EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

FULL PAPER

DOI:10.1002/ejic.201300239

Iron-Catalyzed Ferrocenylmethanol OH Substitution by S, N, P, and C Nucleophiles

Rita Mazzoni,[a] Mauro Salmi,[a] Stefano Zacchini,[a] and Valerio Zanotti*[a]

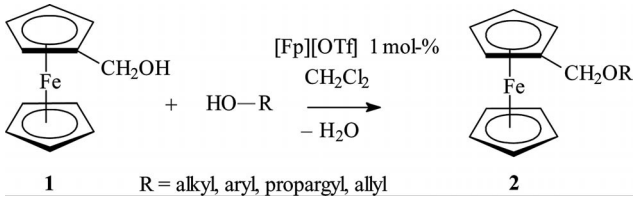
Keywords: Iron / Ferrocene / Nucleophilic substitution / Phosphanes / C–C bond formation / Sustainable chemistry

The iron complex [Fp][OTf] {Fp^+ = $[Fe(CO)_2(Cp)]^+$, OTf^- = $SO_3CF_3^-$} is an efficient catalyst for the direct substitution of the OH group in ferrocenylmethanol [Fc–CH_2OH] by thiols, aromatic amines, diphenylphosphane, and carbon nucleophiles (furan, pyrrole, and indole). This approach offers a convenient route to ferrocenes containing side chains with different functional groups. The advantages of the method are associated with the use of a catalyst based on iron, which is a nontoxic and readily available transition metal, and in the direct OH substitution, which produces water as the only byproduct.

Introduction

The increasing demand for green and sustainable chemical transformations has produced an impressive effort to design more efficient and environmentally benign bond-forming reactions.[1] In this respect, a highly challenging task is the direct use of alcohols instead of alkyl halides in reactions with nucleophiles, which is one of the most useful protocols for carbon–carbon and carbon–heteroatom bond formation. The use of alcohols is advantageous from the viewpoint of atom efficiency and because water is the only byproduct. However, this approach is limited by the poor leaving-group ability of the OH group. A number of synthetic protocols have been recently developed to promote OH substitution, based on organometallic catalysts, but most significant results are essentially limited to π-activated alcohols, such as allyl, benzyl, and propargyl alcohols. Examples include Pd-catalyzed nucleophilic allylic[2] and benzylic[3] substitution, ruthenium-catalyzed propargylic OH substitution,[4] and gold-catalyzed dehydrative transformation of unsaturated alcohols.[5]

Activated alcohols also include ferrocenylmethanol [Fc–CH_2OH] (**1**, Fc = ferrocenyl) and related α-substituted species, such as 1-ferrocenylethanol [Fc–CH(Me)OH], ferrocenyl(phenyl)methanol [Fc–CH(Ph)OH], and diferrocenylmethanol [Fc_2–CHOH], in which OH displacement is favored by formation of a relatively stabilized carbenium cation.[6] Direct nucleophilic substitution of the OH group in ferrocenyl alcohols is generally accomplished by using Lewis acids catalysts (e.g., indium tribromide,[7] ytterbium triflate,[8] or bismuth nitrate).[9] A procedure based on cerium ammonium nitrate (CAN), which presumably takes advantage of one-electron oxidation properties of the catalyst, has been described.[10] Secondary and tertiary ferrocenyl alcohols, which generate more stable carbenium cations, can undergo OH substitution even "on water" and without added Lewis acids.[11] The activation of ferrocenylmethanol provides a convenient and straightforward approach to functionalized ferrocenes, which are extremely valuable organometallic scaffolds for the construction of molecules with applications in catalysis, materials science, and biomedicinal chemistry.[12] We have recently shown that dehydrative etherification of ferrocenylmethanol **1** with a variety of alcohols is efficiently catalyzed by the iron complex [Fp][OTf] {Fp^+ = $[Fe(CO)_2(Cp)]^+$, OTf^- = $SO_3CF_3^-$}[13] (Scheme 1).



Scheme 1.

An advantage of our method over other previously reported approaches is the use of a catalyst based on iron, which is a nontoxic, environmentally benign and cost-effective transition metal.[14] In light of the above considerations, we decided to extend our investigations on [Fp][OTf]-catalyzed OH substitution in ferrocenylmethanol to a broader

[a] Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna,
Viale Risorgimento 4, 40136 Bologna, Italy
Fax: +39-0512093690
E-mail: valerio.zanotti@unibo.it
Homepage: http://www.unibo.it/docenti/valerio.zanotti

variety of nucleophies (thiols, amines, carbon nucleophiles, etc.) to generate C–C and C–heteroatom bonds. The aim was to demonstrate that iron-catalyzed OH substitution can provide a new and convenient approach to ferrocene functionalization.

Results and Discussion

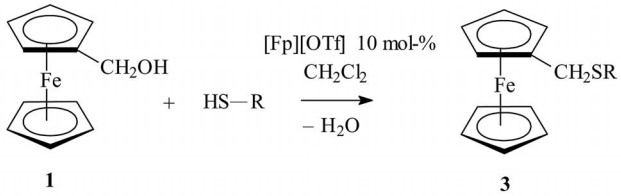
Reactions of Ferrocenylmethanol with Thiols

Based on the results shown in Scheme 1 and in consideration of the analogies between alcohols and thiols, we first investigated the OH substitution by thiols. The conditions under which these reactions have been performed require the use of a slight excess of thiol with respect to **1** (1:1.5 ratio) in the presence of [Fp][OTf] (10 mol-% to **1**) in CH_2Cl_2 solution at room temperature. The reaction (Table 1) leads to the formation of the corresponding ferrocenyl thioethers **3a**–**i** in high yields.

Compounds **3a**–**i** have been characterized by NMR spectroscopy and elemental analysis. Their spectroscopic data have been compared with those reported in the literature, if available. Indeed, complexes **3a**, **3g**,[15] **3b**,[16] **3c**,[17] **3e**,[10b] **3h**,[18] and **3i**[19] have been previously obtained by different methods. Moreover, the molecular structure of **3b** has been determined by X-ray diffraction. The ORTEP diagram is shown in Figure 1, and the main bond lengths and angles are reported in Table 2.

The unit cell of **3b** contains two independent molecules with almost identical geometries and bonding parameters. Complex **3b** is a monosubstituted ferrocene with the two Cp-rings almost parallel [the angles between the least-

Table 1. Reactions of ferrocenylmethanol with thiols catalyzed by [Fp][OTf].



1 **3**

Entry[a]	Thiol	Product	Yield (%)[a]	Entry[a]	Thiol	Product	Yield (%)[b]
1	CH_3CH_2SH	**3a**	93	6	HS⁄⁄SH	**3f**	81
2	SH	**3b**	88	7	HO⁄⁄SH	**3g**	91
3	CH_2SH	**3c**	90	8	HO(OH)⁄⁄SH	**3h**	83
4	SH	**3d**	84	9	NH_2 SH	**3i**	94
5	SH	**3e**	87				

[a] Reaction conditions: **1**/thiol ratio = 1:1.5, in CH_2Cl_2 at room temperature. [b] Isolated yields after 1 h reaction.

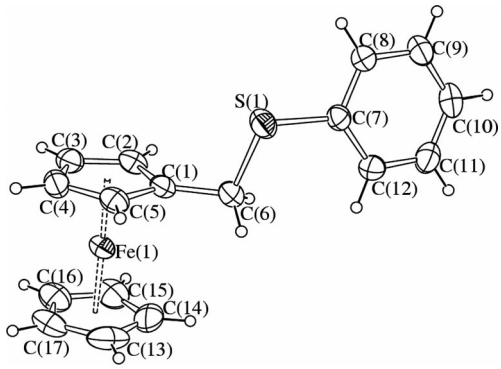


Figure 1. ORTEP diagram of **3b**. Thermal ellipsoids are drawn at 30% probability level. Only one of the two independent molecules present in the unit cell is represented.

Table 2. Selected bond lengths [Å] and angles [°] for **3b**.

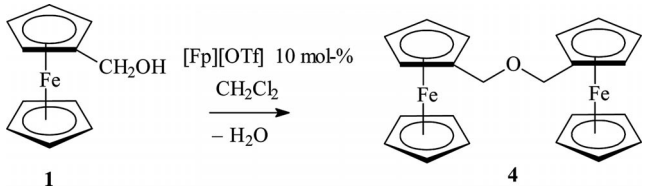
	Molecule 1	Molecule 2
Fe(1)–Cp(1)[a]	2.028(3)–2.040(3)	2.030(2)–2.045(3)
	Average 2.034(6)	Average 2.036(6)
Fe(1)–Cp(2) [b]	2.018(3)–2.045(3)	2.021(3)–2.039(3)
	Average 2.027(6)	Average 2.031(6)
C–C Cp(1) [a]	1.399(4)–1.422(3)	1.391(4)–1.422(4)
	Average 1.409(9)	Average 1.409(9)
C–C Cp(2)[b]	1.366(4)–1.450(5)	1.382(4)–1.417(6)
	Average 1.390(9)	Average 1.400(9)
C(1)–C(6)	1.488(4)	1.488(3)
C(6)–S(1)	1.827(3)	1.822(2)
S(1)–C(7)	1.762(3)	1.765(2)
Sum angles Cp(1)[a]	540.0(5)	540.0(5)
Sum angles Cp(2)[b]	540.1(5)	540.1(5)
C(1)–C(6)–S(1)	107.56(18)	107.20(18)
C(6)–S(1)–C(7)	103.69(12)	103.89(12)

[a] Cp(1) is defined by atoms C(1), C(2), C(3), C(4), and C(5). [b] Cp(2) is defined by atoms C(13), C(14), C(15), C(16), and C(17).

squares mean planes of the five-membered rings are 1.3 and 1.0° for the two independent molecules. The Fe–C interactions with the substituted C_5 ring [average 2.034(6) and 2.036(6) Å] are substantially longer than those with the unsubstituted Cp ring [average 2.027(6) and 2.031(6) Å].[13]

The reactions shown in Table 1 are interesting examples of the relatively uncommon catalytic OH substitution by thiols; thioethers are usually obtained upon reaction of halides with thiolates. Indeed, dehydrative thioetherification, catalyzed by transition-metal complexes, is essentially limited to allylation of thiols based on ruthenium catalysts.[20] Direct reactions between ferrocenyl alcohols and thiols mostly concern α-substituted ferrocenyl alcohols such as [Fc–CH(R)OH] (R = Me, Ph, Fc).[10,11,21] However, it has been reported that **3a** and **3g** can be obtained by reaction of **1** with thiols in the presence of acetic acid, but the reaction is performed with a large excess of thiol (50% mixture of water and thiol used as solvent).[15] Interestingly, the catalyst [Fp][OTf] is not inactivated (or "poisoned") by thiols, although these are potentially able to coordinate to the iron complex.[22] For example, the addition of HSPh to [Fp(THF)][BF_4] (THF = tetrahydrofuran) to form [FpPhSH]$^+$ has been described,[23] but the reaction is quite slow and should not interfere significantly.

A further observation is that the iron-catalyzed dehydrative thioetherification of **1** is selective and leads to the formation of one single product. This is particularly evident in the reactions of **1** with species that contain both thiol and hydroxy groups (Table 2, Entries 6 and 7), which, in theory, might produce both thioethers and ethers. Conversely, thioetherification takes place selectively, which is consistent with the stronger nucleophilic properties of thiols compared to alcohols. In addition to these examples, competition between OH and SH is always present in all the reactions examined, as ferrocenylmethanol itself can act as nucleophile, and the self-condensation product [Fc–CH_2OCH_2–Fc] (**4**) might be expected if the added nucleophile (thiol) were to react too slowly. Indeed, it is known that **1**, upon treatment with [Fp][OTf], in the absence of other nucleophiles, generates the symmetric ether **4**, but the reaction is rather sluggish (Scheme 2).[12]



Scheme 2.

Finally, the reaction of **1** with 2-aminobenzenethiol (Table 1, Entry 9) provides a comparison between the amino and thiol groups: again, the reaction is selective and OH displacement is performed exclusively by the thiol function. Therefore, reactions of **1** with thiols containing other functional groups provide both an indication of which nucleophile more effectively replaces the OH group and easy access to ferrocenyl complexes with a functionalized side chain. This pending function is potentially able to coordinate to other metal centers or connect to different molecular fragments, which is an important feature for possible application.

Reactions of Ferrocenylmethanol with Amines, Phosphanes, and Carbon Nucleophiles

After examination of the OH substitution by alcohols and thiols, we turned our attention to group 15 nucleophiles. The reaction of alcohols with amines is a clear-cut but very challenging method for the synthesis of *N*-alkylated amines. One of the most promising approaches to amination of alcohols is based on the oxidation–imination–reduction sequence: the alcohol, once oxidized and attacked by an amine, affords a hemiaminal. This intermediate can dehydrate to an imine and be hydrogenated to generate an amine. Methods in which this sequence is performed as a one-pot reaction and the oxidation step consists of a dehydrogenation are described as "borrowing hydrogen" or "hydrogen autotransfer" reactions. This area has recently witnessed an impressive development, mostly based on

homogeneous ruthenium and iridium catalysts.[24] On the other hand, the direct combination of alcohols and amines does not necessarily imply a redox mechanism; acid-catalyzed nucleophilic OH substitution by amines in π-activated alcohols is also feasible. A few examples of the amination of ferrocenyl alcohols by anilines (arylamines) are known and, although detailed mechanistic investigations have not been presented, it has been suggested that these reactions occur via ferrocenyl carbenium intermediates.[10b,21]

Based on these considerations, we investigated the reactions of **1** with different amines in the presence of [Fp][OTf] as catalyst. The results are shown in Table 3.

In agreement with previous findings,[10b,21] amination reactions are limited to arylamines (Table 3, Entries 1 and 2). The reactions with other amines (Table 3, Entries 3–5) lead to the formation of the symmetric ether **4** as the only observed product. Therefore, amines do not deactivate the catalyst, and self-condensation of **1** takes place, although the reaction is relatively slow and almost complete conversion occurs in ca. 16 h, which is in agreement with the conditions usually observed for the conversion of **1** into **4** in the absence of nucleophiles. The absence of catalyst deactivation is remarkable as amine complexes of Fp^+ are known and can be prepared from $[Fp(Et_2O)][BF_4]$ and alkylamines.[25] On the other hand, it has been reported that Fp^+ also acts as a catalyst in the presence of 1,8-bis(dimethylamino)-naphthalene, which is potentially able to deactivate it.[26]

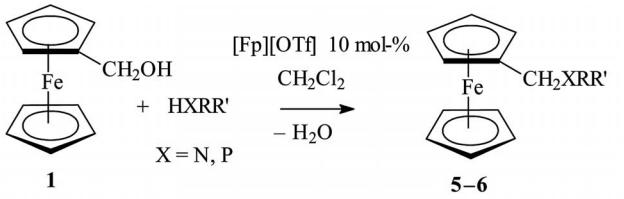
Complexes **5a** and **5b** have been characterized by NMR spectroscopy and elemental analysis; moreover, the molecular structure of **5a** has been determined by the X-ray diffraction (Figure 2 and Table 4).

The unit cell of **5a** contains two independent molecules with almost identical geometries and bonding parameters. Compound **5a** closely resembles **3b**; the replacement of the thioether group with the amino group is the major difference. Hydrogen bonding is present between the N–H group of one molecule and the nitro substituent of the other one [donor–acceptor distance 3.066(2) Å, angle 163(2)°].

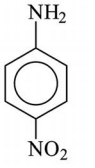
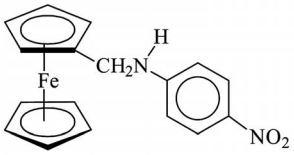
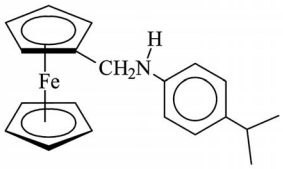
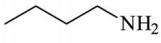
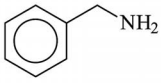
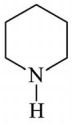
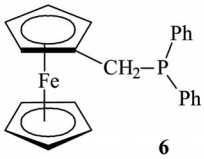
Our results are consistent with those previously reported by Ji and co-workers concerning the reactions of ferrocenyl alcohols with arylamines catalyzed by cerium ammonium nitrate, including the reaction of **1** with *p*-chloroaniline.[10b] In that report, the authors evidenced a higher reactivity for arylamines with electron-withdrawing groups (in the *para* position). Conversely, in our case, we did not observed any relevant effect, and 4-nitroaniline and 4-isopropylaniline (Table 3, Entries 1 and 2, respectively) gave similar results.

An interesting and unprecedented outcome was found in the reaction of **1** with diphenylphosphane (Table 3, Entry 6). Complex **1** undergoes OH displacement by diphenylphosphane to afford the ferrocenylphosphane complex **6**, but the reaction is not selective and a comparable amount of the self-condensation product **4** is also formed. Ferrocenes containing a phosphane group at the α-position of the side chain are known. Examples include $[FcCH_2PH_2]$[27] and $[FcCH_2PR(CH_2CH_2OH)]$[28] (R = Me, CH_2CH_2OH), which exhibit interesting chemistry associated with the coordinating properties of the phosphorus atom.[27] These complexes are not prepared from ferrocenyl alcohols by direct OH nucleophilic substitution; the hydroxy group must be converted into a better leaving group, which usually requires a sequence of transformations. For example, $[FcCH(Me)P(CH_2CH_2OH)_2]$ is obtained by conversion of ferrocenyl alcohol into acetate, which is reacted further with diethylamine, followed by methyl iodide to generate

Table 3. Reactions of ferrocenylmethanol with amines catalyzed by [Fp][OTf].



1 **5–6**

Entry[a]	Nucleophile	Product	Yield(%)[b]
1		 **5a**	92
2		 **5b**	86
3		**4**	85[c]
4		**4**	85[c]
5		**4**	85[c]
6	$PHPh_2$	 **6**	**6**: 41 + **4**: 36

[a] Reaction conditions: **1**/nucleophile ratio = 1:1.5, in CH_2Cl_2 at room temperature. [b] Isolated yields after 2 h of reaction. [c] Isolated yields after 16 h of reaction.

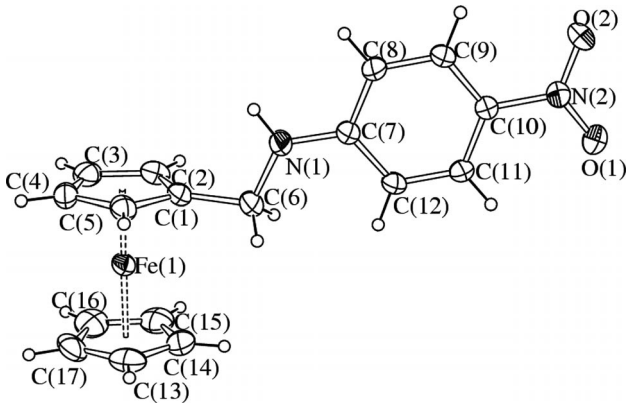


Figure 2. ORTEP diagram of **5a**. Thermal ellipsoids are drawn at 30% probability level. Only one of the two independent molecules present in the unit cell is represented.

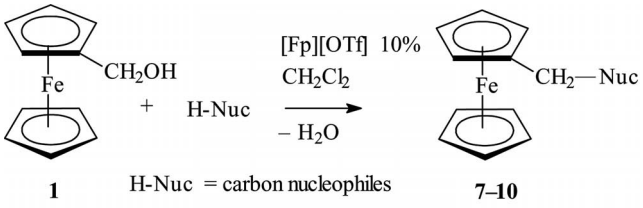
Table 4. Selected bond lengths [Å] and angles [°] for **5a**.

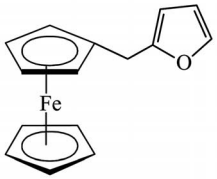
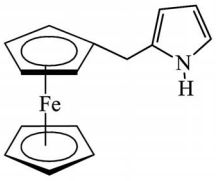
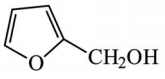
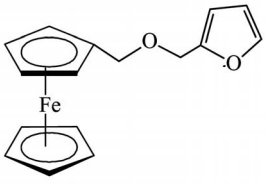
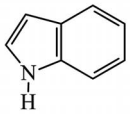
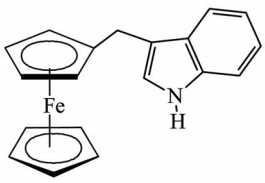
	Molecule 1	Molecule 2
Fe(1)–Cp(1)[a]	2.0248(19)–2.041(2) average 2.036(4)	2.028(2)–2.047(2) average 2.038(4)
Fe(1)–Cp(2)[b]	2.026(2)–2.042(2) average 2.033(4)	2.005(9)–2.036(8) average 2.02(2)
C–C Cp(1)[a]	1.400(4)–1.421(3) average 1.412(7)	1.391(4)–1.422(3) average 1.409(7)
C–C Cp(2)[b]	1.388(4)–1.402(4) average 1.396(9)	1.399(10)–1.434(10) average 1.41(2)
C(1)–C(6)	1.497(3)	1.489(3)
C(6)–N(1)	1.457(3)	1.457(3)
N(1)–C(7)	1.352(3)	1.351(3)
Sum angles Cp(1)[a]	539.9(4)	540.0(4)
Sum angles Cp(2)[b]	540.0(4)	540.0(16)
C(1)–C(6)–N(1)	111.03(18)	110.68(18)
C(6)–N(1)–C(7)	123.32(18)	123.64(18)

[a] Cp(1) is defined by atoms C(1), C(2), C(3), C(4), and C(5). [b] Cp(2) is defined by atoms C(13), C(14), C(15), C(16), and C(17).

[FcCH(Me)NEt_2Me][I]. This latter undergoes nucleophilic substitution by the phosphane.[29] The introduction of a side chain containing a phosphane group is also a fundamental step in the modular approach to ferrocenyl diphosphane ligands (Josiphos-type),[30] which are among the most versatile chelating phosphorus ligands for catalytic applications.[31] In particular, the introduction of a phosphorus moiety in the pseudo-benzylic position (α position) is accomplished by nucleophilic substitution of suitable leaving groups. In general, these are dimethylamino (from Ugi's amine) or methoxy groups, and the nucleophilic substitution takes place with retention of configuration.[32] Moreover, transformation of OH into OMe also allows the *ortho*-lithiation of the Cp ring, which is necessary for the introduction of a second phosphorus function directly on the cylopentadienyl ring. In light of these considerations, the formation of **6**, although low yielding, appears unique, in that it results from the direct reaction of ferrocenylmethanol with a secondary phosphane. Again, it has to be outlined that the catalytic activity of [Fp][OTf] is retained despite the presence of a reagent (PPh_2H) that can react with the catalyst. Indeed, the complex $[FpPPh_2H]^+$ is known,[33] and one of the possible synthetic routes is the reaction of [Fp(THF)][PF_6] with PPh_2H.[34] Moreover, we have verified that, under our reaction conditions, but without ferrocenylmethanol, the catalyst rapidly reacts with PPh_2H to form [FpPPh_2H][OTf]. Therefore, it is surprising that the catalytic activity of [Fp][OTf] is preserved and results in the formation of both C–P and C–O bonds (products **6** and **4**, respectively).

Table 5. Reactions of ferrocenylmethanol with carbon nucleophiles catalyzed by [Fp][OTf].



Entry[a]	Nucleophile	Products	Yield (%)[b]
1		 **7**	55
2		 **8**	51
3		 **9**	80
4		 **10**	75

[a] Reaction conditions: **1**/nucleophile ratio = 1:1.5, in CH_2Cl_2 at room temperature. [b] Isolated yields after 4 h of reaction.

Finally, we have investigated the nucleophilic substitution of the hydroxy group in **1** with carbon nucleophiles (Table 5). Our results evidence that the iron complex [Fp][OTf] is also a good catalyst for OH substitution in **1** by different carbon nucleophiles to result in the formation of a C–C bond at the α position of the side chain.

The reactions reported in Table 5 involve active C–H bonds in heterocyclic aromatic compounds such as pyrrole, furan, and indole. Unexpectedly, thiophene and other active methylene species (acetylacetone and dimethylmalonate) were unreactive. This is in contrast with previous findings in similar reactions performed in acetic acid,[21] or with cerium ammonium nitrate[10a] or $InBr_3$[7] as catalyst, and even in water,[11] in which diketones and keto esters were reactive. On the other hand, these previously reported examples almost exclusively involve secondary ferrocenyl alcohols [e.g., Fc–CH(Me)OH], which are more reactive than **1**. Thus, our synthetic approach is somewhat complementary. For example, **1** was previously found to be unreactive toward pyrrole,[10a] whereas, in our case (Table 5, Entry 2), the reaction takes place in moderate yield. Concerning the reaction with furfuryl alcohol (Table 5, Entry 3), which in theory displays two competitive nucleophilic sites (the hydroxy and the active methylene carbon), we exclusively observed C–O bond formation to yield the etherification product **9** (Table 5, Entry 3). Finally, the reaction with indole catalyzed by [Fp][OTf] gives results similar to those reported for the ferrocenyl alkylation of indoles promoted by a Bi^{III} catalyst, which also afforded **10** in comparable yield.[9]

Conclusions

The iron complex [Fp][OTf] is an excellent catalyst in the direct ferrocenylmethanol OH substitution. Different nucleophiles have been examined including thiols, arylamines, diphenylphosphane, and carbon nucleophiles, which lead to the formation of C–S, C–N, C–P, and C–C bonds. Therefore, this approach offers functionalized ferrocenes containing a side chain with functional groups. Interestingly, [Fp][OTf] acts as a Lewis acid catalyst despite the presence of nucleophiles (thiols, amines, and phosphane) that can potentially react and give stable addition products. Compared to previously reported methods for the direct OH substitution of ferrocenyl alcohols, our approach exhibits two distinct features: one is the use of an iron catalyst and mild reaction conditions without the need for a large excess of the nucleophile. The second aspect is that direct OH substitution can be performed on ferrocenylmethanol instead of secondary ferrocenyl alcohols, which are favored as they generate more stable carbenium cations. Finally, our results provide an unprecedented example of direct-catalyzed OH substitution of ferrocenylmethanol by diphenylphosphane.

Experimental Section

General: All reactions were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were performed on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K with a Perkin–Elmer Spectrum 2000 FTIR spectrophotometer, and elemental analyses were performed with a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed with a Varian Mercury Plus 400 instrument and were recorded at 298 K. ^1H and ^{13}C chemical shifts were referenced to internal tetramethylsilane (TMS). NMR spectra were assigned through DEPT experiments and ^1H–^{13}C correlation measured through gradient-selected heteronuclear single quantum coherence (gs-HSQC) and gs-HMBC experiments. All reagents were commercial products (Aldrich) of the highest purity available and were used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Owing to its high reactivity, the iron complex [Fp][OTf] was freshly prepared immediately before use, by reacting $[Fe_2(Cp)_2(CO)_4]$ with AgOTf, according to the procedure previously reported.[13]

[Fc–CH_2SR] [R = Et, 3a; R = Ph, 3b; R = CH_2Ph, 3c; R = $CH_2CH{=}CH_2$, 3d; R = C_9H_7, 3e; R = $(CH_2)_3SH$, 3f; R = CH_2CH_2OH, 3 g; R = $CH_2CH(OH)CH_2OH$, 3h; R = *o*-$NH_2C_6H_4$, 3i]: The catalyst [Fp][OTf] (0.05 mmol) in CH_2Cl_2 solution (10 mL) was added to a solution of ferrocenylmethanol (**1**, 108 mg, 0.50 mmol) and ethanethiol (0.05 mL, 0.75 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred at room temperature for 1 h. After removal of the solvent and chromatography of the residue on alumina with petroleum ether (b.p. 40–60 °C) as eluent, **3a** was obtained as a yellow solid, yield 121 mg, 93%. $C_{13}H_{16}FeS$ (260.18): calcd. C 60.01, H 6.20; found C 60.09, H 6.32. ^1H NMR ($CDCl_3$): δ = 4.18 (m, 2 H, Cp), 4.14 (s, 5 H, Cp_{free}), 4.11 (m, 2 H, Cp), 3.53 (s, 2 H, CpCH_2), 2.49 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, SCH_2CH$_3$), 1.23 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, SCH$_2$CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 85.4 ($C_{ipso\text{-}Cp}$), 68.6 (Cp_{free}), 68.5, 67.8 (Cp), 31.4 (CpCH_2), 25.8, 14.5 (SCH$_2$CH$_3$) ppm.

Compounds **3b**–**i** were prepared by the same procedure as that described for **3a**, by reacting **1** with the appropriate thiol. Crystals of **3b** suitable for X-ray analysis were obtained by slow evaporation from a CH_2Cl_2 solution.

3b: Yield 135 mg, 88%. $C_{17}H_{16}FeS$ (308.22): calcd. C 66.25, H 5.23; found C 66.37, H 5.14. ^1H NMR ($CDCl_3$): δ = 7.49–7.13 (5 H, Ph), 4.13–4.11 (7 H, Cp_{free} and Cp), 4.06 (m, 2 H, Cp), 3.89 (s, 2 H, CpCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 136.0 ($C_{ipso\text{-}Ph}$), 129.8–126.1 (C_{arom}), 84.3 ($C_{ipso\text{-}Cp}$), 68.7 (Cp_{free}), 68.6, 67.9 (Cp), 34.8 (CpCH_2) ppm.

3c: Yield 145 mg, 90%. $C_{18}H_{18}FeS$ (322.25): calcd. C 67.09, H 5.63; found C 66.97, H 5.13. ^1H NMR ($CDCl_3$): δ = 7.30–7.12 (5 H, Ph), 4.07 (m, 2 H, Cp), 4.03 (7 H, Cp_{free} and Cp), 3.58 (s, 2 H, CH_2Ph), 3.34 (s, 2 H, CpCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.4 ($C_{ipso\text{-}Ph}$), 129.4–126.9 (C_{arom}), 84.9 ($C_{ipso\text{-}Cp}$), 68.7 (Cp_{free} and Cp), 67.9 (Cp), 36.2 (CH_2Ph), 31.2 (CpCH_2) ppm.

3d: Yield 114 mg, 84%. $C_{14}H_{16}FeS$ (272.19): calcd. C 61.78, H 5.92; found C 61.87, H 5.93. ^1H NMR ($CDCl_3$): δ = 5.73 (m, 1 H, CH=CH$_2$), 5.24 (m, 2 H, CH=CH_2), 4.17 (m, 2 H, Cp), 4.12 (s, 5 H, Cp_{free}), 4.11 (m, 2 H, Cp), 3.45 (s, 2 H, CpCH_2), 3.06 (m, 2 H, SCH$_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 133.4, 115.9 (CH=CH$_2$), 84.1 ($C_{ipso\text{-}Cp}$), 67.8 (Cp_{free}), 67.7, 66.9 (Cp), 33.7 (CpCH_2), 31.0 (SCH$_2$) ppm.

3e: Yield 156 mg, 87%. $C_{21}H_{18}FeS$ (368.28): calcd. C 70.40, H 5.06; found C 70.27, H 5.13. ^1H NMR ($CDCl_3$): δ = 8.01–7.43 (7 H, C_9H_7), 4.19 (m, 2 H, Cp), 4.18 (s, 5 H, Cp_{free}), 4.11 (m, 2 H, Cp), 4.04 (s, 2 H, CpCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 134.5–125.6

(C_{arom}), 84.3 ($C_{ipso\text{-}Cp}$), 68.8 (Cp_{free}), 68.7, 68.0 (Cp), 34.8 (Cp*C*H_2) ppm.

3f: Yield 124 mg, 81%. $C_{14}H_{18}FeS_2$ (306.27): calcd. C 54.90, H 5.92; found C 54.77, H 5.93. ^{1}H NMR ($CDCl_3$): δ = 4.18 (m, 2 H, Cp), 4.13 (s, 5 H, Cp_{free}), 4.12 (m, 2 H, Cp), 3.51 (s, 2 H, CpCH_2), 3.13 (t, $^3J_{H,H}$ = 6.5 Hz, 2 H, CH_2CH$_2$CH$_2$SH), 2.57 (m, 2 H, CH$_2$CH_2CH$_2$SH), 1.84 (m, 2 H, CH$_2$CH$_2$CH_2SH), 1.34 (t, $^3J_{H,H}$ = 8.1 Hz, 1 H, SH) ppm. ^{13}C NMR ($CDCl_3$): δ = 85.0 ($C_{ipso\text{-}Cp}$), 68.7 (Cp_{free}), 68.6, 68.0 (Cp), 33.1 (Cp*C*H$_2$), 31.8, 30.1, 23.4 (CH$_2$CH$_2$CH$_2$SH) ppm.

3g: Yield 126 mg, 91%. $C_{13}H_{16}FeOS$ (276.18): calcd. C 56.54, H 5.84; found C 56.60, H 5.73. ^{1}H NMR ($CDCl_3$): δ = 4.17 (m, 2 H, Cp), 4.13 (s, 5 H, Cp_{free}), 4.12 (m, 2 H, Cp), 3.66 (m, 2 H, CH$_2$CH_2OH), 3.52 (s, 2 H, CpCH_2), 2.66 (t, $^3J_{H,H}$ = 6.0 Hz, 2 H, CH_2CH$_2$OH), 2.31 (br, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 84.7 ($C_{ipso\text{-}Cp}$), 68.7 (Cp_{free}), 68.5, 68.0 (Cp), 60.2 (CH$_2$*C*H$_2$OH), 34.8 (*C*H$_2$CH$_2$OH), 31.4 (Cp*C*H$_2$) ppm.

3h: Yield 127 mg, 83%. $C_{14}H_{18}FeO_2S$ (306.20): calcd. C 54.91, H 5.92; found C 54.77, H 5.99. ^{1}H NMR ($CDCl_3$): δ = 4.19 (m, 2 H, Cp), 4.16 (m, 2 H, Cp), 4.13 (s, 5 H, Cp_{free}), 3.69 (m, 2 H, CH_2OH), 3.55 (s, 2 H, CpCH_2), 3.50 (m, 1 H, C*H*OH), 2.92 (br. s, 1 H, OH), 2.60, (m, 2 H, SCH$_2$), 2.40 (br. s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 84.6 ($C_{ipso\text{-}Cp}$), 69.9, 68.7 (Cp), 68.8 (Cp_{free}), 68.1 (CH$_2$OH), 65.4 (CHOH), 35.3 (SCH$_2$), 32.1 (Cp*C*H$_2$) ppm.

3i: Yield 152 mg, 94%. $C_{17}H_{17}FeNS$ (323.23): calcd. C 63.17, H 5.30; found C 63.11, H 5.39. ^{1}H NMR ($CDCl_3$): δ = 7.31–6.64 (4 H, Ph), 4.26 (br, 2 H, NH$_2$), 4.10 (s, 5 H, Cp_{free}), 4.08 (m, 2 H, Cp), 4.04 (m, 2 H, Cp), 3.72 (s, 2 H, CpCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 148.4 ($C_{q\text{-}Ph}$), 136.4–114.9 (C_{arom}), 84.9 ($C_{ipso\text{-}Cp}$), 68.6 (Cp and Cp_{free}), 68.0 (Cp), 35.7 (Cp*C*H$_2$) ppm.

[Fc–CH$_2$NHR] (R = *p*-NO$_2$C$_6$H$_4$, 5a; R = *p*-*i*PrC$_6$H$_4$, 5b): Compounds **5a**–**b** were prepared by the same procedure described above for **3a** (except for a longer reaction time, 2 h) by reacting **1** with the appropriate amine. Crystals of **5a** suitable for X-ray analysis were obtained by slow evaporation from a CH_2Cl_2 solution.

5a: Yield 154 mg, 92%. $C_{17}H_{16}FeN_2O_2$ (336.17): calcd. C 60.74, H 4.80; found C 60.77, H 4.89. ^{1}H NMR ($CDCl_3$): δ = 8.10 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, Ph), 6.56 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, Ph), 4.76 (br., 1 H, NH), 4.24 (m, 2 H, Cp), 4.20 (s, 5 H, Cp_{free}), 4.19 (m, 2 H, Cp), 4.06 (d, $^3J_{HH}$ = 5.0 Hz, 2 H, CpCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.9 ($C_{ipso\text{-}Ph}$), 138.0, 126.5, 111.0 (C_{arom}), 84.4 ($C_{ipso\text{-}Cp}$), 68.6 (Cp_{free}), 68.4, 68.2 (Cp), 42.9 (Cp*C*H$_2$) ppm.

5b: Yield 143 mg, 86%. $C_{20}H_{23}FeN$ (333.25): calcd. C 72.08, H 6.96; found C 71.99, H 5.89. ^{1}H NMR ($CDCl_3$): δ = 7.08 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, Ph), 6.63 (m, $^3J_{H,H}$ = 8.0 Hz, 2 H, Ph), 4.25 (m, 2 H, Cp), 4.18 (s, 5 H, Cp_{free}), 4.14 (m, 2 H, Cp), 3.95 (s, 2 H, CpCH_2), 3.79 (br., 1 H, NH), 2.83 (sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, CH$_3$C*H*CH$_3$), 1.22 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 146.4, 138.1, 127.1, 112.9 (C_{arom}), 86.7 ($C_{ipso\text{-}Cp}$), 68.5 (Cp_{free}), 68.1, 67.8 (Cp), 43.7 (Cp*C*H$_2$), 33.2 (CH$_3$*C*HCH$_3$), 24.3 (CH$_3$) ppm.

[Fc–CH$_2$PPh$_2$] (6): A solution of **1** (110 mg, 0.51 mmol) in CH_2Cl_2 (20 mL) was treated with diphenylphosphane (142 mg, 0.76 mmol) in the presence of [Fp][OTf] (0.05 mmol). The resulting mixture was stirred at room temperature for 2 h. After solvent removal and chromatography of the residue on alumina with petroleum ether (b.p. 40–60 °C) as eluent, **6** was obtained in the first yellow fraction (80 mg, 41%), followed by a second orange fraction containing **4** (74 mg, 36%). $C_{23}H_{21}FeP$ (384.23): calcd. C 71.90, H 5.51; found C 71.81, H 5.39. ^{1}H NMR ($CDCl_3$): δ = 7.50–7.29 (10 H, Ph), 4.10 (s, 5 H, Cp_{free}), 3.98 (m, 2 H, Cp), 3.92 (m, 2 H, Cp), 3.16 (s, 2 H, CpCH$_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.8–128.3 (C_{arom}), 84.3 ($C_{ipso\text{-}Cp}$), 69.1, 67.3 (Cp), 68.7 (Cp_{free}), 29.7 (Cp*C*H$_2$) ppm.

[Fc–CH$_2$R] (R = C$_4$H$_3$O, 7; R = C$_4$H$_4$N, 8; R = C$_5$H$_5$O$_2$, 9): Complexes **7**, **8**, and **9** were prepared by the same procedure described above for **6**, by reacting **1**(110 mg, 0.51 mmol) with furan, pyrrole, and 2-furfuryl alcohol, respectively. A longer reaction time (4 h) was required.

7: Yield 75 mg, 55%. $C_{15}H_{14}FeO$ (266.12): calcd. C 67.70, H 5.30; found C 67.61, H 5.38. ^{1}H NMR ($CDCl_3$): δ = 7.34 (m, 1 H, CH_{furan}), 6.31 (m, 1 H, CH_{furan}), 6.04 (m, 1 H, CH_{furan}), 4.13 (m, 2 H, Cp), 4.10 (s, 5 H, Cp_{free}), 4.08 (m, 2 H, Cp), 3.67 (s, 2 H, CpCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 154.9, 140.8, 110.1, 105.4 (C_{furan}), 85.4 ($C_{ipso\text{-}Cp}$), 68.7 (Cp_{free}), 68.4, 67.4 (Cp), 28.4 (Cp*C*H$_2$) ppm.

8: Yield 69 mg, 51%. $C_{15}H_{15}FeN$ (265.13): calcd. C 67.95, H 5.70; found C 67.91, H 5.68. ^{1}H NMR ($CDCl_3$): δ = 7.97 (br. s, NH), 6.64 (m, 1 H, $CH_{pyrrole}$), 6.12 (m, 1 H, $CH_{pyrrole}$), 5.94 (m, 1 H, $CH_{pyrrole}$), 4.14 (s, 5 H, Cp_{free}), 4.12 (m, 1 H, Cp), 4.11 (m, 1 H, Cp), 3.71 (s, 2 H, CpCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 129.90 ($C_{q\text{-}pyrrole}$), 116.05, 108.11, 105.39 ($C_{pyrrole}$), 86.6 ($C_{ipso\text{-}Cp}$), 68.7 (Cp_{free}), 68.5, 67.7 (Cp), 28.1 (Cp*C*H$_2$) ppm.

9: Yield 121 mg, 80%. $C_{16}H_{16}FeO_2$ (296.14): calcd. C 64.89, H 5.45; found C 64.82, H 5.36. ^{1}H NMR ($CDCl_3$): δ = 7.43 (m, 1 H, CH_{furan}), 6.37 (m, 1 H, CH_{furan}), 6.32 (m, 1 H, CH_{furan}), 4.42 (s, 2 H, OCH$_2$), 4.33 (s, 2 H, CpCH_2), 4.24 (m, 2 H, Cp), 4.16 (m, 2 H, Cp), 4.13 (s, 5 H, Cp_{free}) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.9 ($C_{q\text{-}furan}$), 142.6, 110.1, 109.0 (C_{furan}), 82.9 ($C_{ipso\text{-}Cp}$), 69.4 (OCH$_2$), 68.5, 68.0 (Cp), 68.4 (Cp_{free}), 63.3 (Cp*C*H$_2$) ppm.

[Fc–CH$_2$-indole] (10): Complex **10** was prepared by the same procedure as that for the synthesis of **7**, **8**, and **9** by reacting **1** (110 mg, 0.51 mmol) with indole, yield 118 mg, 75%. $C_{19}H_{17}FeN$ (315.20): calcd. C 72.40, H 5.44; found C 72.52, H 5.38. ^{1}H NMR ($CDCl_3$): δ = 7.87 (br s, 1 H, NH), 7.62 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, CH_{indole}), 7.33 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, CH_{indole}), 7.18 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, CH_{indole}), 7.11 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, CH_{indole}), 6.87 (s, 1 H, CH_{indole}), 4.20 (m, 2 H, Cp), 4.16 (s, 5 H, Cp_{free}), 4.08 (m, 2 H, Cp), 3.85 (s, 2 H, CpCH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 136.2, 127.3 ($C_{q\text{-}indole}$), 121.9, 121.6, 119.2, 118.94, 116.83, 111.03 (C_{indole}), 85.0 ($C_{ipso\text{-}Cp}$), 68.7, 67.2 (Cp), 68.6 (Cp_{free}), 25.5 (Cp*C*H$_2$) ppm.

X-ray Crystallography: The crystal data and collection details for **3b** and **5a** are reported in Table 6. The asymmetric units of both crystals contain two independent molecules with almost identical geometries and bonding parameters. The diffraction experiments were performed with a Bruker APEX II diffractometer equipped with a CCD detector by using Mo–K_α radiation. The data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[35] Structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data).[36] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by using a riding model, except for the N–H groups in **5a**, which were located in the Fourier map and refined isotropically by using 1.2 times the U_{iso} value of the parent N atom. Similar U restraints (standard uncertainty 0.01) were applied to all C atoms. One Cp ring of one of the two independent molecules of **5a** is disordered and, thus, it has been split into two images and refined with one occupancy parameter. The H atoms were placed in calculated positions and treated isotropically.

Table 6. Crystal data and experimental details for **3b** and **5a**.

	3b	**5a**
Formula	$C_{17}H_{16}FeS$	$C_{17}H_{16}FeN_2O_2$
Fw	308.21	336.17
T [K]	295(2)	295(2)
λ [Å]	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	9.830(2)	11.2600(12)
b [Å]	13.265(3)	12.9225(14)
c [Å]	13.613(5)	12.9652(14)
α[°]	113.050(4)	65.7970(10)
β [°]	99.908(4)	70.5980(10)
γ [°]	108.921(3)	65.3390(10)
Cell volume [Å^3]	1451.0(7)	1533.9(3)
Z	4	4
$\sigma_{calcd.}$ [g cm^{-3}]	1.411	1.456
μ [mm^{-1}]	1.165	0.991
F(000)	640	696
Crystal size [mm]	0.16×0.14×0.10	0.25×0.44×0.18
θ limits [°]	1.73–26.00	1.76–26.00
Reflections collected	15138	15667
Independent reflections	5676 [R_{int} = 0.0257]	5977 [R_{int} = 0.0200]
Data/restraints/parameters	5676/204/343	5977/322/449
Goodness of fit on F^2	1.018	1.037
R_1 [$I>2\sigma(I)$]	0.0349	0.0318
wR_2 (all data)	0.0892	0.0878
Largest diff. peak and hole [e Å^{-3}]	0.482/–0.193	0.349/–0.197

Acknowledgments

The authors thank the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR), PRIN 09 project: Designing metal containing molecular fragments for advanced chemical applications) and the University of Bologna for financial support.

[1] a) I. T. Horvath, P. T. Anastas, *Chem. Rev.* **2007**, *107*, 2169–2173; b) R. A. Sheldon, *Chem. Soc. Rev.* **2012**, *41*, 1437–1451; c) P. T. Anastas, M. M. Kirchhoff, *Acc. Chem. Res.* **2002**, *35*, 686–694.
[2] for a recent review article see: B. Sundararaju, M. Achard, C. Bruneau, *Chem. Soc. Rev.* **2012**, *41*, 4467–4483.
[3] a) H. Hikawa, Y. Ino, H. Suzuki, Y. Yokoyama, *J. Org. Chem.* **2012**, *77*, 7046–7051; b) K. J. Miller, M. M. Abu-Omar, *Eur. J. Org. Chem.* **2003**, 1294–1299.
[4] a) Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, *J. Am. Chem. Soc.* **2002**, *124*, 11846–11847; b) Y. Nishibayashi, H. Imajima, G. Onodera, M. Hidai, S. Uemura, *Organometallics* **2004**, *23*, 26–30; c) Y. Nishibayashi, M. D. Milton, Y. Inada, M. Yoshikawa, I. Wakiji, M. Hidai, S. Uemura, *Chem. Eur. J.* **2005**, *11*, 1433–1451; d) Y. Inada, Y. Nishibayashi, S. Uemura, *Angew. Chem.* **2005**, *117*, 7893; *Angew. Chem. Int. Ed.* **2005**, *44*, 7715–7717; e) V. Cadierno, J. Díez, S. E. García-Garrido, J. Gimeno, *Chem. Commun.* **2004**, 2716–2717; f) E. Bustelo, P. H. Dixneuf, *Adv. Synth. Catal.* **2005**, *347*, 393–397.
[5] B. Biannic, A. Aponick, *Eur. J. Org. Chem.* **2011**, 6605–6617.
[6] H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, *36*, 66–77.
[7] P. Vicennati, P. G. Cozzi, *Eur. J. Org. Chem.* **2007**, 2248–2253.
[8] R. Jiang, Y. Shen, Y. Zhang, X. Xu, J. Shao, S. Ji, *Chin. J. Chem.* **2011**, *29*, 1887–1893.
[9] R. Jiang, X.-P. Xu, T. Chen, H.-Y. Li, G. Chen, S.-J. Ji, *Synlett* **2009**, *17*, 2815–2820.
[10] a) X. Xu, R. Jiang, X. Zhou, Y. Liu, S. Ji, Y. Zhang, *Tetrahedron* **2009**, *65*, 877–882; b) R. Jiang, Y. Zhang, Y. C. Shen, X. Zhu, X. P. Xu, S. J. Ji, *Tetrahedron* **2010**, *66*, 4073–4078.
[11] a) P. G. Cozzi, L. Zoli, *Green Chem.* **2007**, *9*, 1292–1295; b) P. G. Cozzi, L. Zoli, *Angew. Chem.* **2008**, *120*, 4230; *Angew. Chem. Int. Ed.* **2008**, *47*, 4162–4166.
[12] a) A. Togni, T. Hayashi, Ferrocenes: Homogeneous Catalysis, Organic Synthesis Materials Science, Wiley-VCH, Weinheim, Germany, **1995**; b) P. Stepnicka, *Ferrocenes: Ligands, Materials and Biomolecules*, Wiley, Chichester, **2008**.
[13] L. Busetto, R. Mazzoni, M. Salmi, S. Zacchini, V. Zanotti, *RSC Adv.* **2012**, *2*, 6810–6816.
[14] Selected examples include: a) *Iron Catalysis in Organic Chemistry* (Eds: B. Plietker) Wiley-VCH, Weinheim **2008**; b) A. Correa, O. G. Mancheño, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108–1117; c) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500–1511; d) R. M. Bullock, *Angew. Chem.* **2007**, *119*, 7504; *Angew. Chem. Int. Ed.* **2007**, *46*, 7360–7363; e) G. Cahiez, V. Habiak, C. Duplais, A. Moyeux, *Angew. Chem.* **2007**, *119*, 4442; *Angew. Chem. Int. Ed.* **2007**, *46*, 4364–4366; f) S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 3363; *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321; g) R. Mazzoni, M. Salmi, V. Zanotti, *Chem. Eur. J.* **2012**, *18*, 10174–10194.
[15] C. S. Combs, C. I. Ashmore, A. F. Bridges, C. R. Swanson, W. D. Stephens, *J. Org. Chem.* **1969**, *34*, 1511–1512.
[16] B. Misterkiewicz, C. Kajdas, M. Dominiak, J. Dabrowski, J. Wasilewski, *Chem. Ind.* **1981**, *12*, 433–434.
[17] M. Uher, S. Toma, *Collection Czechoslov. Chem. Commun.* **1971**, *36*, 3056–3059.
[18] B. Czech, A. Czech, S. I. Kang, R. A. Bartsch, *Chem. Lett.* **1984**, 37–40.
[19] N. Oda, T. Ueda, I. Ito, *Chem. Pharm. Bull.* **1979**, *27*, 2855–2857.
[20] a) T. Kondo, Y. Morisaki, S. Y. Uenoyama, K. Wada, T. A. Mitsudo, *J. Am. Chem. Soc.* **1999**, *121*, 8657–8658; b) A. B. Zaitsev, H. F. Caldwell, P. S. Pregosin, L. F. Veiros, *Chem. Eur. J.* **2009**, *15*, 6468–6477; c) P. Jaisankar, S. Tanaka, M. Kitamura, *J. Org. Chem.* **2011**, *76*, 1894–1897.
[21] R. Jiang, X.-Q. Chu, X.-P. Xu, B. Wu, S.-J. Ji, *Aust. J. Chem.* **2011**, *64*, 1530–1537.
[22] a) M. Ahmad, R. Bruce, G. R. Knox, *J. Organomet. Chem.* **1966**, *6*, 1–10; b) D. G. McGuire, M. A. Khan, M. T. Ashby, *Inorg. Chem.* **2002**, *41*, 2202–2208.
[23] P. M. Treichel, L. D. Rosenhein, *Inorg. Chem.* **1981**, *20*, 942–944.
[24] a) G. Guillena, D. J. Ramon, M. Yus, *Chem. Rev.* **2010**, *110*, 1611–1641; b) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703.
[25] C. M. M'thiruaine, H. B. Friedrich, E. O. Changamu, M. D. Bala, *Inorg. Chim. Acta* **2011**, *336*, 105–115.
[26] M. E. Dudley, Md. M. Morshed, C. L. Brennan, M. S. Islam, M. S. Ahmad, M.-R. Atuu, B. Branstetter, M. M. Hossain, *J. Org. Chem.* **2004**, *69*, 7599–7608.
[27] N. J. Goodwin, W. Henderson, B. K. Nicholson, J. Fawcett, D. R. Russell, *J. Chem. Soc., Dalton Trans.* **1999**, 1785–1793.
[28] N. J. Goodwin, W. Henderson, B. K. Nicholson, J. K. Sarfo, J. Fawcett, D. R. Russell, *J. Chem. Soc., Dalton Trans.* **1997**, 4377–4384.
[29] T. V. V. Ramakrishna, A. J. Elia, A. Vij, *J. Organomet. Chem.* **2000**, *602*, 125–132.
[30] a) A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066; b) A. Togni, *Angew. Chem.* **1996**, *108*, 1581; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1475–1477.
[31] a) I. R. Butler, *Eur. J. Inorg. Chem.* **2012**, 4387–4406; b) P. Barbaro, C. Bianchini, G. Giambastiani, S. L. Parisel, *Coord. Chem. Rev.* **2004**, *248*, 2131–2150; c) A. Fihri, P. Meunier, J. C. Hierso, *Coord. Chem. Rev.* **2007**, *251*, 2017–2055.
[32] a) R. Schuecker, W. Weissensteiner, K. Mereiter, M. Lotz, F. Spindler, *Organometallics* **2010**, *29*, 6443–6458; b) R. J. Kloetz-

ing, M. Lotz, P. Knochel, *Tetrahedron: Asymmetry* **2003**, *14*, 255–264.

[33] a) W. Malisch, K. Thirase, F.-J. Rehmann, J. Reising, N. Gunzelmann, *Eur. J. Inorg. Chem.* **1998**, 1589–1595; b) J. Powell, E. Fuchs, M. R. Gregg, J. Phillips, M. V. R. Stainer, *Organometallics* **1990**, *9*, 387–393; c) H. Nakazawa, Y. Ueda, K. Nakamura, K. Miyoshi, *Organometallics* **1997**, *16*, 1562–1566.

[34] H. Nakazawa, K. Kubo, C. Kai, K. Miyoshi, *J. Organomet. Chem.* **1992**, *439*, C42–C45.

[35] G. M. Sheldrick, *SADABS*, *Program for empirical absorption correction*, University of Göttingen, Germany, **1996**.

[36] G. M. Sheldrick, *SHELX97, Program for crystal structure determination*, University of Göttingen, Germany, **1997**.

Received: February 19, 2013
Published Online: June 19, 2013

