application in a number of different fields including catalysis, bioorganometallic chemistry, and material sciences, and all of these areas have been reviewed extensively.1−4 For applications in catalysis, besides achiral 1,1′-heteroannularly substituted ferrocenes, chiral homoannularly 1,2-substituted derivatives are mainly used. As a consequence, a huge number of methodologies have been developed for the synthesis of 1,2-disubstituted ferrocenes.5c,d

The majority of these approaches make use of ortho-directing groups. For example, both N,N-dimethylaminomethylferrocene5 and chloroferrocene6 can be ortho-deprotonated by treatment with n-butyllithium, and the lithiated intermediates can be further reacted with electrophiles to afford 1,2-disubstituted products (Scheme 1).

Recently, we reported on biferrocene diphosphines as ligands for hydrogenation catalysts.7 The ligand synthesis was achieved by a Negishi coupling reaction, and for this purpose racemic 2-bromo-1-iodoferrocene was required. In this context we questioned whether this derivative could be synthesized in one step from commercially available bromoferrocene. As reported by Butler in 1999,8 in analogy to bromoarenes,9 bromoferrocene and 1,1′-dibromoferrrocene can be ortho-deprotonated with LDA (lithium disopropylamide). Further reaction of the lithiated intermediates with a number of electrophiles gave ortho-substituted bromo- or 1,1′-dibromoferrocenes with moderate yields. We subsequently showed that the ortho-deprotonation of bromoferrocenes can be significantly

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improved by using LiTMP (lithium 2,2,6,6-tetramethylpiperididide) in place of LDA and by optimizing the reaction conditions.\textsuperscript{60} This approach allowed access to a variety of enantiopure 1,2,3- and 1,3-substituted ferrocenes.\textsuperscript{10,11}

Two methods for the preparation of racemic 2-bromo-1-idoferrocene have been reported to date, and these were developed by Butler\textsuperscript{12} and Mongin/Krishna,\textsuperscript{13} respectively. Butler’s procedure starts from 1,1′-dibromoferrrocene, which affords the desired product after consecutive treatment with BuLi, LiTMP, and Zn(TMP)_2. Subsequent reaction with iodine gave 2-bromo-1-idoferrocene in 64% yield. However, significant amounts of byproducts were formed in both types of reaction.

Only in a few cases has bromoferrocene been used as the starting material for \textit{ortho}-deprotonation reactions.\textsuperscript{6,8,10} As a consequence, we questioned whether its scope of application could be extended not only to the synthesis of other 1,2-disubstituted ferrocenes but also to 1,3- or higher-substituted derivatives.

In this work we show how bromoferrocene can be \textit{ortho}-deprotonated selectively by LiTMP and subsequently transformed into a variety of 1,2-di-, 1,2,3-tri-, and 1,3-disubstituted ferrocene derivatives and how the formation of certain byproducts can be suppressed. In addition, the possibility of using this methodology to transform selectively iodo- and chloroferroccenes into their \textit{ortho}-substituted derivatives was evaluated.

\section*{RESULTS AND DISCUSSION}

\textbf{Ortho-Deprotonation of Bromoferroccenes.} Treatment of bromoferrrocene (1) with 1.5 equiv of LiTMP and subsequent reaction with one of the electrophiles DMF, CO\textsubscript{2}, TsCN, CIPPH\textsubscript{2}, or ClSn\textsubscript{Bu}\textsubscript{3} provided the 1,2-disubstituted products 2–6 selectively in 71–84% isolated yield (Scheme 2).\textsuperscript{15} Products with other substitution patterns were not detected in any case. During optimization of the reaction conditions it was noticed that the conversion of bromoferrrocene (1) to products depended significantly on the bromoferrocene/LiTMP ratio. For example, when bromoferrrocene was reacted with 1, 1.25, 1.5, or 2 equiv of LiTMP and when ClSn\textsubscript{Bu}\textsubscript{3} was subsequently used as the electrophile, the conversion of bromoferrrocene to the product 2-bromo-1-tributyllstannylferrocene (6) increased from 75% to 84%, 90%, and 93%, as determined by NMR spectroscopy. On the basis of these data we considered a LiTMP/substrate ratio of 1.5:1 to be a suitable compromise.

Interestingly, when bromoferrocene was reacted with 1.5 equiv of LiTMP and iodine or 1,2-diiodoethane were added to the reaction mixture, not only the desired product 2-bromo-1-idoferrocene (7) but also the trisubstituted derivative 2-bromo-1,3-dioidoferrocene (9) and other differently substituted monobromo-iodoferrocenes were obtained (Scheme 3). The structural integrity of 9 was confirmed by an X-ray diffraction study (Figure 1).

In this particular case, one might assume that the electrophile (I\textsubscript{2} or ICH\textsubscript{2}CH\textsubscript{2}I) reacts faster with \textit{ortho}-lithiated bromoferrocene 2-Li-1 to form the desired product 7 than with the excess LiTMP still present in the reaction mixture. This would allow excess LiTMP to further \textit{ortho}-deprotonate 7 next to either the bromo or the iodo substituent. Subsequent reaction with the electrophile would lead to products 9 and 11, respectively. Similarly, 12 would be formed from 9. Only 10 would not be accessible from 1 through a sequence of \textit{ortho}-deprotonation/iodination reactions, but this could result from an iodide scrambling process (a detailed discussion is provided below). It appeared, however, that all byproducts were formed in routes that involve compound 7 as the intermediate. On the basis of this assumption, the reaction was carried out in the inverse mode (slow addition of lithiated 1 to the electrophile).

The \textit{ortho}-lithiated bromoferrocene 2-Li-1 was added slowly at −78 °C to a solution of either ICH\textsubscript{2}CH\textsubscript{2}I or ICF\textsubscript{2}CF\textsubscript{2}I in THF, and this reversal of the addition completely suppressed the formation of byproducts to give 7 in 65% and 73% isolated yield, respectively (Scheme 2). Running the reaction in the inverse mode ensures that during the whole reaction period the electrophile is present in large excess rather than LiTMP.

Alternatively, 2-bromo-1-idoferrocene (7) could be obtained in 81% yield and with excellent purity by reaction of 6 in CH\textsubscript{2}Cl\textsubscript{2} with a solution of iodine in CH\textsubscript{2}Cl\textsubscript{2} (Scheme 4). The use of 1,1,2,2-tetra bromoethane as the electrophile and running the reaction in the inverse mode also allowed access to 1,2-dibromoferrocene (8)\textsuperscript{16} in 68% yield (Scheme 2).

We subsequently attempted to carry out a further selective \textit{ortho}-deprotonation on 2-substituted bromoferrocenes. It is clear that a second \textit{ortho}-deprotonation can be expected to take place selectively only if the substituent adjacent to the bromo substituent does not itself show \textit{ortho}-directing properties. Examples of such reactions have been reported previously by Butler,\textsuperscript{16} our group,\textsuperscript{10,11a} and others.\textsuperscript{31,13b,c}

In this work the 2-bromo-1-tributylstannylferrocene derivative 6 was reacted with LiTMP, and the lithiated intermediate was quenched with ClSn\textsubscript{Bu}\textsubscript{3} to provide the 1,2,3-trisubstituted product 13 in good yield (76–82%, Scheme 4). However, when 2-bromo-1-idoferrocene (7) was \textit{ortho}-deprotonated with LiTMP and subsequently reacted with ICH\textsubscript{2}CH\textsubscript{2}I, besides the
starting material and bromoferrocene a selection of five additional monobromo-iodoferrocenes were detected by NMR spectroscopy together with two unidentified byproducts, with the desired product 2-bromo-1,3-diiodoferrocene (9) being only a minor component (15%). In this case, the formation of byproducts could not be suppressed by carrying out the reaction in the inverse mode (for a discussion of this reaction see below). Nevertheless, in analogy to the synthesis of 7, product 9 could be obtained by reaction of 13 with iodine in 83% yield (Scheme 4).

While a wide variety of 1,2-disubstituted ferrocenes can easily be obtained by ortho-deprotonation of suitable monosubstituted precursors, 1,3-disubstituted derivatives are significantly more difficult to synthesize. Only Brown and co-workers had reported a methodology that allowed the selective meta-deprotonation of a monosubstituted ferrocene derivative. In the majority of cases 1,3-disubstituted ferrocenes have been prepared by removal of the central substituent of a 1,2,3-trisubstituted precursor. We therefore questioned whether the bromo substituent of derivative 13 could be replaced selectively by a proton. It is well known from the work of Kagan that the use of BuLi followed by treatment with an appropriate electrophile leads to the selective exchange of the 4-tolylsulfonyl group of 14 (Scheme 5, top), and, as a consequence, it seemed likely that the bromide of 13 could also be exchanged with other groups, including a proton.

In order to identify an appropriate reagent, the model compound 2-bromo-1-tributylstannylferrocene (6) was first reacted with NaBH₄, LiAlH₄, Pd(H₂), PrMgCl-LiCl, BuLi, PhLi, and BuLi, and the reaction mixtures were quenched with water. Only with PrMgCl-LiCl and BuLi could the bromide be exchanged quantitatively with a proton without harming the tributylstannyl residue (15, Scheme 5). For practical applications additional electrophiles were applied. Treatment of 6 with 1.5 equiv of BuLi followed by quenching with either DMF or ICF₂CF₂I gave derivatives 16 (80%) and 17, respectively. Derivative 17 was further transformed into 1,2-diiodoferrocene 18 (66% based on 6; Scheme 5, bottom).

On the basis of the results obtained with 6, removal of the bromo substituent of 13 was attempted with PrMgCl-LiCl and BuLi. Reaction of 13 at −78 °C with BuLi and CH₂OH as the proton source worked best, and the 1,3-disubstituted product 19 was isolated in almost quantitative yield. Treatment of 19 with I₂ in CH₂Cl₂ gave 1,3-diiodoferrocene (20) (69%, based on 13, Scheme 6).

In summary, 1,3-diiodoferrocene (20) was accessible in gram quantities from commercially available bromoferrocene (1) in four steps with an overall yield of 41–44%. It is clear that 20 constitutes a valuable starting material for the synthesis of a variety of 1,3-disubstituted ferrocene derivatives. For example, both iodides could be exchanged quantitatively by treatment with BuLi (4 equiv) at −78 °C. Reactions of the lithiated
intermediate with dimethylformamide (DMF), diethyl carbonate (DEC), and tosylcyanide (TsCN) led to derivatives 21−23 in 80%, 57%, and 67% yield, respectively. Furthermore, dialdehyde 21 was transformed into 1,3-divinylferrocene (24) (79% yield), a derivative that may be of interest in materials chemistry.

Ortho-Deprotonation of Chloro- and Iodoferrocenes. Since the use of LiTMP allowed bromoferrocene (1) to be selectively ortho-deprotonated and further transformed into a variety of 2-substituted bromoferrrocenes, we questioned whether this methodology could also be applied to chloroferrocene (26) and iodoferrocene (25) (Scheme 7).

According to a recent report, chloroferrocene (26) was ortho-deprotonated with LiTMP, and hexachloroethane was added to the lithiated intermediate. This reaction resulted in 1,2-dichloroferrocene (27) along with higher-substituted derivatives such as 1,3-trichloroferrocene.

In this case we also noticed that on running the reaction in the inverse mode the formation of higher-substituted derivatives could be suppressed to a very high extent. In addition to 1,2-dichloroferrocene (27) (38% yield), 2-chloro-1,3-dibutylstannylferrocene (28) (62%) was prepared and further transformed into 2-chloro-1-iodoferrocene (29) (94%).

In contrast to chloroferrocene (26), iodoferrocene (25) could not be transformed selectively into its 2-substituted derivatives. When 25 was deprotonated with LiTMP and subsequently reacted with an electrophile, regardless of the mode of addition, a variety of products were formed in all cases. For example, the use of ICH2CH2I as the electrophile led to a number of differently substituted iodoferrocenes in addition to ferrocene itself.

In order to gain further insights into the reactivity of differently substituted haloferrocenes, the ortho-deprotonation of 10 substrates with LiTMP was investigated (Chart 1). All substrates were deprotonated under comparable conditions with LiTMP, and the lithiated species were reacted further with either CH3OH, CD3OD, ICH2CH2I, ClSnnBu3, or Cl3CCl3. The results of these reactions are summarized in Table 1.

The results obtained after quenching with CH3OH clearly show that, regardless of the reaction conditions applied, all iodo-substituted derivatives (7, 9, 18, 20, 25, and 29; Table 1, entries 1, 4, 6, 18, 19, and 23) resulted in a mixture of products. For example, the reaction of 1,2-diiodoferrocene (18) with LiTMP (Scheme 8; Table 1, entry 4) resulted, after quenching with CH3OH, in a mixture of five (including starting material) out of seven possible iodo-substituted ferrocenes, with 1,3-diiodoferrocene (20) being the main component (67%). For a compilation of all possible homoannularly substituted iodo- and bromoferrrocenes see Chart 2 (top).

These results indicate that even in the absence of an external iodide source an intermolecular iodide transfer reaction had taken place. In each case, LiTMP had clearly induced an intermolecular iodide scrambling process. Such general reaction behavior, and especially the fact that LiTMP had isomerized 1,2-diiodoferrocene (18) to 1,3-diiodoferrocene (20), is reminiscent of the so-called “halogen dance” reaction, which is particularly well documented for halide-substituted aromatic heterocycles. Typically, a base-like LiTMP induces an isomerization process that involves deprotonation, lithium/halide exchange, and protonation steps.

The fact that LiTMP already scrambled the iodo substituents of iodoferrocenes before an electrophile had been added to the reaction mixture clearly indicates that a selective ortho-substitution of iodoferrocenes cannot be expected. This fact...
became even clearer when CD$_3$OD was used to quench the deprotonation reaction of 18. According to 1H and 13C NMR spectroscopy, the product mixture contained—in addition to all protonated products (18, 20, 25, 30, 31; Scheme 8, top)—at least five additional deuterated derivatives that must be the result of the reaction of lithiated intermediates with CD$_3$OD (Scheme 8, bottom).

In a similar way to 18, identical deuteration experiments were carried out with the iodo-substituted substrates 7, 9, 20, and 25 (Supporting Information, Table S3, entries 1–3, 5–7), and in each case mixtures of protonated and deuterated products were obtained. This indicates that after deprotonation not only had an iodide scrambling occurred but also this process led to a mixture of lithiated intermediates. It is clear that the reaction of such a mixture with an electrophile would lead to complex product mixtures.

The bromo-substituted ferrocenes were investigated next. The reactivity of the bromo substituent of bromoferrocene (1) and derivatives 7, 8, and 9 depended on the reaction temperature as well as on the number of bromo substituents. Only starting material was recovered when bromoferrocene (1) was deprotonated with LiTMP at −30 °C and then reacted with CH$_3$OH (Table 1, entry 8). As discussed above, the use of other electrophiles resulted exclusively in 1,2-substituted bromoferrocenes, and this indicates that the deprotonation reaction had occurred exclusively at one of the ortho-positions (Scheme 2). However, when 1,2-dibromoferrocene (8) was treated at −30 °C with LiTMP, a slow reaction took place that led to a mixture of four products, with the starting material still being the major component (94%; Scheme 9, top; Table 1, entry 12). When the deprotonation of 8 was carried out at room temperature, a mixture of six (including starting material...
out of seven bromo-substituted ferrocenes (Chart 2) was obtained, with the starting material now being a minor component (6%; Scheme 9, bottom; Table 1, entry 13). In summary, at −30 °C the bromo substituent of ortho-deprotonated bromoferrocene (1) did not exchange, while those in 1,2-dibromoferrocene did, albeit at a very slow rate. At room temperature extensive bromide scrambling took place.

The monobromo-substituted derivatives 2-bromo-1-iodoferrocene (7) and 2-bromo-1,3-diodoferrocene (9) showed very similar behavior. At a deprotonation temperature of −30 °C only the iodides scrambled (Table 1, entries 18, 25). At room temperature, in addition to the iodides, the bromides also exchanged (Table 1, entries 19, 26).

For example, when derivative 7 was deprotonated with LiTMP at −30 °C and subsequently reacted at −78 °C with ICH2CH2I (described above), five additional monobromoiodoferrocenes were obtained besides starting material and bromoferrocene (1) (Table 1, entry 20). After addition of the electrophile the reaction temperature was raised to 20 °C, and, in this case, a complex mixture of more than 14 products was obtained; these included iodoferrocenes, bromoferrocenes, and bromoiodoferrocenes (Table 1, entry 22).
In contrast to the bromo substituents of 7, 8, and 9, the chlorides of 1,2-dichloroferrocene (27) and 2-chloro-1-idoferrocene (29) did not exchange either at −30 °C or at room temperature. In the case of 27 only starting material was recovered (Table 1, entries 16, 17), while 29 gave nearly identical mixtures of monochloro-idoferrocenes at both temperatures (Table 1, entries 23, 24).

**CONCLUSIONS**

Chloroferrocene (26) and bromoferrocene (1) can be deprotonated easily by treatment with LiTMP at −30 °C. Subsequent reactions with electrophiles led selectively to ortho-substituted bromo- and chloroferrocenes. On using chloroferrocene as the substrate, excellent selectivity could be achieved only when the reaction was carried out in inverse mode instead of straight mode. Otherwise higher-substituted derivatives were formed. On employing bromoferrocene (1), most reactions could be carried out in straight mode, and only some electrophiles (e.g., ICH3CH2I, ICF3CFI, CI3CCCl3) required the inverse reaction mode. For example, deprotonated bromoferrocene reacted with ICH3CH2I in inverse mode to afford the desired 2-bromo-1-idoferrocene, whereas in straight mode the formation of several higher-substituted products was observed. It seems reasonable to assume that in the latter case the excess of LiTMP present in the reaction mixture deprotonates the product, which reacts further to give higher-substituted derivatives. On carrying out the reaction in inverse mode, however, the presence of a large excess of electrophile is ensured rather than LiTMP during the whole reaction period.

In contrast to bromo- and chloroferrocene (1 and 26), iodoferrocene (25) could not be substituted selectively. Although deprotonation with LiTMP occurred easily, even in the absence of an additional electrophile, the iodo substituent of deprotonated iodoferrocene scrambled, and this process resulted, after protonation with H2O or CH3OH, in a mixture of ferrocene plus a number of differently substituted iodoferrocenes. Such a scrambling process at −30 °C was observed for all iodo-substituted ferrocenes tested, including 2-bromo-1-idoferrocene (7) and 2-bromo-1,3-iodoferrocene (9). Therefore, these derivatives and their analogues could not be substituted selectively.

In contrast to bromoferrocene (1), at −30 °C the bromides of deprotonated 1,2-dibromoferrocene (8) scrambled very slowly, whereas at room temperature this process was fast and led to six out of seven differently substituted bromoferrocenes (including starting material). This finding shows that the scrambling process depends not only on temperature but also on the degree of substitution. Higher levels of halo substitution clearly ease this scrambling process. The chlorides of the deprotonated chloro-substituted ferrocenes chloroferrocene (26), 1,2-dichloroferrocene (27), and 2-chloro-1-idoferrocene (29) did not scramble, even at room temperature.

It is clear that in order to achieve high selectivity it is necessary to suppress efficiently both the scrambling process and product deprotonation.

The fact that bromoferrocene (1) can be ortho-deprotonated with LiTMP without bromide scrambling allowed the selective synthesis of a number of 2-substituted bromoferrocenes. The product 2-bromo-1-tributylstannylferrocene (6) was found to be particularly useful since it could be further ortho-deprotonated adjacent to the bromo substituent and then reacted to afford 1,3-bis(tributylstannyl)-2-bromoferrocene (13). A further two-step transformation gave 1,3-dioidoferrocene (20) (41–44% overall yield, based on 1), which we consider to be a very valuable starting material for the synthesis of a variety of 1,3-disubstituted ferrocenes. For example, on using nBuLi both iodides of 20 could be exchanged quantitatively. Reaction of the 1,3-dilithiated ferrocene with DMF, diethyl carbonate, and toslycyanide gave the corresponding 1,3-disubstituted aldehyde 21 (80%), ester 22 (57%), and cyanide 23 (67%), respectively. Since ferrocenyl iodides can be easily transformed to provide other functional groups or can be subjected to different coupling reactions, a variety of additional 1,3-disubstituted ferrocenes should now be accessible via 1,3-dioidoferrocene.

**EXPERIMENTAL SECTION**

**General Details.** All reactions were carried out under an argon atmosphere using standard Schlenk techniques and dry solvents. Solvents and solutions were degassed by three freeze–pump–thaw cycles. Column chromatography was performed either on silica gel (Merck, 40–63 μm) or on aluminum oxide (Merck, aluminum oxide 90). Eluents heptane (heptane fraction), ethyl acetate (EA), and dichloromethane (DCM) were of technical grade and were distilled before use. NMR spectra were recorded in CDCl3; chemical shifts are referenced to CDCl3 (δ(C): 7.26 ppm) and CDCl3 (1H: 7.70 ppm). 13C NMR spectra are referenced to 85% H3PO4 (31P: 0 ppm). For the assignment of peaks, the following abbreviations are used: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. Coupling constants in 1H NMR spectra are due to 3J1−1H, 3J1−13C, or 3J1−19Sn−1H coupling. High-resolution mass spectra were recorded on an ESI-QqTOF MS system. A commercial source of bromoferrocene (1) that contained 5% ferrocene was dried under vacuum (rt, 0.5 Torr, 3 h) before use. For running reactions at −30 °C (±4 °C) an FT900 immersion cooler was used.

**Lithium 2,2,6,6-Tetramethylpiperidide.** To a degassed solution of 2,2,6,6-tetramethylpiperidide (2.26 g, 16 mmol) in THF (9.5 mL) was added dropwise at 0 °C a solution of nBuLi (9.4 mL, 1.6 M in hexane, 15 mmol), and the clear yellow solution (referred to as LiTMP in THF/hexane) was stirred at the same temperature for 30 min.

**1-Bromo-2-formylferrocene (1).** To a degassed solution of bromoferrocene (1) (0.566 g, 2.14 mmol) in THF (10 mL) was added dropwise at −78 °C a solution of nBuLi (3.20 mmol) in THF/hexane. The reaction mixture was stirred for 30 min at −78 °C and for an additional 3 h at −30 °C. To the resulting orange-red suspension was added neat DMF (1.561 g, 21.36 mmol), and stirring was continued for 90 min at −30 °C. The reaction mixture was warmed to rt, quenched by the addition of water (20 mL), and extracted with Et3O (3 × 20 mL). The combined organic phases were washed with brine (3 × 20 mL) and dried over MgSO4. Column chromatography on aluminum oxide (heptane/EtO = 1:1) gave product 2 in 80% yield (0.500 g, 1.707 mmol). 1H NMR (400 MHz, CDCl3): δ 4.33 (s, 5H, J = 1.5 Hz, H7, H4); 4.28 (dd, J1 = 2.7 Hz, J2 = 1.5 Hz, H1, H5); 4.85 (dd, J1 = 2.7 Hz, J2 = 1.5 Hz, H2, H6). 13C{1H} NMR (100.6 MHz, CDCl3): δ 66.6 (Cp), 71.1 (Cp), 72.1 (SC, C5), 75.0 (Cp), 75.6 (C2), 80.0 (C1), 192.8 (CHO), HR-MS (ESI in MeOH/MeCN): m/z [M]+ calculated for C10H10BrFeO 291.9186; found 291.9195. For additional spectroscopic data see refs 15 and 28.

**1-Bromo-2-hydroxycarbonylferrocene (3).** To a degassed solution of bromoferrocene (1) (0.491 g, 1.85 mmol) in THF (10 mL) was added dropwise at −78 °C a solution of LiTMP (2.78 mmol) in THF/hexane. The reaction mixture was stirred for 30 min at −78 °C and for 3 h at −30 °C. The resulting orange-red suspension was filtered via a Teflon cannula onto 300 g of crushed dry ice. The reaction mixture was stirred until it reached rt, and to the orange-brown solution was added aqueous NaOH (15 mL, 0.5 M). The phases were separated, and the organic phase was extracted twice with NaOH (25 mL, 0.5 M). The combined aqueous phases were acidified at rt to pH 3 by
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addition of ortho-phosphoric acid (80%). The precipitate was filtered off, dissolved in ethyl acetate, and dried over MgSO4. Removal of the solvent under reduced pressure gave 84% of product 3 (0.483 g, 1.56 mmol) as orange crystals. Mp: 165 °C. dec. 1H NMR (400 MHz, CDCl3): δ 4.32 (s, SH, Cp′), 4.43 (t, J = 2.8 Hz, H1, H4), 4.74 (dd, J1 = 1.5 Hz, J2 = 2.8 Hz, 1H, H5), 4.87 (dd, J1 = 1.5 Hz, J2 = 2.8 Hz, 1H, H3). COOH proton not observed. 13C{1H} NMR (100 MHz, CDCl3): δ 70.2, 70.3 (2C, C3 + C4), 72.7 (SC, Cp′), 75.4 (CS), 78.3 (C1), 174.84 (COOH), signal of C2 not observed. HR-MS (ESI) in MeOH/MeCN: m/z [M + Na]+ calc 330.9033 for C11H10BrFeNaO2 found 330.9023.

1-Bromo-2-cyanoverrocene (4). To a degassed solution of bromoverrocene (1) (0.484 g, 1.83 mmol) in THF (10 mL) was added dropwise at −78 °C a solution of LiTMP (2.74 mmol) in THF/hexane. The reaction mixture was stirred for 30 min at −78 °C and subsequently transferred within 10 min via a Teﬂon cannula to a degassed solution of tosylcyanide (0.671 g, 3.71 mmol) in THF (3.5 mL), which had been precooled to −78 °C. The reaction mixture was stirred for another 30 min at −78 °C and for 40 min at rt. The reaction mixture was quenched by the addition of water (20 mL), and the aqueous phase was extracted with EtO2 (3 × 20 mL). The combined organic phases were washed with brine (3 × 20 mL) and dried over MgSO4. Column chromatography on silica gel (hexane/Et2O 9:1) gave product 4-Bromo-1-iodoferrocene (4) (0.500 g, 1.89 mmol) in 79% yield (0.377 g, 1.30 mmol). Mp: 91–92 °C. mp 73.1 (d, J = 2.3 Hz, C5), 84.9 (d, J = 9.2 Hz, PhA, ortho), 138.6C (d, J = 18.4 Hz, 2C, PhA, para), 136.9 (d, J = 18.4 Hz, 2C, PhA, ipso), 138.6 (d, J = 11.1 Hz, PhA, meta), 2.55 mmol) as orange-red crystals. Mp: 91 °C. 1H NMR (400 MHz, CDCl3): δ 75.1 (C1), 75.1 (C2), 69.4 (2C, C3 + C5), 73.5 (C6), 35.4 (C7), 35.4 (C8), 1.40 (m, 6H, CH2), 1.14 (m, 6H, CH2). HR-MS (ESI) in MeOH/MeCN: m/z [M + Na]+ calc 554.0294 for C28H21BrFeNa, found 554.0283.

2-Bromo-1-idoferrocene (7). Method A. To a degassed solution of bromoverrocene (1) (0.500 g, 1.89 mmol) in THF (5 mL) was added dropwise at −78 °C a solution of LiTMP (2.83 mmol) in THF/hexane. The reaction mixture was stirred for 30 min at −78 °C and for an additional 3 h at −30 °C. The resulting orange-red suspension was cooled to −78 °C and subsequently transferred within 15 min via a Teﬂon cannula to a degassed and precooled (−78 °C) solution of ICl/CH2Cl2 (1.064 g, 7.375 mmol) in THF (5 mL). Stirring was continued for 90 min at −78 °C. The reaction mixture was quenched by the addition of methanol (2 mL) and diluted with EtO2 (20 mL). The organic phase was washed with water (2 × 20 mL) and brine (2 × 20 mL) and dried over MgSO4. Column chromatography on silica gel (hexane) gave product 7 in 65% yield (0.476, 1.22 mmol) as orange crystals. On a 5 g scale compound 7 was isolated in 63% yield.
The use of IF3/CCl4 as the electrophile (1.336 g, 3.776 mmol, 5 mL THF) gave 7 in 73% isolated yield (0.535 g, 1.37 mmol).

Method B. To a degassed solution of 2-bromo-1-tributylstannylferrocene (6) (1.048 g, 1.892 mmol) in DCM (6 mL) was added at rt via a Teﬂon cannula a degassed solution of Li (0.568 g, 22.4 mmol) in DCM (14 mL). The reaction mixture was stirred for 16 h at rt, quenched with saturated aqueous Na2S2O4 (10 mL), and diluted with water (10 mL). The aqueous phase was extracted with EtO2 (2 × 5 mL), and the combined organic phases were washed with brine (2 × 20 mL). The solvents were removed under reduced pressure, and to the residue were added KF (3 g) and methanol (10 mL). The resulting suspension was stirred for 30 min and ﬁltered through a plug of aluminum oxide (eluent DCM), and the solvents were removed under reduced pressure. The residue was taken up in EtO2 (30 mL), washed with water (3 × 10 mL) and brine (10 mL), and dried over MgSO4. Column chromatography on aluminum oxide (heptane + methanol) gave product 7 in 81% yield (0.600 g, 1.54 mmol) as orange-brown crystals. Mp: 74 °C. 1H NMR (400 MHz, CDCl3): δ 4.19 (t, J = 2.6 Hz, 1H, H4), 4.22 (s, SH, Cp′), 4.43 (dd, J1 = 2.6 Hz, J2 = 1.4 Hz, 1H, H5), 4.52 (dd, J1 = 2.6 Hz, J2 = 1.4 Hz, 1H, H3). 13C{1H} NMR (100 MHz, CDCl3): δ 46.2 (C1), 68.4 (C4), 69.6 (C3), 73.5 (C9), 73.6 (C5), 84.5 (C2), 84.5 (C2). HR-MS (ESI) in MeOH/MeCN: m/z [M]+ calc 389.8240 for C28H21BrFeNa, found 389.8204. For additional spectroscopic data see ref 12 and 13.

1,2-Dibromoverrocene (8). To a degassed solution of bromoverrocene (1) (1.000 g, 3.775 mmol) in THF (10 mL) was added dropwise at −78 °C a solution of LiTMP (0.663 mmol) in THF/hexane. The reaction mixture was stirred for 30 min at −78 °C and for an additional 3 h at −30 °C. The resulting orange-red suspension was cooled to −78 °C and subsequently transferred dropwise via a Teﬂon cannula to a degassed solution of Br2/CHCl2Br2 (2.610 g, 7.551 mmol) in THF (6 mL) that had been precooled to −78 °C. The reaction mixture was stirred for an additional 90 min at −78 °C and subsequently quenched by the addition of methanol (2 mL). The organic phase was diluted with EtO2 (30 mL), washed with brine (3 × 30 mL), and dried over MgSO4. Column chromatography on aluminum oxide (heptane) gave product 8 in 67% yield (0.878 g, 2.55 mmol) as orange-red crystals. Mp: 91 °C. 1H NMR (400 MHz, CDCl3): δ 6.41 (t, J = 2.7 Hz, 1H, H4), 4.26 (s, SH, Cp′), 4.44 (dd, J1 = 2.7 Hz, 2H, H3 + H5). 13C{1H} NMR (100.6 MHz, CDCl3): δ 65.9 (C4), 68.9 (2C, C3 + C5), 73.2 (SC, Cp′), 80.3 (2C, C1 + C2). HR-MS (ESI) in MeOH/MeCN: m/z [M]+ calc 434.8322 for C28H19Br2Fe, found 434.8309. For additional spectroscopic data see ref 14c.
The reaction mixture was added via a Teflon cannula at rt (12 g) and methanol (20 mL). The resulting suspension was stirred for 30 min and filtered through a plug of aluminum oxide (elucent DCM), and the solvents were removed under reduced pressure. The residue was taken up in EtO (30 mL), washed with water (3 × 10 mL) and brine (10 mL), and dried over MgSO₄. Column chromatography on silica (CH₂Cl₂/heptane = 7:3) gave product 18 in 83% yield (0.515 g, 0.997 mmol) as orange crystals. A second fraction of the product was obtained by further column chromatography (heptane). On a larger scale, the desired product was obtained with a 70% yield (30 g, 5.193 mmol) as orange crystals. For additional spectroscopic data see refs 20, 28a, and 29.

1,2-Diiodoferrocene (18). To a degassed solution of 1-ido-2-butyldiiodoferrocene (17) (1.100 g, 3.968 mmol) in THF (30 mL) was added at rt via a Teflon cannula a degassed solution of I₂ (1.007 g, 3.968 mmol) in DCM (22 mL). The reaction mixture was added dropwise at −78 °C and stirred for 16 h at rt, quenched with saturated aqueous Na₂SO₄ (5 mL), and diluted with water (10 mL). The atmosphere was extracted with Et₂O (2 × 30 mL) and brine (2 × 30 mL) and dried over MgSO₄. Column chromatography on silica (CH₃OH/CH₂Cl₂ = 1:9) gave product 18 (1.102 g, 2.846 mmol) as orange crystals. HR-MS (ESI, MeOH/MeCN): m/z [M+H]⁺ calcd 447.0433 for C₃₆H₂₅Fe₂I₂Sb, found 447.0439. For additional spectroscopic data see refs 20, 28a, and 29.
was added at rt water (80 mL), and the phases were separated. The aqueous phase was extracted twice with Et2O (100, 50 mL). The combined organic phases were washed with brine (100 mL) and dried over MgSO4. Removal of the solvents under reduced pressure gave a mixture of the desired product 19 in 95% yield together with 2% of 1,1′-bis(tributylstannyl)ferrocene as a byproduct (total yield: 5.070 g, 69%). The byproduct could not be removed by column chromatography on aluminum oxide (heptane), and the product mixture was therefore used without further purification in the synthesis of 1,3-diidoferrocene (20). 1H NMR (400 MHz, CDCl3): δ 9.02 (t, J = 0.9 Hz, 18H, CH3), 0.99–1.05 (m, 12H, CH3), 1.30–1.42 (m, 12H, CH2), 1.54–1.64 (m, 12H, CH2), 3.82–3.85 (m, J = 3.7 Hz, H1, H2), 4.04 (s, 5H, Cp), 4.17–4.20 (m, J = 0.9 Hz, 2H, H4 + H5). 13C{1H} NMR (100.6 MHz, CDCl3): δ 10.3 (J1 = 1.3 Hz, 1H, H2), 1.49 (d, J = 1.3 Hz, 1H, H1), 2.93 (J = 1.4 Hz, 1H, H2). 19F{1H} NMR (100.6 MHz, CDCl3): δ −145.3 (2C, CH3), 60.9 (2C, CH3), 72.0 (2C, C1 + C3), 74.3 (2C, C1 + C3), 170.1 (2C, CO). HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd 533.0452 for C31H22F6NaFeO3 found 533.0450.

1,3-Dicyanoferrocene (23). To a degassed solution of 1,3-diodoferrocene (20) (0.250 g, 0.571 mmol) in THF (4 mL) was added at −78 °C BuLi (1.5 mL, 1.6 M in hexane, 2.4 mmol). The mixture was stirred for 15 min at −78 °C, and the resulting suspension was added to a degassed and precooled (−78 °C) solution of tosylcyanide (0.620 g, 3.42 mmol) in THF (10 mL). The reaction mixture was stirred for 30 min at −78 °C and for an additional 75 min at rt. To the reaction mixture were added aqueous NaOH (2 mL, 1 M) and EtOH (10 mL), and the phases were separated. The organic phase was washed with NaOH (2 × 10 mL, 1 M), aqueous NH4Cl (10 mL), water (2 × 10 mL), and brine (2 × 10 mL), and dried over MgSO4. Column chromatography on aluminum oxide (heptane/EA = 4:1) gave product 23 in 67% yield (0.090 g, 0.381 mmol) as an orange solid. Mp: 135 °C. 1H NMR (400 MHz, CDCl3): δ 4.56 (s, 5H, Cp), 4.89 (d, J = 1.3 Hz, 2H, H4 + H5), 5.14 (s, J = 1.3 Hz, 1H, H2). 19F{1H} NMR (100.6 MHz, CDCl3): δ −55.2 (2C, C1 + C3), 73.2 (5C, Cp), 73.7 (2C, C4 + C5), 74.2 (ZC, 117.5 (2C, CN). HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd 237.0115 for C14H10F6N2 found 237.0101.

1,3-Diethenylferrocene (24). A suspension of [MePPh3]Br (1.007 g, 2.819 mmol), KO’Bu (0.316 g, 2.82 mmol), and dibenzo-18-crown-6 (0.004 g, 0.011 mmol) in THF (3.7 mL) was stirred at rt for 3 h, and to this mixture was added a Teflon cannula a solution of 1,3-diformylferrocene (21) (0.325 g, 1.34 mmol) in THF (6.3 mL). Stirring at rt was continued for 16 h. To the reaction mixture were added water (5 mL) and EtOH (10 mL). The phases were separated, and the organic phase was washed with water (2 × 10 mL) and brine (2 × 10 mL) and dried over MgSO4. Column chromatography on silica (heptane) gave product 24 in 79% yield (0.253 g, 1.06 mmol) as a yellow solid. Mp: 27 °C. 1H NMR (400 MHz, CDCl3): δ 4.04 (s, 5H, Cp), 4.40 (d, J = 1.4 Hz, 1H, H2), 4.59 (s, J = 1.4 Hz, 1H, H2), 5.03 (dd, Jd = 1.0 Hz, Jz = 1.5 Hz, 2H, CH2), 5.36 (dd, Jd = 1.75 Hz, Jz = 1.5 Hz, 2H, CH2), 6.43 (dd, Jd = 1.75 Hz, Jz = 1.07 Hz, 2H, CH), 7.53 (2C, C1 + C3), 74.5 (2C, C4 + C5), 70.4 (2C, C1 + C3), 111.3 (2C, CH2), 134.7 (2C, CH). HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd 238.0435 for C14H10F6N2 found 238.0436.

Chloroferrocene (26). To a degassed solution of iodoferrocene (25) (3.000 g, 9.618 mmol) in THF (20 mL) was added at −78 °C BuLi (6.6 mL, 1.6 M in hexane, 10.56 mmol). The mixture was stirred for 15 min at −78 °C and then transferred via a Teflon cannula to a precooled (−78 °C) solution of Cl3CCl3 (2.732 g, 11.54 mmol) in THF (10 mL). The reaction mixture was stirred for an additional 90 min at −78 °C. Methanol (2 mL) was added, and the mixture was then stirred at rt. Water (10 mL) and EtOH (20 mL) were added, and the phases were separated. The organic phase was washed with water (2 × 20 mL) and brine (2 × 20 mL) and dried over MgSO4. In order to remove excess Cl3CCl3 by sublimation, the residue (2.354 g) was transferred to a Kugelrohr distillation apparatus and held for 15 min at 50 °C and at a pressure of 0.1 Torr. The remaining solid (2.221 g) was subjected to column chromatography on aluminum oxide (heptane) to give chloroferrocene (26) containing 2% ferrocene in 83% yield (1.754 g, 7.955 mmol) as a yellow solid. 1H NMR (400 MHz, CDCl3): δ 4.05 (pt, 2H, Cp), 4.23 (s, 5H, Cp), 4.38 (pt, 2H, Cp). 19F{1H} NMR (100.6 MHz, CDCl3): δ −66.0 (2C, C1 + C3), 67.8 (2C, CH2), 70.2 (2C, Cp), 92.4 (C1). HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd 219.9742 for C13H10FeCl2 found 219.9732. For additional spectroscopic data see ref 23.

1,3-Bis(ethoxycarbonyl)ferrocene (22). To a degassed solution of 1,3-diodoferrocene (20) (2.000 g, 4.568 mmol) in THF (32 mL) was added at −78 °C BuLi (12 mL, 1.6 M in hexane, 19.2 mmol). The suspension was stirred for 15 min at −78 °C and then added to a degassed and precooled (−78 °C) solution of diethyl carbonate (20.51 g, 174 mmol) in THF (20 mL). The reaction mixture was stirred for an additional 2 h at −78 °C. The cooling bath was removed, and ethanol (5 mL) was added. Water (20 mL) and Et2O (50 mL) were added at rt, and the phases were separated. The organic phase was washed with brine (3 × 30 mL) and dried over MgSO4. Column chromatography on aluminum oxide (heptane/EA = 9:1 → 17:3) gave product 22 in 57% yield (0.860 g, 2.61 mmol) as a yellow-orange solid. Mp: 99 °C. 1H NMR (400 MHz, CDCl3): δ 1.36 (t, J = 7.3 Hz, 6H, CH3), 4.24 (s, 5H, Cp), 4.92 (q, J = 7.3 Hz, 4H, CH2), 4.98 (d, J = 1.4 Hz, 2H, CH4 + H5), 5.43 (t, J = 1.4 Hz, 1H, H2). 19F{1H} NMR (100.6 MHz, CDCl3): δ −145.3 (2C, CH3), 60.5 (2C, CH3), 71.3 (5C, Cp), 71.9 (2C), 72.7 (2C, C4 + C5), 74.4 (2C, C1 + C3), 70.1 (2C, CO). HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd 353.0452 for C13H10FeCl2O found 353.0450.
an additional 3 h at −30 °C. The resulting orange-red suspension was cooled to −78 °C and transferred dropwise within 75 min via a Teflon cannula to a degassed solution of Cl2C6Cl4 (4.575 g, 19.33 mmol) in THF (17 mL) that had been precooled to −78 °C. The reaction mixture was stirred for 1 h at −78 °C and subsequently quenched with the addition of methanol (6 mL). The organic phase was diluted with Et2O (50 mL), washed with water (100 mL) and brine (100 mL), and dried over MgSO4. Removal of the solvents gave a mixture of product and starting material that could not be fully separated by column chromatography on aluminum oxide (heptane). Recrystallization of a fraction (2.085 g, 27/26 = 9:1) from heptane (5 mL) gave a precipitate (1.450 g) that was again recrystallized from heptane (8 mL). The final yellow product 27 (1.107 g, 4.343 mmol, 38%) contained 1.2% starting material 26. Mp: 71 °C. 1H NMR (400 MHz, CDCl3): δ 3.39 (t, J = 2.7 Hz, 1H, H4), 4.27 (s, 5H, Cp'), 4.37 (d, J = 2.7 Hz, 2H, H3 + H5). 13C{1H} NMR (100.6 MHz, CDCl3): δ 62.9 (C4), 65.9 (2C, C3 + C5), 72.5 (5C, Cp'), 91.1 (2C, C1 + C2). HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd 253.9352 for C10H8ClFe, found 253.9344. For additional spectroscopic data see Supporting Information.

2-Chloro-1-tributylstannylferrocene (28). To a degassed solution of chloroferrocene (26) (1.982 g, 8.899 mmol) in THF (20 mL) was added dropwise at −78 °C a solution of LiTMP (13.48 mmol) in THF/hexane. The reaction mixture was stirred for 30 min at −78 °C and for an additional 3 h at −30 °C. The resulting orange-red suspension was cooled to −78 °C and added dropwise to a precooled (−78 °C) solution of chlorotributylstannane (5.120 g, 15.73 mmol) in THF (15 mL). The reaction mixture was stirred at this temperature for an additional 90 min and subsequently quenched with methanol (5 mL). The organic phase was diluted with Et2O (2 × 50 mL) and brine (2 × 50 mL), and dried over MgSO4. Column chromatography on aluminum oxide (heptane) gave product 28 in 62% yield (2.855 g, 5.603 mmol) as a dark-orange red oil. 1H NMR (600 MHz, CDCl3): δ 0.92 (t, J = 7.3 Hz, 9H, CH3), 1.04–1.22 (m, 6H, CH2), 1.32–1.43 (m, 6H, CH2), 1.50–1.69 (m, 6H, CH2), 3.85–3.89 (m, 1H, H5), 4.17–4.19 (m, 1H, H4), 4.50–4.52 (m, 1H, H3). 13C{1H} NMR (150.9 MHz, CDCl3): δ 24.4 (3C, CH2), 27.4 (J = 60.2 Hz, 3C, CH2), 29.2 (J = 19.5 Hz, 3C, CH2), 68.5 (J = 30.94 Hz, C4), 69.7 (C3), 70.0 (3C, Cp'), 70.3 (C1), 72.3 (J = 35.2 Hz, C5), 99.3 (C2). HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd 510.0799 for C27H39Cl2FeSn, found 510.0772.

2-Chloro-1-tributylstannylferrocene (29). To a degassed solution of 2-chloro-1-tributylstannylferrocene (28) (2.855 g, 5.603 mmol) in DCMM (25 mL) was added at rt via a Teflon cannula a degassed solution of I2 (0.568 g, 2.24 mmol) in DCMM (35 mL). The reaction mixture was stirred for 16 h at rt, quenched with saturated aqueous Na2SO4 (5 mL), and diluted with water (30 mL). The aqueous phase was extracted with Et2O (2 × 10 mL), and the combined organic phases were washed with brine (2 × 75 mL) and dried over MgSO4. The solvents were removed under reduced pressure, and to the residue were added KF (3 g) and methanol (60 mL). The resulting suspension was stirred for 30 min and filtered through a plug of aluminum oxide (wetted with methanol), and the solvents were removed under reduced pressure. The residue was taken up in heptane (50 mL) and filtered again through a short plug of aluminum oxide. Column chromatography on aluminum oxide (heptane) gave product 29 in 94% yield (1.825 g, 5.269 mmol) as yellow-orange crystals. Mp: 59 °C. 1H NMR (400 MHz, CDCl3): δ 4.15 (t, J = 2.7 Hz, 1H, H4), 4.23 (s, 5H, Cp'), 4.35 (dd, J1 = 2.7 Hz, J2 = 1.5 Hz, 1H, H5), 4.50 (dd, J1 = 2.7 Hz, J2 = 1.5 Hz, 1H, H3). 13C{1H} NMR (100.6 MHz, CDCl3): δ 43.3 (C1), 67.0, 67.1 (2C, C3 + C4), 72.7 (C5), 73.3 (3C, Cp'), 96.6 (C2). HR-MS (ESI, MeOH/MeCN): m/z [M]+ calcd 345.8709 for C10H8ClFeI, found 345.8701.

**Method A.** To the resulting suspension was added via a syringe either CH3OH (1 mL) or CD3OH (1 mL), and the reaction mixture was warmed to rt and diluted with Et2O (10 mL).

**Method B (Straight Mode).** To the resulting suspension was added at −78 °C 2.0 mmol of an electrophile [neat ClSnBu3 via a syringe; a solution of ICH2CH2I, ICF2CF2I, or Cl3CCl3 in THF (3.5 mL) via a cannula]. The reaction mixture was stirred for 90 min at the stated reaction temperature (Table 1), quenched by the addition of CH3OH (2 mL), and diluted with Et2O (10 mL).

**Method C (Inverse Mode).** The resulting suspension was added dropwise via a cannula to a precooled (−78 °C) solution of 2 mmol of electrophile in THF (3.5 mL). The reaction mixture was stirred for 90 min at the stated reaction temperature (Table 1), quenched by the addition of CH3OH (2 mL), and diluted with Et2O (10 mL).

To a degassed solution of substrate (18), 7–9, 18, 20, 25–27, and 29 (1.00 mmol) in THF (3.5 mL) was added dropwise (via a cannula; 30 drops/min) at −78 °C a solution of 1.5 mmol of LiTMP in THF/hexane. The reaction mixture was stirred for 30 min at −78 °C and 3 h at −30 °C and was subsequently cooled to −78 °C.

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**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information

Figures, tables with geometric data, and a CIF for 9 as well as figures of NMR spectra of starting materials and products are given. Further NMR data for ortho-deprotonation reactions as well as the results of deuterium experiments are listed. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00464

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The authors declare no competing financial interest.


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