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Twofold Ferrocene C–H Lithiations For One-Step Difunctionalizations

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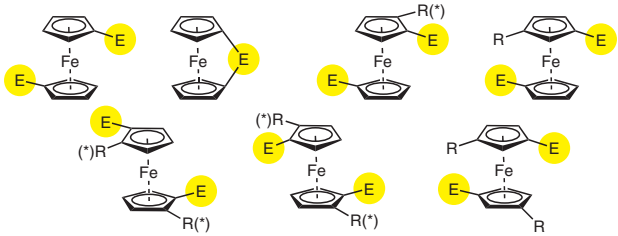

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Abstract For some aromatics, a twofold C–H deprotolithiation can be achieved, allowing these compounds to be subsequently difunctionalized in one step. This short review brings together examples in which ferrocenes are converted in this way.

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4 Ferrocenes Substituted by Aminoalkyls
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Key words ferrocene, deprotolithiation, dilithio compounds, electrophilic trapping, planar chirality, chiral directing group, chiral ligand, ferrocenophane

William Erb obtained his Ph.D. in organic chemistry in 2010 under the supervision of Prof. Jieping Zhu on the total synthesis of natural products and palladium-catalyzed reactions. During the next four years of postdoctoral studies he worked in various laboratories on different research projects from organocatalysis to supramolecular chemistry with an emphasis on the development of new methodologies (University of Bristol, Prof. Varinder Aggarwal, UK - ESPCI, Prof. Janine Cossy, Paris - LCMT, Prof. Jacques Rouden, Caen - COBRA, Prof. Géraldine Gouhier, Rouen). He was appointed assistant professor at the University of Rennes (France) in 2015 where he is mainly working on the development of original ferrocene functionalizations.
Florence Mongin obtained her Ph.D. in chemistry in 1994 from the University of Rouen (France) under the supervision of Prof. Guy Queguiner. After a two-year stay at the Institute of Organic Chemistry of Lausanne (Switzerland) as a postdoctoral fellow with Prof. Manfred Schlosser, she returned to the University of Rouen as an Assistant Professor in 1997 (HDR in 2003). She took up her present position in 2005 as Professor at the University of Rennes (France) and was appointed Junior Member of the Institut Universitaire de France in 2009. Her present scientific interests include the functionalization of aromatic compounds including heterocycles with recourse to bimetallic bases or combinations.

1 Introduction

Aromatic organolithiums can be prepared by different methodologies including halogen/metal exchange, C–H lithiation, transmetalation, and C–heteroatom bond cleavage.[1] Twofold C–H deprotonation followed by electrophilic trapping has attracted numerous synthetic organic chemists because the approach allows two functionalizations to be achieved at once in a one-pot process. Substrates benefiting from relatively acidic hydrogens, either because the corresponding carbanions are stabilized by electron delocalization or inductively owing to the presence of electron-withdrawing groups, can be readily dideprotonated. In contrast, twofold sp^2-C–H lithiation of substrates such as ferrocenes, benzenes, and benzo-fused derivatives, for which the pK_a values are ~30–35 or above, presents an important synthetic challenge. Indeed, because of the highly ionic character of their C–Li bonds, the corresponding dilithio compounds are very reactive.

Since the discovery and structural elucidation of ferrocene in 1951,[2] the first sandwich compound rapidly became a key player in chemistry due to unequalled redox properties, three-dimensional structure, and air and thermal stability.[3] It has since been incorporated into various ligands (in particular chiral ones) for homogeneous catalysis,[4] in materials endowed with various (e.g., optical, electronic, and magnetic) properties,[3,5] and in biologically active compounds.[6]

Among the methods used to functionalize ferrocenes, deprotometalation is probably the most convenient strategy, allowing various derivatives to be prepared regioselectively.[4b,d,h,7] In this short review, our goal is to update the approaches to dideprotolithiate and subsequently difunctionalize ferrocene and its derivatives.

2 Bare Ferrocene

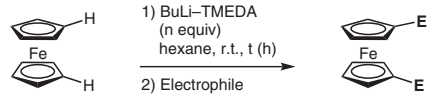
The dideprotolithiation of ferrocene[8] being more likely than that of benzene,[9] it quickly established itself as a reaction competitive to monolithiation.[10] Dismutation of lithioferrocene to afford 1,1′-dilithioferrocene and ferrocene is at the origin of this issue.[11] In spite of thorough studies in order to get clean ferrocene monolithiation,[12] competitive formation of 1,1′-dilithioferrocene could only be avoided in the presence of catalytic potassium *tert*-butoxide.[13] What was initially a problem, competitive dideprotolithiation, turned out to be an opportunity, with numerous studies dedicated to the synthesis of 1,1′-difunctionalized ferrocenes using this possibility.

Tetrahydrofuran (THF) is not a solvent in which alkyllithium-mediated dimetalation of ferrocene can be carried out efficiently. Indeed, subsequent electrophilic trapping shows that, in addition to remaining starting material, mixtures of monolithio- and 1,1′-dilithioferrocenes are, in general, formed.[13]

In 1964, Eberhardt and Butte discovered the impact of ligands, TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and sparteine, in enhancing the reactivity of the alkyllithium reagents through the formation of chelates.[14] Unlike butyllithium, the butyllithium–TMEDA chelate (2.0 to 2.5 equiv; formed from the components after stirring for a few minutes at 25 °C) can easily 1,1′-dimetalate ferrocene in hexane at 25 °C, a result first evidenced by Rausch and Ciappenelli in 1967.[15] Subsequent quenching using various electrophiles allowed many 1,1′-disubstituted ferrocenes to be obtained (Table 1).[15,16]

As exemplified in Table 2, ferrocenophanes can be similarly obtained from 1,1′-dilithioferrocene, but by trapping with bis-electrophiles such as dichlorides.[16m,p,17] Ferrocenophanes (or *ansa*-bridged systems) are a widely developed field[18] on which there is much to be said, even including examples with nickel, palladium, and platinum bridges.[19] It has been illustrated here (not exhaustively) to highlight the variety of electrophiles that can be employed to intercept 1,1′-dilithioferrocene.

Table 1 Dideprotolithiation of Ferrocene in Hexane Followed by Different Electrophilic Trappings



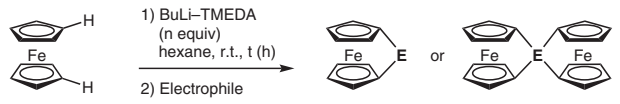
n equiv, t (h)	Electrophile (E)	Yield[a] (%)
2.5, 6	CO_2 then H^+ (CO_2H)	94[15]
2.5, 6	$Ph_2C{=}O$ [$C(OH)Ph_2$]	80[15]
2.5, 6	pyridine (2-pyridyl)	30[15]
2.2, overnight	DMF (CHO)	85[16a]
2.1, 22	$H_2C{=}NMe_2I$[b] (CH_2NMe_2)	57[16b]
2.2, overnight	$ClCO_2$*i*-Pr (CO_2*i*-Pr)	58 (18)[16c]
2.2, overnight	ClCOPh (COPh)	65 (16)[16c]
2.2, overnight	ClTs (Cl)	64 (15)[16c]
2.2-2.5, 6 to overnight	$(CCl_3)_2$ (Cl)	60,[16d] 75[16e]
2.5, 6	Br_2 (Br)	23[16d]
2.2, overnight	$(CBrCl_2)_2$ (Br)	89[16c]
2.1, overnight	$(CHBr_2)_2$ (Br)	67[16f]
2.2 to 2.5, 6 to 16	I_2 (I)	55,[16d] 60,[16c] 72[16g]
2.2, overnight	NFSI[c] (F)	2,[16e] 9[16h]
2.5, 6	$(ClBNMe_2)_2$ [$(BNMe_2)_2$]	58[16i]
2.5, 6	$ClSiMe_3$ ($SiMe_3$)	n.r.[16j]
2.5, 6	$ClSi(OMe)_3$ [$Si(OMe)_3$]	52[16k]
2.3 to 2.5, 6 to 16	$ClSi(OEt)_3$ [$Si(OEt)_3$]	64,[16l] 50[16m]
2.0, 18	ClP*t*-Bu_2 (P*t*-Bu_2)	n.r.[16n]
2.0, 18	ClP(Ph)*t*-Bu [P(Ph)*t*-Bu]	60[16o]
2.2, overnight	$ClPPh_2$ (PPh_2)	73[16c]
2.2, 12	$ClP(NEt_2)_2$ [$P(NEt_2)_2$]	80[16p]
2.2, overnight	$ClPO(OEt)_2$ [$PO(OEt)_2$]	60 (22)[16c]
2.4, 24	$ClPO(O$*i*-$Pr)_2$ [$PO(O$*i*-$Pr)_2$]	82[16q]
2.1, 3	$(SMe)_2$ (SMe)	70[16r]
2.1, 3	$(S$*i*-$Pr)_2$ (S*i*-Pr)	73[16r]
2.0, overnight	$(SPh)_2$ (SPh)	70[16c]
2.0, 18	$IAsMe_2$ ($AsMe_2$)	54[16s]
2.0, 18	$ClAsPh_2$ ($AsPh_2$)	57[16s]

[a] Yield in parenthesis is of the competitively formed 1-substituted ferrocene; n.r. = yield not reported.
[b] Eschenmoser's salt.
[c] *N*-Fluorobenzenesulfonimide.

Using diethyl ether as hexane cosolvent still proved convenient to access 1,1′-disubstituted ferrocenes (Table 3).[20]

Solid-state structures were recorded for chelates of 1,1′-dilithioferrocene with PMDTA (PMDTA = *N*,*N*,*N*′,*N*″,*N*″-pen-

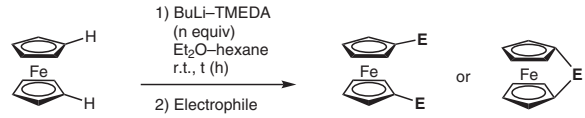
Table 2 Dideprotolithiation of Ferrocene in Hexane Followed by Conversions into Ferrocenophanes



n equiv, t (h)	Electrophile (E)	Yield[a] (%)
2.3, 16	Cl_2SiCl_2 ($SiCl_2$)	50,[16m] 80–90[17a]
2.5, 18	Cl_2SiPh_2 ($SiPh_2$)	32[17b,c]
2.3, 16	Cl_2SiMe_2 ($SiMe_2$)	60[17d]
2.3, 16	Cl_2SiCl_2 (Si)	17,[17b] 56,[16p] 70[17e]
2.3, 16	$Cl_2Si(CH_2)_3$ [$Si(CH_2)_3$]	71,[16p] 79[17e]
2.3, 16	Cl_2SiMe(5-norbornyl) [SiMe(5-norbornyl)]	50[17f]
2.3, 16	$Cl_2SiMe(CH{=}CH_2)$ [$SiMe(CH{=}CH_2)$]	60[17f]
2.3, 16	Cl_2SiHMe (SiHMe)	80[17f]
2.5, 18	Cl_2SiH_2 (SiH_2)	38[17g]
2.5, 18	Cl_2PPh (PPh)	51[17b]
2.0, 18	Cl_2PMe (PMe)	19[17h]
2.0, 18	Cl_2Pt-Bu (Pt-Bu)	46[17i]
2.0, 18	Cl_2P(menthyl) [P(menthyl)]	35[17j]
2.5, 6	Cl_2PNi-Pr_2 (PNi-Pr_2)	42[17k]
2.5, 18	$S(O_2SPh)_2$ (S)	28[17l,m]
2.5, 18	Cl_2GePh_2 ($GePh_2$)	19[17b,n]
2.3, 16	Cl_2GeMe_2 ($GeMe_2$)	30–35[17b,n]
2.3, 16	Cl_2GeEt_2 ($GeEt_2$)	30–35[17b,n]
2.5, 6	Cl_2GeCl_2 (Ge)	n.r.[17o]
2.0, 18	Cl_2AsPh (AsPh)	34[17h]
2.5, 18	$Se(S_2CNEt_2)_2$ (Se)	23[17l]
2.5, 18	Se_8 (SeSeSe)	31[17p]
2.0, 18	$Cl_2B{=}N(SiMe_3)_2$ [$B{=}N(SiMe_3)_2$]	35[17q,r]
2.0, 18	$Cl_2B{=}N(SiMe_3)t$-Bu [$B{=}N(SiMe_3)t$-Bu]	44[17q,r]
2.0, 18	$Cl_2B{=}Ni$-Pr_2 ($B{=}Ni$-Pr_2)	38[17q]

[a] n.r. = yield not reported.

Table 3 Dideprotolithiation of Ferrocene in Diethyl Ether/Hexane Followed by Different Electrophilic Trappings



n equiv, t (h)	Electrophile (E)	Yield[a] (%)
2.5, 24	DMF (CHO)	85[20a,b]
2.5, 24	PhCHO [CH(OH)Ph]	91[20a]
2.5, 24	$(CH_2O)_n$ [CH_2OH]	43[20a]
2.7, 24	Ph_2CO [C(OH)Ph]	93[20c]
2.5, 24	$ClCH_2OMe$ (CH_2OMe)	33[20a]
2.2, 19.5	$ClC{=}SNMe_2$ [$C{=}SNMe_2$]	54[20d]
2.1, 18	2,4,6-i-$Pr_3C_6H_2SO_2N_3$ (N_3)	62[20e]
2.2, 14	$(CBrF_2)_2$ (Br)	60[20f]
2.2, 6	$B(OBu)_3$ then hydrolysis [$B(OH)_2$]	60[20g]
2.0, 18	$Cl_2AlC(SiMe_3)_2SiMe_2$(2-pyridyl) [$AlC(SiMe_3)_2SiMe_2$(2-pyridyl)]	31[20h]
2.0, 18	$Cl_2Al[C(SiMe_3)_2SiMe_2NMe_2]$ {$Al[C(SiMe_3)_2SiMe_2NMe_2]$}	97[20i]
2.5, 24	$ClSiMe_3$ ($SiMe_3$)	80[20a]
2.1, 3	$(SMe)_2$ (SMe)	51 (10)[20j]
2.1, 3	$(SPh)_2$ (SPh)	80[20j]
2.0, 18	$Cl_2GaC(SiMe_3)_2SiMe_2$(2-pyridyl) [$GaC(SiMe_3)_2SiMe_2$(2-pyridyl)]	59[20k]
2.0, 18	$Cl_2GaC(SiMe_3)_2SiMe_2NMe_2$) [$GaC(SiMe_3)_2SiMe_2NMe_2$)]	68[20i]
2.0, 18	$[Cl_2InC(SiMe_3)_2SiMe_2$(2-pyridyl)$]_2$ [$InClC(SiMe_3)_2SiMe_2$(2-pyridyl)]	57[20k]
2.5, 6	$ClSnBu_3$ ($SnBu_3$)	68[20l]
2.2, 17	Cl_2Snt-Bu_2 (Snt-Bu_2)	65[20m,n]
2.2, 17	$Cl_2Sn(Mes)_2$ [$Sn(Mes)_2$][b]	85[20m]

[a] Yield in parenthesis is of the competitively formed 1-substituted ferrocene.
[b] Mes = 2,4,6-trimethylphenyl.

tamethyldiethylenetriamine; more soluble)[21] and TMEDA.[22] The latter can be displaced by THF upon recrystallization.[18b]

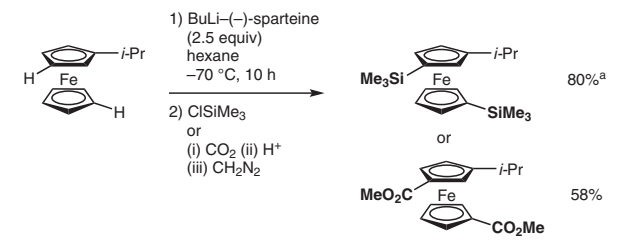
That 1,1′-dilithioferrocene is favored under these conditions was attributed to its insolubility in hexane[16c] and diethyl ether.[20a] In order to avoid the presence of the more soluble monosubstituted product, Jahn and co-workers removed the hexane supernatant by filtration and washed the bright orange precipitate of 1,1′-dilithioferrocene before adding THF in order to make it react with electrophiles.[16c] Removing the solvent is also useful when it is necessary to know exactly the quantity of formed 1,1′-dilithioferrocene, for instance in order to add the appropriate amount of bis-electrophile for a more controlled synthesis of *ansa*-bridged derivatives.[23]

3 Ferrocenes Substituted by Alkyl or Silyl Groups

In 1964, Benkeser and Bach reported a study in which alkylated ferrocenes were treated by butyllithium in diethyl ether at room temperature for long reaction times before interception with chlorotrimethylsilane. Mixtures resulting from non-regioselective mono- and dideprotonation (positions 3 or/and 1′) were produced.[24] A similar result was noticed in 1995 by Manners, O'Hare, and co-workers on 1,1′-dimethylferrocene by using butyllithium–TMEDA in hexane.[25] While dideprotonation is favored over monometalation when bis(tetrahydroindenyl)iron is treated by the chelate butyllithium–TMEDA at 60 °C in hexane, mixtures of

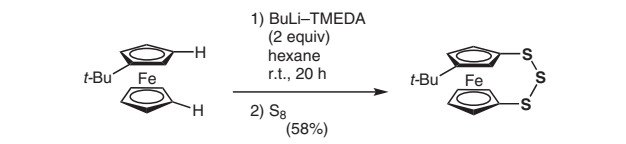
regioisomers (1,1′-, 1,2′-, and 2,2′-disubstituted) are again obtained, a result evidenced by using chlorodiphenylphosphine as electrophile.[26]

According to Aratani, Gonda, and Nozaki, hexane is a more suitable solvent than diethyl ether to dilithiate isopropylferrocene. In 1969, the efficient formation of 1′,3-disubstituted derivatives was reported by using butyllithium and (–)-sparteine at –70 °C for 10 hours before trapping (Scheme 1). A marginal enantiomeric excess was recorded, probably due to the lack of coordinating atom in this ferrocene substituent.[27]



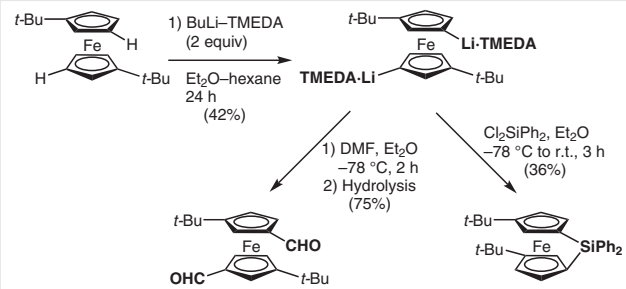
Scheme 1 Double deprotolithiation of isopropylferrocene using butyllithium–(–)-sparteine in hexane at –70 °C. [a] 12% yield using Et_2O as solvent.

Replacing isopropyl by *tert*-butyl similarly leads to 1′,3-disubstituted derivatives upon treatment by butyllithium–TMEDA in hexane. As already shown from bare ferrocene,[28] interception of the 1′,3-dilithio compound with sulfur here produces the corresponding 1,2,3-trithia[3]ferrocenophane (Scheme 2).[29] By starting from ferrocenophanes in which the cyclopentadienyl groups are connected through a tetramethyldimethylene or a trimethylene bridge, the corresponding 1,2,3-trithia[3]ferrocenophanes are still generated, but in very low yields.[30]



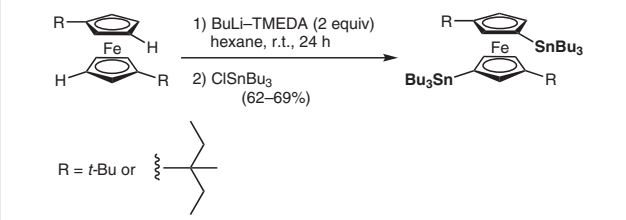
Scheme 2 Double deprotolithiation of *tert*-butylferrocene using butyllithium–TMEDA in hexane

When submitted to the butyllithium–TMEDA chelate (2.4 equiv) in hexane at r.t. for 20 hours, 1,1′-trimethyleneferrocene mainly leads to mixtures.[31] In the case of 1,1′-di-*tert*-butylferrocene, the reaction rather takes place regio- and stereoselectively (C_2-symmetry) by using butyllithium–TMEDA in diethyl ether, as shown by interception with DMF[32] or dichlorodiphenylsilane[23] to respectively produce the expected dicarbaldehyde or ferrocenophane. In the former case, it is important to isolate and analyze the intermediate 3,3′-dilithio product (which contains two molecules of TMEDA) before quenching it in order to calculate the required amount of electrophile (Scheme 3).[23]



Scheme 3 Double deprotolithiation of 1,1′-di-*tert*-butylferrocene using butyllithium–TMEDA

During the synthesis of a stable ferrocene-based *N*-heterocyclic carbene, Siemeling and co-workers prepared the same 1,1′-di-*tert*-butyl-3,3′-dilithioferrocene, and converted it into the corresponding dibromo, bis(trimethylsilyl), and diazido derivatives.[33] Lentz and co-workers employed both the 1,1′-di-*tert*-butyl- and the 1,1′-bis(1-ethyl-1-methylpropyl)ferrocene to generate the 3,3′-dilithio derivatives and make them react with chlorotributylstannane (Scheme 4).[34]

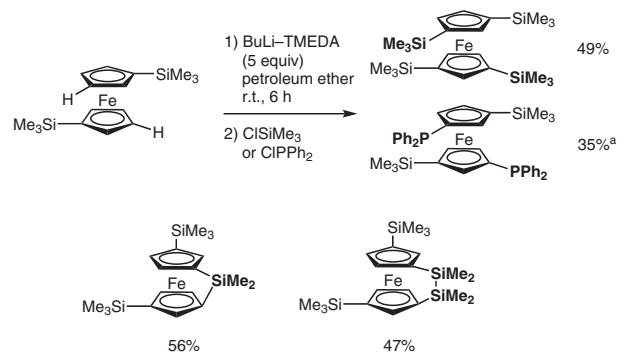


Scheme 4 Double deprotolithiation of hindered 1,1′-dialkylferrocenes followed by trapping with chlorotributylstannane

When compared with an alkyl group, a diphenylphosphino behaves differently since it is electron-accepting. As a consequence, when present on ferrocene adjacent deprotonation is observed. But, probably due to steric hindrance and low ability to coordinate lithium, deprotonation remote from the phosphine is favored. Thus, the 1′,3-dilithiated product predominates after a long contact between (diphenylphosphino)ferrocene and 2:1 butyllithium–TMEDA in diethyl ether at room temperature.[35]

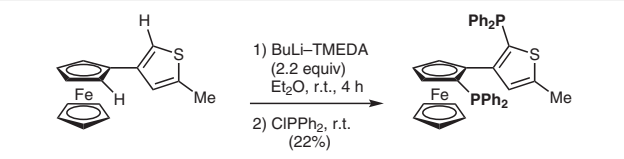
When (electron-withdrawing) silylated substituents are present on ferrocene substrates, the dilithiation takes place at a remote position, but preferably on the same ring. Thus, in 1992 Roberts, Silver, and co-workers reported that upon addition of excess butyllithium–TMEDA chelate to 1,1′-bis(trimethylsilyl)ferrocene, the reaction occurs at the 3,3′-positions to furnish, after quenching, tetrasubstituted derivatives (Scheme 5, top). Trapping the 3,3′-dilithio derivative with chlorodiphenylphosphine selectively leads to C_2-symmetric diastereomers, i.e. to the smallest steric interactions between the silyl groups in the lithio intermediate. Further metalation of the tetrasubstituted ferrocenes

proves difficult, probably due to important steric hindrance.[16j] In 1995, this 1,1′-bis(trimethylsilyl)-3,3′-dilithioferrocene was converted into silicon-bridged [1]- and [2]ferrocenophanes upon addition of dichlorodimethylsilane and 1,2-dichloro-1,1,2,2-tetramethylsilane, respectively (Scheme 5, bottom).[36]



Scheme 5 Double deprotolithiation of 1,1′-bis(trimethylsilyl)ferrocene using butyllithium–TMEDA. [a] Only one diastereomer isolated.

To our knowledge, dilithiation of phenylferrocenes has never been described. Nevertheless, albeit in a low yield, (5-methyl-2-thienyl)ferrocene was converted into a diphosphine by consecutive treatment with butyllithium–TMEDA and chlorodiphenylphosphine, as shown in Scheme 6.[37]

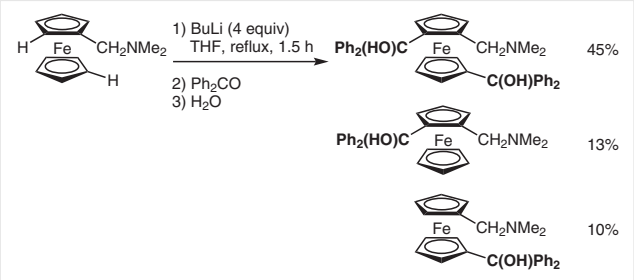


Scheme 6 Double deprotolithiation of (5-methyl-2-thienyl)ferrocene followed by phosphination

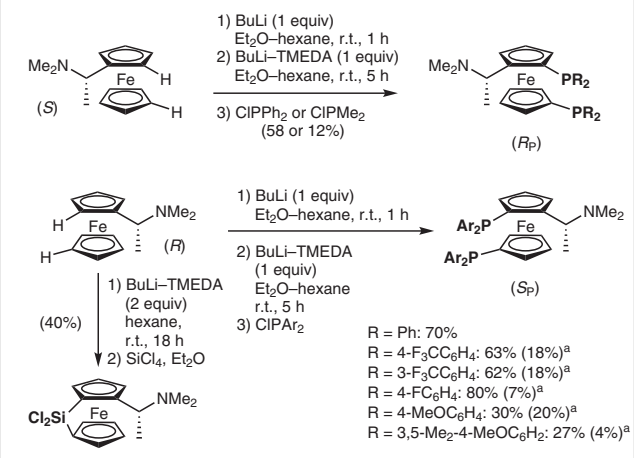
4 Ferrocenes Substituted by Aminoalkyls

In 1965, Slocum, Rockett, and Hauser documented the formation of a mixture of 1′,2-dilithiated, 2-lithiated, and 1′-lithiated products upon treatment of [(dimethylamino)methyl]ferrocene by butyllithium in THF at reflux. After interception with benzophenone, the corresponding alcohols were obtained in 45%, 13%, and 10% yields, respectively (Scheme 7).[9] An improved procedure was later developed[38] in order to convert it into the 1′,2-diphosphine.[39]

Thus, in 1980, Kumada and co-workers difunctionalized (*S*)-[1-(dimethylamino)ethyl]ferrocene in diethyl ether by stepwise treatment with butyllithium and butyllithium–TMEDA, e.g. to provide the (*S*,*R*$_P$)-1,1′-diphosphines shown in Scheme 8 (top).[38,40] In 1987, it was shown that it is similarly possible to enantioselectively obtain ferrocenophanes by starting from an enantiopure [1-(dimethylamino)ethyl]ferrocene (Scheme 8, bottom, left).[41] Under these conditions, one can assume a first stereoselective lithiation next to the chiral directing group followed by a second deprotonation at the remote cyclopentadienyl ring. With the aim of obtaining chiral ferrocenylphosphine–transition metal complexes for asymmetric catalysis, the study was extended by Hayashi and Yamazaki to the synthesis of different bis(diarylphosphino) derivatives starting from (*R*)-[1-(dimethylamino)ethyl]ferrocene (Scheme 8, bottom, right). As shown in Scheme 8, a sufficiently long reaction time for the dilithiation step is crucial for the success of the reaction.[42]

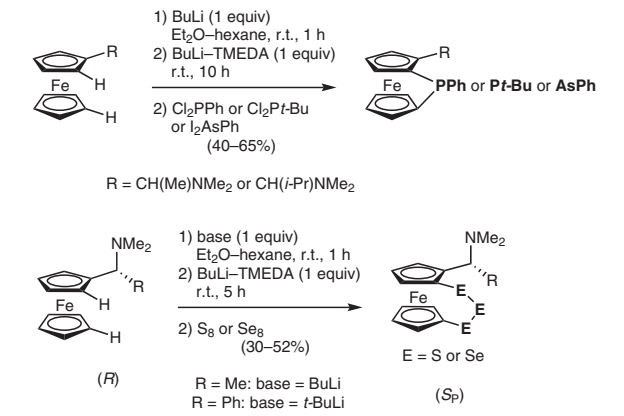


Scheme 7 Double deprotolithiation of [(dimethylamino)methyl]ferrocene using butyllithium in refluxing THF



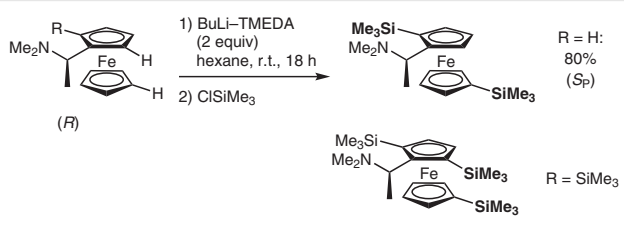
Scheme 8 Dideprotolithiation of [1-(dimethylamino)ethyl]ferrocenes followed by phosphination or silylation. [a] Yield for the monophosphine competitively formed.

In 1983, Cullen and co-workers reported the synthesis of [1]ferrocenophanes from [1-(dimethylamino)alkyl]ferrocenes. The latter can be similarly attacked by butyllithium then butyllithium–TMEDA in diethyl ether/hexane to afford the 1′,2-dilithio derivatives, which are next trapped with dichlorophosphines and diiodophenylarsine (Scheme 9, top).[17i,43] Probably inspired by the enantioselective functionalizations described above (Scheme 8), Fukuzawa and Wachi extended the protocol to the synthesis of 1,1′-trichalcogena[3]ferrocenophanes (Scheme 9, bottom).[44]



Scheme 9 Dideprotolithiation of substituted ferrocenes followed by conversions into [1]- and [3]ferrocenophanes

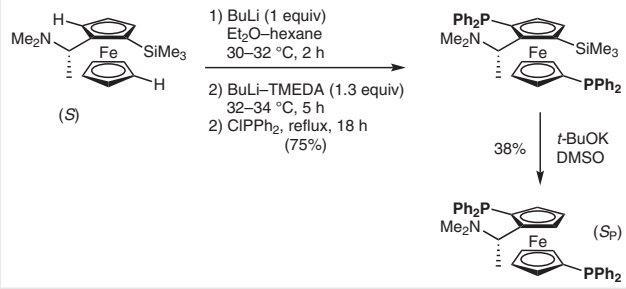
In 1986, Cullen and co-workers showed that 1′,2-dilithiation of (*R*)-[1-(dimethylamino)ethyl]ferrocenes can be performed by using the chelate butyllithium–TMEDA at once, as evidenced by subsequent reaction with chlorotrimethylsilane (Scheme 10).[45] Replacing chlorotrimethylsilane by elemental sulfur[45] or 1,2-dibromo-1,1,2,2-tetrachloroethane[46] led to the corresponding 1,2,3-trithia[3]ferrocenophane or 1′,2-dibromide, respectively. Even if mixtures are formed, the silanes produced according to Scheme 10 can undergo dilithiation under similar conditions.[45]



Scheme 10 Dideprotolithiation of (*R*)-[1-(dimethylamino)ethyl]ferrocenes followed by silylation

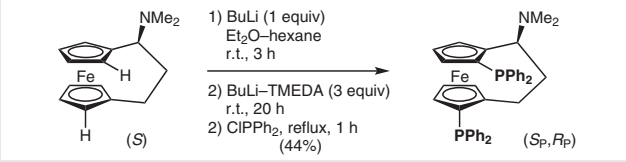
(*S*)-[1-(Dimethylamino)ethyl]ferrocene can be converted into (*S*,R_P)-1,1′-diphosphines. The second reaction depicted in Scheme 10 (bottom) shows that a trimethylsilyl group can protect the position usually deprotonated next to the 1-(dimethylamino)ethyl group and reroute the reaction to the other adjacent position. Such a possibility was employed in 1989 by Pastor and Togni to access, after deprotection, (*S*,S_P)-1,1′-diphosphines (Scheme 11).[47]

From [1-(dimethylamino)ethyl]ferrocene, 1′,2-dilithiation was evidenced together with 2-lithiation upon reaction with butyllithium (1.5 equiv) in diethyl ether–hexane for long lithiation periods.[48] In the case of the bridged aminoferrocene shown in Scheme 12, four isomeric diphosphines



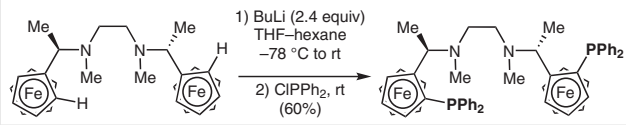
Scheme 11 Dideprotolithiation of trimethylsilyl-protected (*S*)-[1-(dimethylamino)ethyl]ferrocene followed by phosphination and deprotection

were produced, the major one being isolated in 44% yield. The first lithiation occurs at the 2-position closest to nitrogen (albeit with a stereoselectivity different from that observed for the nonbridged substrate) while the second one (mediated by butyllithium–TMEDA) takes place at the opposite 2′-position on the other cyclopentadienyl ring.[49]



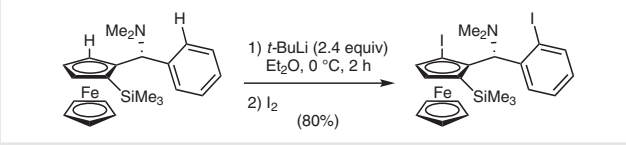
Scheme 12 Dideprotolithiation of a bridged aminoferrocene followed by phosphination

Although dilithiation generally occurs on each cyclopentadienyl of a substituted ferrocene, Kim, Jeong, and coworkers documented an example in which a (*R*,*R*)-diferrocenyl diamine is attacked at both ferrocenes to stereoselectively afford a C_2-symmetric diphosphine (Scheme 13).[50]



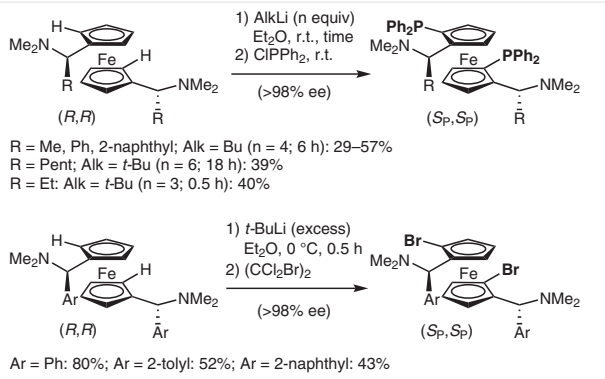
Scheme 13 Dideprotolithiation of a diferrocenyl diamine followed by phosphination

As exemplified by Fukuzawa and co-workers in 2007, if a phenyl group is connected at the α-position of an (aminomethyl)ferrocene, it can be attacked by the base at the same time as the ferrocene ring to provide a difunctionalized product after electrophilic trapping (Scheme 14).[51]



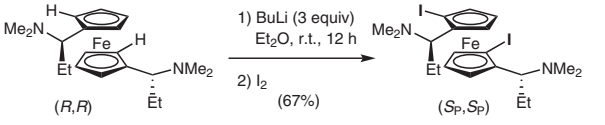
Scheme 14 Dideprotolithiation of an α-(dimethylamino)benzylferrocene followed by iodolysis

In studies published at the end of the 1990s, Schwink and Knochel studied the behavior of ferrocenes 1,1′-disubstituted by identical 1-(dimethylamino)alkyl groups (Scheme 15). By using an excess of butyllithium or *tert*-butyllithium in diethyl ether, the 2,2′-dilithio products are formed. The stereoselectively proves to be in favor of the C_2-symmetric isomers, as demonstrated by interception with chlorodiphenylphosphine or 1,2-dibromo-1,1,2,2-tetrachloroethane.[52] In 2006, 2,2′-disubstituted 1,1′-trichalcogena[3]ferrocenophanes were synthesized by employing this protocol.[44]



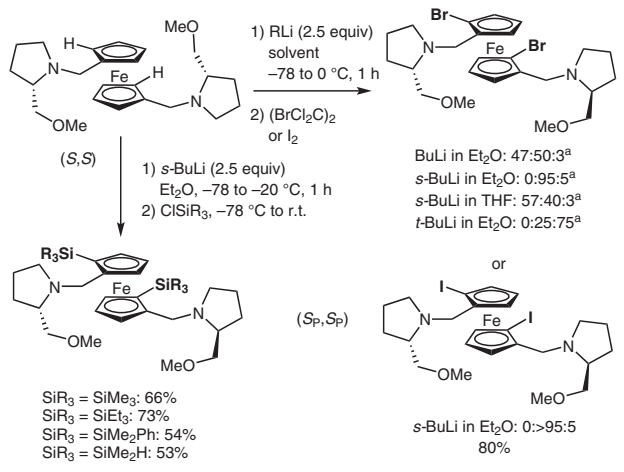
Scheme 15 Dideprotolithiation of (*R*,*R*)-1,1′-disubstituted ferrocene diamines followed by phosphination or bromolysis

In 1998, the scope of the reaction was enlarged to the 1-(dimethylamino)propyl group by Kang and co-workers.[53] The corresponding 2,2′-diiodo derivative is generated in high yield and stereoselectivity (Scheme 16).[54]



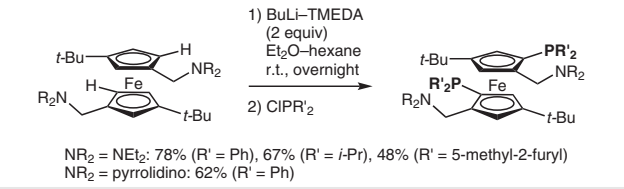
Scheme 16 Dideprotolithiation of (*R*,*R*)-1,1′-disubstituted ferrocene diamines followed by iodolysis

With the aim of building 2-phospha[3]ferrocenophanes with planar chirality, Marinetti and co-workers studied the behavior of different alkyllithiums toward the ferrocene diamine (derived from ferrocene-1,1′-dicarbaldehyde) depicted in Scheme 17.[55] The choice of the base proves to be crucial. By using *sec*-butyllithium in diethyl ether, the reaction takes place in good yield and excellent diastereoselectivity, as demonstrated by quenching the dilithio product with 1,2-dibromo-1,1,2,2-tetrachloroethane,[55] chlorosilanes,[55,56] and iodine.[57] It could be deduced from the configuration displayed by the major stereoisomer that a chiral induction similar to that exhibited by the pyrrolidine group during the monofunctionalization of (*S*)-[2-(methoxymethyl)pyrrolidino]ferrocene using butyllithium takes place.[58]



Scheme 17 Dideprotolithiation of (*S*,*S*)-1,1′-bis[2-(methoxymethyl)pyrrolidino]ferrocene by using different alkyllithiums. [a] The (S_P)-monobromo/*dl*-dibromo/*meso*-dibromo ratios are given.

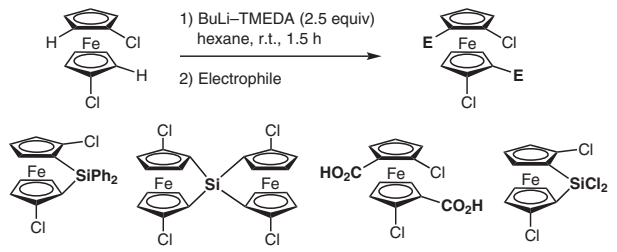
In order to reach tetradentate ligands bearing phosphino, aminomethyl, and *tert*-butyl groups, in 2015 Pirio, Hierso and co-workers compared two strategies, (i) the assembly of ferrocene from the appropriate cyclopentadienyl rings and (ii) the successive functionalization of 1,1′-di-*tert*-butylferrocene. While the former furnishes a 1:1 mixture of *meso* and *rac* stereoisomers, the latter proved to be diastereoselective. Thus, *dl*-2,2′-di-*tert*-butylferrocene-1,1′-dicarbaldehyde (prepared according to Scheme 3) was submitted to reductive amination, and the aminomethyl-substituted ferrocenes regioselectively dilithiated to introduce the required phosphino groups (Scheme 18). It is worth noting that dilithiation of 1,1′-bis[(diethylamino)methyl]ferrocene is not stereoselective.[59]



Scheme 18 Double deprotolithiation of *dl*-1,1′-bis[(dialkylamino)methyl]-3,3′-di-*tert*-butylferrocene followed by phosphination

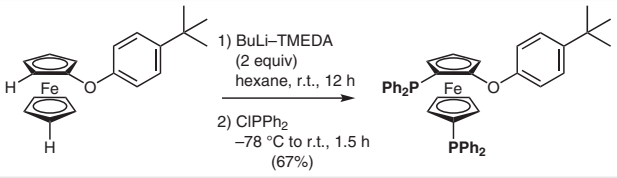
5 Ferrocenes Substituted by Halogens or Oxygen-Based Groups

1,1′-Dichloroferrocene can be 2,2′-dilithiated under conditions employed for ferrocene. Thus, Osborne, Rosseinsky and co-workers obtained various tetrasubstituted derivatives upon treatment by butyllithium–TMEDA in hexane and subsequent electrophilic interception, (Scheme 19).[17o]



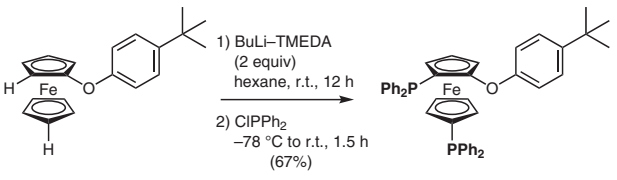
Scheme 19 Dideprotolithiation of 1,1′-dichloroferrocene followed by electrophilic trapping (yields not reported)

The stereoselectivity issue of the reaction was later studied by Sünkel and co-workers. After trapping the dilithio compound with dimethyl disulfide, they obtained both the *dl* and the *meso* compound in an approximate 2:1 ratio (Scheme 20).[60] Dideprotonation of 1,1′-bis(methylthio)ferrocene was attempted, but only mixtures were obtained.[60–62]



Scheme 20 Dideprotolithiation of 1,1′-dichloroferrocene followed by reaction with dimethyl disulfide

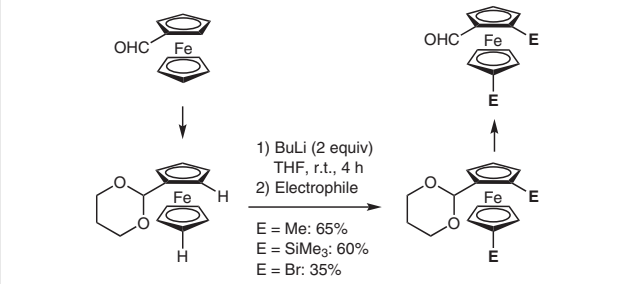
In 2010, Schaarschmidt and Lang reported the synthesis of a 1′,2-diphosphine by starting from an aryl ferrocenyl ether and using butyllithium–TMEDA in hexane (Scheme 21). The phenyl group was only attacked in the presence of a larger amount of base, to form tri- or tetrafunctionalized derivatives.[63]



Scheme 21 Twofold 1′,2-functionalization of an aryl ferrocenyl ether

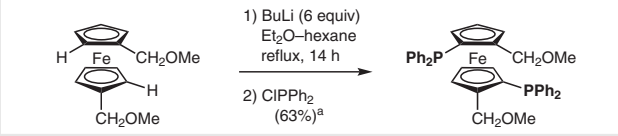
6 Ferrocenes Substituted by Alkoxyalkyls or Acetals

The acetal of ferrocenecarbaldehyde with propane-1,3-diol can be readily turned into different 1′,2-disubstituted derivatives in the presence of butyllithium (2 equiv) in THF, as reported by Loh and co-workers in 2007 (Scheme 22).[64]



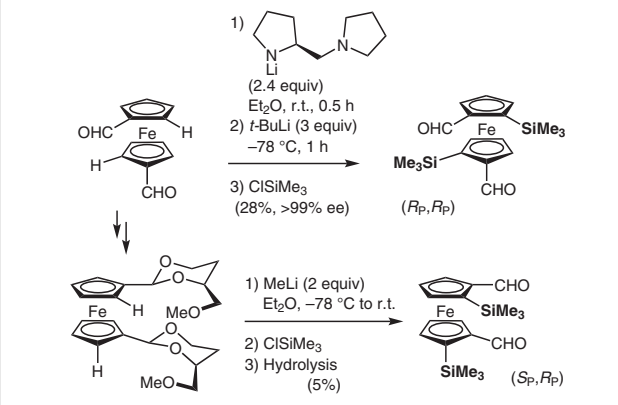
Scheme 22 Twofold 1′,2-functionalization of ferrocenecarbaldehyde acetal

From 1,1′-bis(methoxymethyl)ferrocene, a large excess of butyllithium is required in diethyl ether to achieve dimetalation, a reaction that favors the stereoisomers of C_2-symmetry (Scheme 23).[20a,65] *tert*-Butyllithium is less suitable, leading to a complex mixture.[66]



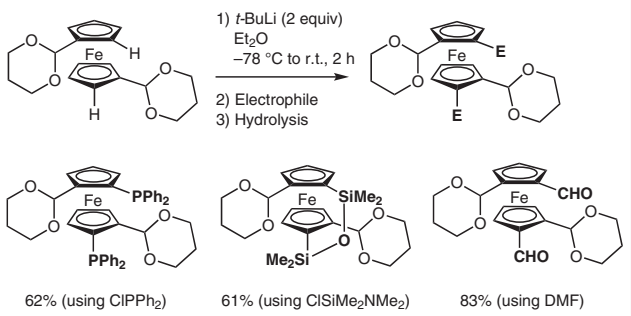
Scheme 23 Dideprotolithiation of 1,1′-di(methoxymethyl)ferrocene followed by conversion into a diphosphine. [a] Together with 3% of the *meso* compound.

After addition of the lithium salt of (+)-(*S*)-1-(pyrrolidin-2-ylmethyl)pyrrolidine to ferrocene-1,1′-dicarbaldehyde in order to form the diaminal dianion, 2,2′-dilithiation becomes possible by using *tert*-butyllithium in excess. By this way, in 1998 Manoury, Balavoine, and co-workers achieved the enantioselective synthesis of a C_2-symmetric tetrasubstituted ferrocene (Scheme 24, top).[67] In turn, the *meso* product was generated stereoselectively by starting from the chiral 1,1′-diacetal shown in Scheme 24 (bottom), but in a very low yield explained by important monofunctionalization.[68]



Scheme 24 Enantioselective dideprotolithiation of a diaminal dianion of ferrocene-1,1′-dicarbaldehyde followed by silylation

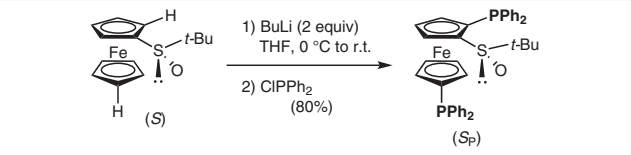
The behavior of the acetal of ferrocene-1,1′-dicarbaldehyde and propane-1,3-diol was documented by Connell and co-workers in 2009. The C_2-symmetric 2,2′-disubstituted products were isolated in good yields after deprotonation using *tert*-butyllithium in diethyl ether followed by trapping with electrophiles (Scheme 25, left and middle).[69] In order to access ferrocene-1,1′,2,2′-tetracarbaldehyde, DMF was also employed as the electrophile by Hildebrandt and co-workers in 2016 (Scheme 25, right).[70]



Scheme 25 Twofold 2,2′-functionalization of the diacetal of ferrocene-1,1′-dicarbaldehyde

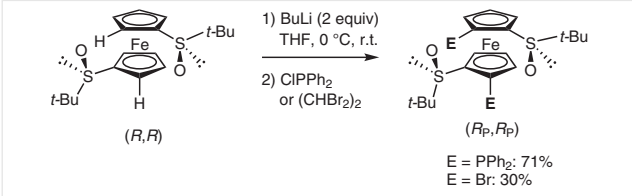
7 Ferrocenes Substituted by Sulfoxides

In the course of the development of diastereoselective syntheses on ferrocene derivatives, Kagan and co-workers showed that *tert*-butyl sulfoxide is a powerful substituent to induce 1′,2-deprotolithiation. Thus, upon consecutive treatment with butyllithium (2 equiv, THF, 0 °C to r.t.) and chlorodiphenylphosphine, (*S*)-(*tert*-butylsulfinyl)ferrocene was diastereoselectively converted into the corresponding (S,S_P)-1′,2-diphosphine, isolated in 80% yield (Scheme 26). Note that the oxygen present in the directing group faces the pro-*S* ferrocene position, a result coming from the *anti* orientation of the *tert*-butyl with respect to the iron atom.[71]



Scheme 26 Dideprotolithiation of (*S*)-(*tert*-butylsulfinyl)ferrocene followed by conversion into a diphosphine

If a second *tert*-butylsulfinyl group is present at the 1′-position, ferrocene is logically 2,2′-dilithiated. Thus, Zhang and co-workers succeeded in obtaining the tetrasubstituted ferrocenes stereoselectively with butyllithium in THF (Scheme 27).[72]

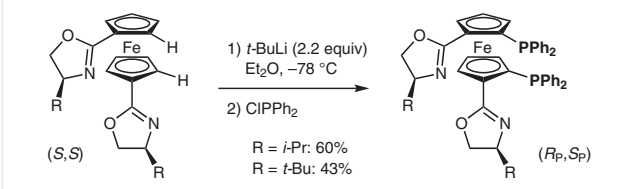


Scheme 27 Dideprotolithiation of (*R*,*R*)-1,1′-bis(*tert*-butylsulfinyl)ferrocene followed by electrophilic trapping

8 Ferrocenes Substituted by Oxazolines

Oxazolylferrocenes have attracted scientific interest because of applications in asymmetric catalysis.[73] The ligands developed in this part have notably found applications in asymmetric allylic substitution and hydrogenation reactions.[74]

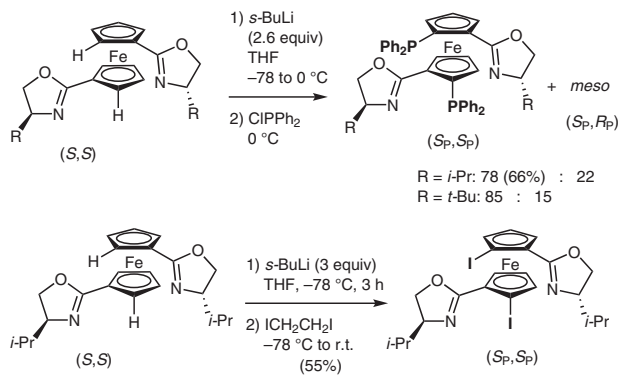
Whereas (*S*,*S*)-1,1′-bis(4-alkyloxazolin-2-yl)ferrocenes are mainly monofunctionalized using butyllithium, 2,2,′-dilithiation occurs with *tert*-butyllithium and *sec*-butyllithium. In 1995, Park and co-workers trapped the dilithio product, obtained by using *tert*-butyllithium at –78 °C in diethyl ether, with chlorodiphenylphosphine to obtain *meso* diphosphines (Scheme 28).[75]



Scheme 28 Dideprotolithiation of (*S*,*S*)-1,1′-bis(4-alkyloxazolin-2-yl)ferrocene followed by conversion into diphosphines

In 1996, Ikeda and co-workers ensured the 2,2′-dideprotolithiation of 1,1′-bis(4-alkyloxazolin-2-yl)ferrocene by using *sec*-butyllithium in THF, this time preferentially affording, and in high yield, C_2-symmetric ferrocene phosphines (Scheme 29, top).[76] Kang and co-workers also used *sec*-butyllithium in THF to prepare the corresponding diiodide (Scheme 29, bottom).[54]

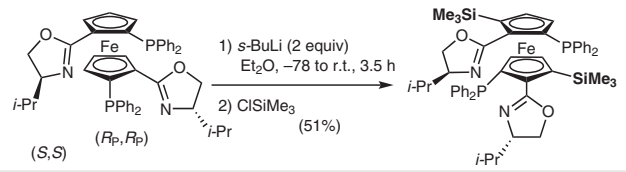
In fact, the outcome of the reaction heavily depends on the reaction parameters (temperature, solvent, base), as documented by Park, Ahn, and co-workers in 1996. By using alkyllithiums (*s*-BuLi or *t*-BuLi; 1 equiv) to monolithiate, and then chlorodiphenylphosphine, opposite stereoselectivities are noticed in diethyl ether (R_P) and THF (S_P) for the obtained phosphines. With an excess of base (*s*-BuLi or *t*-BuLi; 2 equiv) to ensure 2,2′-dilithiation, the *meso* product is observed as major product in diethyl ether (*s*-BuLi or *t*-BuLi) or THF using *t*-BuLi,[77] while the (S_P,S_P)-phosphine only forms as major product using *s*-BuLi in THF, in accordance with the previous studies.[77,78]



Scheme 29 Dideprotolithiation of (*S*,*S*)-1,1′-bis(4-alkyloxazolin-2-yl)ferrocenes followed by phosphination or iodolysis

As for mono-4-alkyloxazolin-2-yl-substituted ferrocenes, the first lithiation is controlled by coordination of the oxazoline nitrogen to the base. The stereoselectivity noticed can be rationalized by the steric hindrance existing between the oxazoline alkyl group and the aggregated base, leading to an alkyl substituent toward the other cyclopentadienyl ring in THF. In less coordinating diethyl ether, the nitrogens of both oxazolines would participate in the first lithiation, and the second lithiation ring would be directed by the remote oxazoline oxygen.[75–77,79] With oxazolines, the chelation is different from what happens with ferrocene sulfoxides and amines, for which the bulky groups are orientated *anti* to the iron atom.

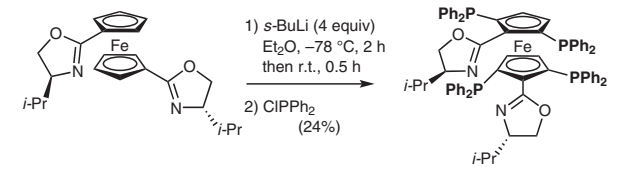
Further dilithiation of a C_2-symmetric 1,1′-bis(4-alkyloxazolin-2-yl)-2,2′-bis(diphenylphosphino)ferrocene is still possible next to the oxazoline ring, as demonstrated by Park and co-workers in the course of the synthesis of 1,1′,2,2′,3,3′-hexasubstituted ferrocenes (Scheme 30).[80]



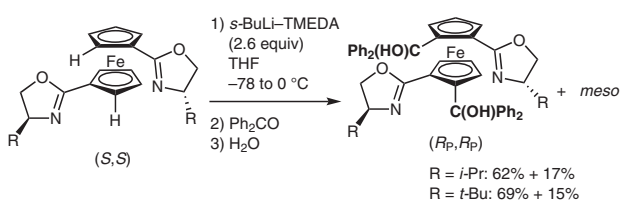
Scheme 30 Dideprotolithiation of a C_2-symmetric 1,1′-bis(4-alkyloxazolin-2-yl)-2,2′-bis(diphenylphosphino)ferrocene followed by silylation

With oxazolines as directing group, even tetralithiation becomes possible. By starting from the valine-derived 1,1′-bis(4-alkyloxazolin-2-yl)ferrocene shown in Scheme 31, it was achieved (albeit in moderate yield) in order to prepare a tetrakisphosphine by using an excess of *tert*-butyllithium in diethyl ether.[80]

In 2000, Ikeda and co-workers combined *sec*-butyllithium with TMEDA in THF to dideprotolithiate (*S*,*S*)-1,1′-bis(4-alkyloxazolin-2-yl)ferrocenes. If no improvement was noticed concerning the stereoselectivity (similar to that observed using *sec*-butyllithium in THF; Scheme 29), higher yields were obtained after interception with benzophenone (Scheme 32).[81]



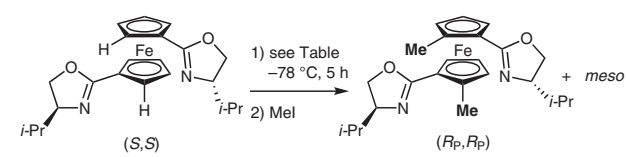
Scheme 31 Tetrafold deprotolithiation of (*S*,*S*)-1,1′-bis(4-isopropyloxazolin-2-yl)ferrocene ferrocene followed by phosphination



Scheme 32 Dideprotolithiation of (*S*,*S*)-1,1′-bis(4-alkyloxazolin-2-yl)ferrocene followed by electrophilic trapping using benzophenone

Interestingly, in diethyl ether, a selectivity improvement was observed by replacing *sec*-butyllithium with *sec*-butyllithium–TMEDA (see Table 4), whereas *tert*-butyllithium and butyllithium proved inappropriate. Methyl iodide was employed by Richards and co-workers as an electrophile in this study. Using instead hexachloroethane or 1,2-dibromo-1,1,2,2-tetrachloroethane also gives the expected halides; nevertheless, due to instability, their purification is precluded and yields of 39% (chloro) and 70% (bromo) were recorded for the whole process leading to the corresponding methyl halogeno esters.[82]

Table 4 Dideprotolithiation of (*S*,*S*)-1,1′-Bis(4-isopropyloxazolin-2-yl)ferrocene under Different Reaction Conditions Followed by Electrophilic Trapping[82]



Base (2.6 equiv), solvent	TMEDA (2.6 equiv)	Ratio C_2-symmetric/*meso*
s-BuLi, THF	no	3.8:1
s-BuLi, THF	yes	4:1
s-BuLi, Et_2O	yes	10:1
t-BuLi, Et_2O	yes	2:1
BuLi, Et_2O	yes	10:1[a]
s-BuLi, hexanes	yes	no lithiation[b]

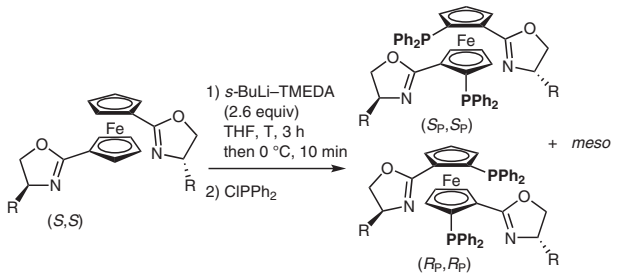
[a] About 50% of monomethylated product also obtained.
[b] Due to poor solubility.

In 2015, Zhang and co-workers reported their findings on the effect of the temperature on the stereoselectivity of the reaction using (*S*,*S*)-1,1′-bis(4-alkyloxazolin-2-yl)ferrocenes (Table 5). When the base is added at –90 °C, the S_P,S_P C_2-symmetric is the major product, formed with a small amount of the *meso* product. In contrast, when the base is added at a higher temperature, the formation of the S_P,S_P C_2-symmetric product drastically decreases. In the case of R = *i*-Pr, it is in favor of the *meso* product at temperatures of 25 and 40 °C. With R = *t*-Bu, the *meso* product predominated when the base was added at –10 °C but, at 40 °C, the R_P,R_P C_2-symmetric product is obtained instead. To rationalize these results, the authors proposed a S_P-lithiation favored under kinetic conditions (steric hindrance between the oxazoline alkyl, toward the other cyclopentadienyl ring, and the base for both deprotonations), and a privileged R_P-lithiation under thermodynamic conditions. The nature of the electrophile also has a considerable impact on the stereoselectivity, as shown in Table 6.[74]

Another approach was developed by Arthurs and Richards in order to obtain the most challenging R_P,R_P C_2-symmetric 2,2′-disilylated product. Indeed, they used deuterium as protecting group in order to abstract the required proton.[83]

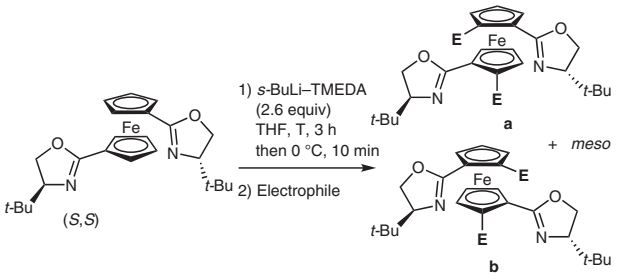
Even if less common, the dimeric ferrocene oxazolines depicted in Scheme 33 were difunctionalized diastereoselectively and in satisfying yields through a dilithio species by using butyllithium in diethyl ether.[84]

Table 5 Dideprotolithiation of (*S*,*S*)-1,1′-Bis(4-alkyloxazolin-2-yl)ferrocenes at Different Reaction Temperatures Followed by Phosphination[74]

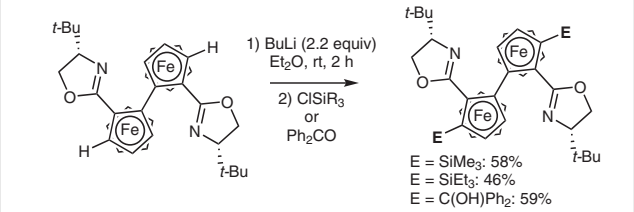


R	T (°C)	Total yield (%)	Ratio S_P,S_P/R_P,R_P/*meso*
i-Pr	–90	55	88:0:12
	25	47	7:0:93
	40	47	5:3:93
t-Bu	–90	53	86:0:14
	–10	51	18:0:82
	40	50	0:82:18

Table 6 Dideprotolithiation of (*S*,*S*)-1,1′-Bis(4-alkyloxazolin-2-yl)ferrocene at Different Reaction Temperatures Followed by Different Electrophilic Trapping[74]



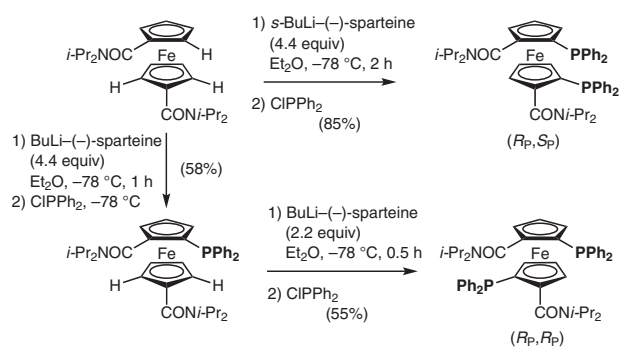
Electrophile (E)	T (°C)	Total yield (%)	Ratio **a**/**b**/*meso*
MeI (Me)	–90	50	84:0:16
	–10	60	45:14:41
	40	52	5:43:52
$ClSiMe_3$ ($SiMe_3$)	–90	70	92:0:8
	–10	75	26:0:74
	40	65	0:58:42
Ph_2CO [$C(OH)Ph_2$]	–90	60	86:0:14
	–10	71	16:0:84
	40	67%	13:42:45



Scheme 33 Dideprotolithiation of a di(oxazolylferrocene) followed by electrophilic trapping

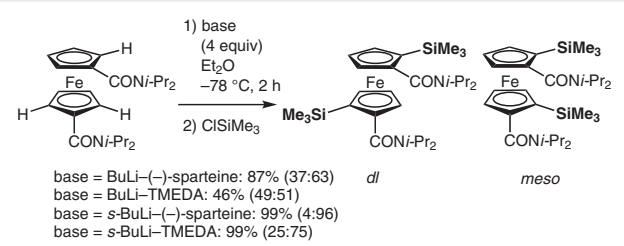
9 Ferrocenes Substituted by Carboxamides

In 1997, Jendralla and Paulus synthesized either the *meso* (Scheme 34, top) or the C_2-symmetric diphosphine (bottom) from *N*,*N*-diisopropylferrocene-1,1′-dicarboxamide. As in the case of the 1,1′-bis(4-alkyloxazolin-2-yl)ferrocenes (Section 8) under similar conditions, the second lithiation of the twofold process occurs with an enantioselectivity opposite to the first one. In contrast, when the monophosphine is isolated before submission to a second deprotolithiation–phosphination sequence, the C_2-symmetric diphosphine becomes the main product.[85] Note that the 2,2′-dilithiation-trapping sequence from *N*,*N*-diisopropylferrocene-1,1′-dicarboxamide can be achieved by using *sec*-butyllithium–TMEDA in diethyl ether at –78 °C and then benzophenone to afford the expected ferrocenediol.[86]



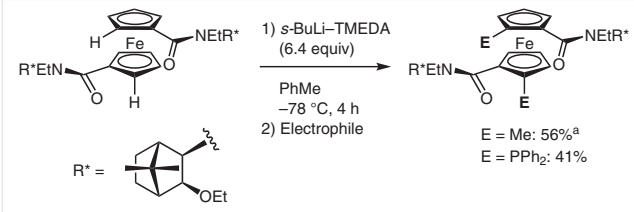
Scheme 34 Enantioselective deprotolithiation on *N*,*N*-diisopropylferrocene-1,1′-dicarboxamide followed by phosphination

In 2006, Snieckus and co-workers, who already experimented the need for isolating the intermediate 1,1′,2-trisubstituted ferrocene in the conversion of *N*,*N*-diisopropylferrocene-1,1′-dicarboxamide into the 1,1′,2,2′-tetrasubstituted derivatives,[78] disclosed their dilithiation-interception results (Scheme 35).[87] By using butyllithium–TMEDA [or –(–)-sparteine] (>2 equiv) in diethyl ether, and chlorotrimethylsilane as electrophilic partner, they obtained disilylated products in good yields, but low levels of diastereoselectivity [and optical purity with (–)-sparteine]. By replacing butyllithium by *sec*-butyllithium, quantitative yields were obtained, but a stereoselectivity in favor of the *meso* product. These results, similar to those of Jendralla and Paulus using chlorodiphenylphosphine,[85] are dependent on the electrophile used. Indeed, turning to iodomethane, iodine, or benzophenone, with butyllithium–(–)-sparteine as base under the same reaction conditions, leads to monofunctionalization, suggesting a deprotonation faster at this low temperature (maybe due to the presence of LiCl) than the reaction between the base and chlorotrimethylsilane.[87]



Scheme 35 Dideprotolithiation of *N*,*N*-diisopropylferrocene-1,1′-dicarboxamide followed by silylation

In order to access ferrocene amido-phosphines, Dimitrov and co-workers examined the dilithiation of ferrocene-1,1′-dicarboxamides. By using the chiral amido group shown in Scheme 36, they could perform the 2,2′-dilithiation by using an excess of *sec*-butyllithium–TMEDA at low temperature.[88]



Scheme 36 Diastereoselective deprotolithiation of a chiral ferrocene-1,1′-dicarboxamide. [a] Together with the *meso* product (7%) and the (R_P)-monofunctionalized product (17%, >99 dr).

10 Conclusion

As shown in this short review, ferrocene dideprotolithiation, which is above all a method to introduce substituents facing each other from their respective cyclopentadienyl group, has aroused the interest of many chemists taking into account the numerous applications that can have these elaborated metallocenes.

We are confident that the scope of this chemistry is expected to continue to grow with the development of other bases with which polydeprotonation of ferrocenes could be more easily modulated. For example, Mulvey and co-workers already showed the possible polydeprotonation of bare ferrocene by employing mixed alkali metal–magnesium[89] or –manganese[90] amides.[91] Finally, by combining deprotolithiation with in situ trapping using softer metallic species, dimetallated ferrocenes bearing sensitive directing groups can be generated and next difunctionalized.[92]

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