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Highly efficient reduction of ferrocenyl derivatives by borane

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Abstract

Borane, as a DMS or a THF complex, can efficiently reduce a large range of ferrocenyl derivatives (aldehydes, ketones, ethers, acetals, carboxylic acids, esters,…) if they bear at least one oxygen at a carbon at the α position. On the contrary, similar molecules, which contain nitrogen instead of oxygen, do not react with borane.

Keywords: Iron; Ferrocene; Reduction; Borane

1. Introduction

Ferrocene chemistry was revived during the last years because ferrocenyl derivatives have found numerous uses in various fields of science from biology to materials chemistry [1]. However, the main achievements with ferrocenes have been found in asymmetric catalysis [2]. During the course of our studies on ferrocenes with various substitution patterns [3,4], we observed that during the protection of a diphenylphosphinoferrocene bearing an aldehyde function by borane, the formyl group was not reduced to a hydroxymethyl group as expected [5] but to a methyl group. This unusual reactivity of borane initiated us to study the reducing power of borane on the various ferrocenyl derivatives.

2. Results and discussion

We first studied the reduction of ferrocenecarboxaldehyde by $BH_3{\cdot}SMe_2$ (see Table 1). Ferrocenecarboxaldehyde (**1a**) was quantitatively reduced into methylferrocene (**13**) even at room temperature (Table 1, entry 1). Two equivalents of borane (0.67 mol of BH_3 per mole of FcCHO) are sufficient for the complete reduction to methylferrocene (**13**) (Table 1, entry 5). Thus each of the 3 hydrogens of borane can be transferred. Further, $BH_3{\cdot}THF$ can be used instead of $BH_3{\cdot}SMe_2$ with a similar efficiency (Table 1, entry 6). Various aldehydes and ketones have been successfully reduced into the corresponding alkylferrocenes (Table 1, entries 7–13). Even hindered compounds like 2-tris(*n*-butyltin)ferrocenecarboxaldehyde (**1b**) and 2-diphenylphosphinoferrocene-carboxaldehyde (**1c**) can be quantitatively converted. In particular, 2-tris(*n*-butyltin)ferrocenecarboxaldehyde (**1b**) have been reduced without any detectable loss of the tris(*n*-butyl)tin group whereas it was completely removed by using $TiCl_4$–$NaBH_3CN$ [6] or $TiCl_4$–$HSiEt_3$ [7] as the reducing agents [8].

Borane is very active in the reduction of aldehydes or ketones. Therefore, as it is interesting to know if ferrocenyl alcohols can also be reduced to alkylferrocenes under similar conditions, various primary, secondary and tertiary α-ferrocenyl alcohols have been tested (see Table 2). Within 30 min the different alcohols were quantitatively converted into the corresponding alkylferrocenes (Table 2, entries 1–7) except for the extremely hindered ferrocenyl(*t*-butyl)methanol (**2d**) which required 4 h to be completely reduced (Table 2, entry 4). Only 1-phenyl-1-ferrocenylethanol (**2f**) could not be reduced as it had been quickly and quantitatively dehydrated to α-ferrocenylstyrene (**24**) (Table 2, entry 6). Moreover, the 2-ferrocenyl-1,2-ethanediol (**2h**) had been selectively transformed to 2-ferrocenylethanol (**26**) even in the presence of a very large excess of

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borane (Table 2, entries 8 and 9); the hydroxy group in the α position from the ferrocene is completely removed leaving the other unactivated hydroxy group untouched.

Owing to the high reducing power of the borane–methylsulfide complex, we tried other functions like ethers and acetals, which are normally not reduced by boranes [5]. These compounds, even the crowded ones, could be easily transformed to the corresponding alkylferrocenes if they bore a ferrocenyl group at the α carbon (Table 3, entries 1–4)

Borane is also known to reduce the carboxylic acids into alcohols [5] efficiently. In our study, ferrocenecarboxylic acid (**7**) was quantitatively reduced into methylferrocene (**13**) (Table 3 entry 5). Similarly, esters are known to be slowly reduced to alcohols. Therefore, the methyl ferrocenecarboxylic ester (**8**) has been tested under the same conditions; the reaction was much slower than for ferrocenecarboxylic acid but yielded exclusively methylferrocene (**13**) without traces of alcohol (Table 3 entry 6). We also tested amides and nitriles that are known to be reduced by borane to amines [5]. *N*,*N*-Dimethyl-ferrocenecarboxamide (**9**) has been quickly reduced with an excess of borane to a mixture of methylferrocene (**13**) (17%) and *N*,*N*-dimethylaminomethylferrocene (**11**) (74%) (Table 3, entry 7). First, we thought that methylferrocene was obtained from *N*,*N*-dimethylaminomethylferrocene. Therefore, increasing the reaction time, should allow more amine to be converted into methylferrocene. However, if the

Table 1
Reduction of ferrocenyl aldehydes and ketones[a]

Entry	Substrate	Borane (amount in equivalents) [b]	Reaction time	Product (yield) [c]
1	FcCHO (**1a**)	$BH_3{\cdot}SMe_2$ (12)	16 h [d]	$FcCH_3$ (**13**) (97%)
2	FcCHO (**1a**)	$BH_3{\cdot}SMe_2$ (12)	15 min	$FcCH_3$ (**13**) (96%)
3	FcCHO (**1a**)	$BH_3{\cdot}SMe_2$ (3)	1 h	$FcCH_3$ (**13**) (97%)
4	FcCHO (**1a**)	$BH_3{\cdot}SMe_2$ (3)	15 min	$FcCH_3$ (**13**) (99%)
5	FcCHO (**1a**)	$BH_3{\cdot}SMe_2$ (2.1)	15 min	$FcCH_3$ (**13**) (98%)
6	FcCHO (**1a**)	$BH_3{\cdot}THF$ (3)	15 min	$FcCH_3$ (**13**) (97%)
7	(*S*)-2-Tris(*n*-butyltin)-ferrocene-carboxaldehyde (**1b**)	$BH_3{\cdot}THF$ (3)	15 min	(*S*)-2-(Tris(*n*-butyltin)) methylferrocene (**14**) (92%)
8	(*S*)-2-Diphenylphosphino-ferrocene-carboxaldehyde (**1c**)	$BH_3{\cdot}THF$ (3)	16 h [d]	(*S*)-2-(Diphenyl(trihydridoboryl) (phosphino)methylferrocene. (**15**) (99%)
9	1,1′-Ferrocene-dicarboxaldehyde (**1d**)	$BH_3{\cdot}THF$ (6)	15 min	1,1′-Dimethylferrocene (**16**) (96%)
10	Acetylferrocene (**1e**)	$BH_3{\cdot}SMe_2$ (3)	15 min	Ethylferrocene (**17**) (99%)
11	1,1′-Diacetylferrocene (**1f**)	$BH_3{\cdot}SMe_2$ (6)	15 min	1,1'-Diethylferrocene (**18**) (99%)
12	$FcC(O)CH_2CH_2CH_3$ (**1g**)	$BH_3{\cdot}SMe_2$ (3)	15 min	$FcCH_2CH_2CH_2CH_3$ (**19**) (97%)
13	FcC(O)Ph (**1h**)	$BH_3{\cdot}SMe_2$ (3)	5 min	$FcCH_2Ph$ (**20**) (99%)

[a] Reaction conditions: in THF at reflux (concentration in substrate = ca. 0.2 mol l^{-1}).
[b] In equivalents/substrat considering 3H available on borane.
[c] Isolated yield.
[d] Reaction carried out at RT instead of THF reflux.

Table 2
Reduction of ferrocenyl alcohols[a]

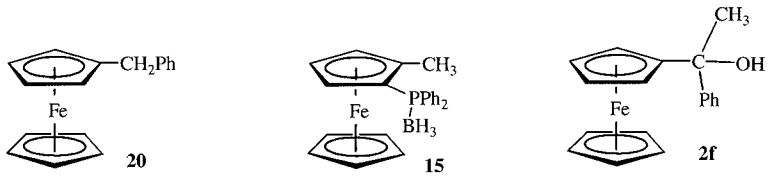
Entry	Substrate	Borane (amount in equivalents) [b]	Reaction time	Product (yield) [c]
1	$FcCH_2OH$ (**2a**)	$BH_3{\cdot}SMe_2$ (3)	15 min	$FcCH_3$ (**13**) (97%)
2	FcCHPhOH (**2b**)	$BH_3{\cdot}SMe_2$ (3)	15 min	$FcCH_2Ph$ (**20**) (98%)
3	(4-Methoxyphenyl)-ferrocenylmethanol (**2c**)	$BH_3{\cdot}SMe_2$ (3)	30 min	(4-methoxyphenyl)-ferrocenylmethane (**21**) (96%)
4	FcCH*t*-BuOH (**2d**)	$BH_3{\cdot}SMe_2$ (3)	4 h	$FcCH_2t$-Bu (**22**)(97%)
5	FcCH*n*-BuOH (**2e**)	$BH_3{\cdot}SMe_2$ (3)	30 min	$FcCH_2n$-Bu (**23**) (99%)
6	$FcC(CH_3)PhOH$ (**2f**)	$BH_3{\cdot}SMe_2$ (3)	15 min	α-ferrocenylstyrene (**24**) (98%)
7	$FcC(CH_3)_2OH$ (**2g**)	$BH_3{\cdot}SMe_2$ (3)	15 min	$FcCH(CH_3)_2$ (**25**)
8	$FcCHOHCH_2OH$ (**2h**)	$BH_3{\cdot}SMe_2$ (6)	1 h	$FcCH_2CH_2OH$ (**26**) (87%)
9	$FcCHOHCH_2OH$ (**2h**)	$BH_3{\cdot}SMe_2$ (24)	1 h	$FcCH_2CH_2OH$ (**26**) (93%)

[a] Reaction conditions: in THF at reflux (concentration in substrate = ca. 0.2 mol l^{-1}).
[b] In equivalents/substrat considering 3H available on borane.
[c] Isolated yield.

Table 3
Reduction of various ferrocenyl compounds[a]

Entry	Substrate	Borane (amount in equivalents) [b]	Reaction time	Product (yield) [c]
1	$FcCH_2OMe$ (**3**)	$BH_3{\cdot}SMe_2$ (12)	15 min	$FcCH_3$ (**13**) (93%)
2	2-Ferrocenyl-1,3-dioxane (**4**)	$BH_3{\cdot}SMe_2$ (12)	15 min	$FcCH_3$ (**13**) (96%)
3	2-Ferrocenyl-1,3-dioxolane (**5**)	$BH_3{\cdot}SMe_2$ (3)	30 min	$FcCH_3$ (**13**) (87%)
4	4-(Methoxymethyl)-2-ferrocenyl)-1,3-dioxane (**6**)	$BH_3{\cdot}SMe_2$ (12)	3 h	$FcCH_3$ (**13**) (97%)
5	FcCOOH (**7**)	$BH_3{\cdot}SMe_2$ (12)	30 min	$FcCH_3$ (**13**) (95%)
6	FcCOOMe (**8**)	$BH_3{\cdot}SMe_2$ (12)	16 h	$FcCH_3$ (**13**) (61%) FcCOOMe **8** (38%)
7	$FcC(O)NMe_2$ (**9**)	$BH_3{\cdot}SMe_2$ (12)	1 h	$FcCH_3$ (**13**) (17%) $FcCH_2NMe_2$ (**11**) (74%)
8	$FcC(O)NMe_2$ (**9**)	$BH_3{\cdot}SMe_2$ (12)	18 h	$FcCH_3$ (**13**) (18%) $FcCH_2NMe_2$ (**11**) (75%)
9	FcCN (**10**)	$BH_3{\cdot}SMe_2$ (12)	16 h	No conversion
10	$FcCH_2NMe_2$ (**11**)	$BH_3{\cdot}SMe_2$ (12)	18 h	No conversion
11	$FcCH_2NMe_3$,I (**12**)	$BH_3{\cdot}SMe_2$ (12)	18 h	No conversion

[a] Reaction conditions: in THF at reflux (concentration in substrate = ca. 0.2 mol l^{-1}).
[b] In equivalents/substrat considering 3H available on borane.
[c] Isolated yield.



Scheme 1.

reaction time was increased from 1 to 18 h, the same reaction mixture was obtained (Table 3, entry 8). Moreover, as the *N*,*N*-dimethylaminomethylferrocene (**11**) did not react with borane (Table 3, entry 11) the amine could not be reduced further to methylferrocene (**13**). Even the methylated (ferrocenylmethyl)-trimethylammonium iodide (**12**) which possesses a much better leaving group than the corresponding amine was left untouched by borane (Table 3, entry 10). Strangely, ferrocenylcyanide (**10**) which possesses a nitrile function, usually reduced by borane [5,9], did not react either (Table 3, entry 9).

During the course of our studies, crystals suitable for X-ray analysis have been obtained for benzylferrocene (**20**), 2-methyl-1-diphenyl(trihydroboryl)phosphino ferrocene (**15**) and for 1-phenyl-1-ferrocenylethanol (**2f**) (see Scheme 1).

The molecular views and the atom-labelling scheme are shown in Figs. 1–3. Important bond distances and bond angles are given in Table 4. In the three compounds mentioned above, the geometry of the ferrocene framework is as expected and the Fe–C and C–C distances are within the usual range found for such molecules. In compounds **20** and **2f**, the Cp rings are perfectly eclipsed whereas in **15** they are slightly staggered. The absolute configuration for molecule **15** was confirmed by refining Flack's enantiopole parameter [10] and agrees with the synthetic pathway used.

In compound **20** (Fig. 1) it is interesting to point out that the benzyl moiety $CH_2C_6H_5$ is pointing away from the ferrocene fragment. The dihedral angle between the phenyl ring and the corresponding Cp ring is 96.8°. Such an arrangement has been already observed in related compounds as the 1,3,1′,3′-tetrabenzylbiferrocene [11] and in the 1,1′-di(*p*-bromobenzyl)biferrocene [12].

Compound **15** (Fig. 2) presents one of the rare structural examples of a ferrocenyl phosphine bearing a BH_3 group. Indeed, to the best of our knowledge, only three structures, the (*S*,*S*)-1,1′-bis((*t*-butyl)methyl-(trihydridoboryl)phosphino) ferrocene [13], the (*S*,*S*)-1,1′-bis(2-methoxyphenyl(phenyl)(trihydridoboryl)-phosphino) ferrocene [14] and the 1,1′-bis(diphenyl(trihydridoboryl)phosphino) ferrocene [15], have been reported so far. The B–P bond length of 1.923(3) Å is comparable to the values found in the above compounds. The phosphorus atom lies 0.124 Å above the plane of the Cp ring whereas the boron atom is displaced by 0.912 Å out of this plane towards the iron. This displacement of the boron towards the iron is

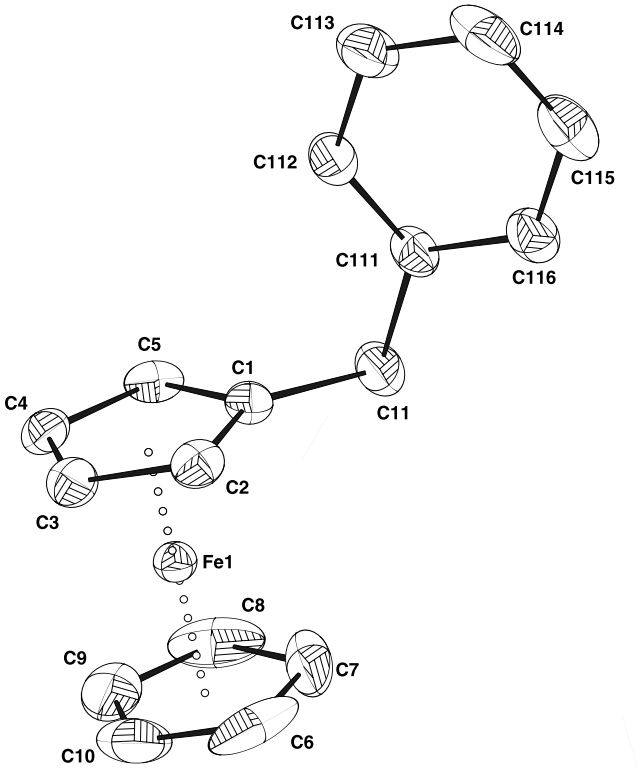


Fig. 1. CAMERON view of molecule **20** with atom labelling scheme. Ellipsoids are drawn at 50% probability.

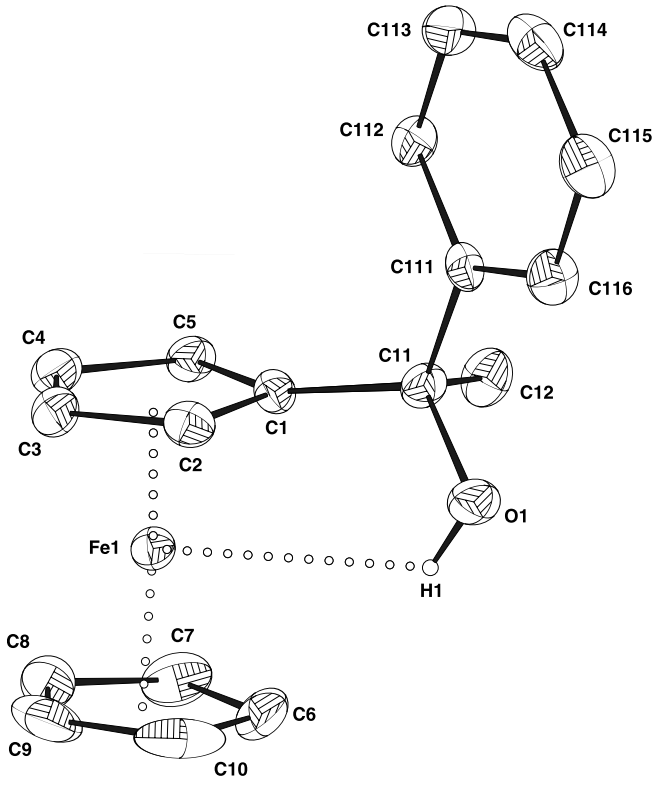


Fig. 3. CAMERON view of molecule **2f** with atom labelling scheme. Ellipsoids are drawn at 50% probability.

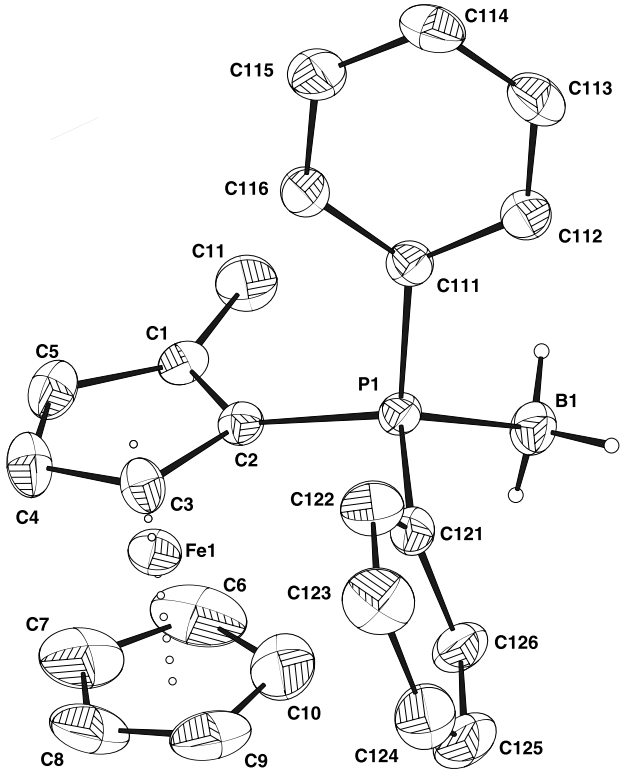


Fig. 2. CAMERON view of molecule **15** with atom labelling scheme. Ellipsoids are drawn at 50% probability.

certainly responsible for the slightly staggered conformation (13.5°) of the Cp rings. Nevertheless, there is a short H–H contact of 2.36 Å between one of the H of the BH_3 group and the H attached to the C(10) atom of the Cp ring below.

In compound **2f** (Fig. 3), there is an unusual intramolecular hydrogen bond between the OH group and the iron as shown not only by the relative orientation of the OH towards the iron but also by the rather short 2.94(3) Å Fe···H distance. This distance is less than the sum of the van der Waals radii (3.77 Å) but definitely more than the sum of the covalent radii (1.75 Å) typical of a weak interaction. This Fe···H interaction is confirmed by the larger dihedral angle, 4.31°, observed between the Cp ring when compare with the values of 0.8 and 1.1° observed in compounds **20** and **15**, respectively. This Fe···H interaction is a good illustration of the basicity of the iron atom in ferrocenes [16]. To the best of our knowledge, there is only one structural example of such intramolecular interaction between a hydroxy group and an iron atom (d_{Fe-H} = 2.99(3) Å) in the η^4-α-[(R_S)-(1*Z*,3*E*)-3-[(*R*)-1-hydroxy-but-3-enyl]-1-*p*-tolylsulfinyl-1,3-pentadien-5-ol]-tricarbonyl-iron(0) complex [17].

In conclusion, borane, as a THF or SMe_2 complex, can efficiently reduce a large range of α-ferrocenyl compounds (aldehydes, ketones, alcohols, carboxylic acids, esters, ethers, acetals,…) to the corresponding

Table 4
Important bond lengths (Å) and bond angles (°)

Compound **20**			
Bond lengths			
C(1)–C(2)	1.417(3)	C(6)–C(7)	1.412(5)
C(1)–C(5)	1.426(3)	C(6)–C(10)	1.365(4)
C(2)–C(3)	1.422(3)	C(7)–C(8)	1.422(4)
C(3)–C(4)	1.413(3)	C(8)–C(9)	1.374(4)
C(4)–C(5)	1.418(3)	C(9)–C(10)	1.344(4)
C(1)–C(11)	1.498(3)	C(11)–C(111)	1.513(3)
Bond angles			
C(2)–C(1)–C(11)	124.97(19)	C(5)–C(1)–C(11)	127.85(18)
C(11)–C(111)–C(112)	121.98(18)	C(11)–C(111)–C(116)	119.26(18)
C(1)–C(11)–C(111)	114.84(16)		
Compound **15**			
Bond lengths			
P(1)–C(111)	1.817(3)	P(1)–C(121)	1.824(3)
P(1)–B(1)	1.923(3)	P(1)–C(2)	1.784(3)
C(1)–C(2)	1.449(4)	C(6)–C(7)	1.378(7)
C(1)–C(5)	1.426(4)	C(6)–C(10)	1.452(7)
C(2)–C(3)	1.439(3)	C(7)–C(8)	1.382(6)
C(3)–C(4)	1.402(4)	C(8)–C(9)	1.355(6)
C(4)–C(5)	1.411(5)	C(9)–C(10)	1.400(7)
C(1)–C(11)	1.488(4)		
Bond angles			
B(1)–P(1)–C(2)	120.38(14)	B(1)–P(1)–C(121)	111.83(14)
B(1)–P(1)–C(111)	109.61(14)	C(2)–P(1)–C(121)	104.11(12)
C(2)–P(1)–C(111)	104.09(12)	C(111)–P(1)–C(121)	105.63(12)
P(1)–C(111)–C(112)	119.7(2)	P(1)–C(111)–C(116)	122.2(2)
C(2)–C(1)–C(11)	127.0(3)	C(5)–C(1)–C(11)	126.2(3)
P(1)–C(2)–C(1)	127.7(2)	P(1)–C(2)–C(3)	125.0(2)
P(1)–C(121)–C(122)	122.2(2)	P(1)–C(121)–C(126)	119.4(2)
Compound **2f**			
Bond length			
C(1)–C(2)	1.431(3)	C(6)–C(7)	1.411(4)
C(1)–C(5)	1.431(3)	C(6)–C(10)	1.424(5)
C(2)–C(3)	1.423(3)	C(7)–C(8)	1.370(4)
C(3)–C(4)	1.429(4)	C(8)–C(9)	1.394(4)
C(4)–C(5)	1.416(3)	C(9)–C(10)	1.407(4)
O(1)–C(11)	1.438(2)	C(1)–C(11)	1.501(3)
C(11)–C(12)	1.527(3)	C(11)–C(111)	1.515(3)
O(1)–H(1)	0.84(3)	H(1)–Fe(1)	2.94(3)
Bond angles			
O(1)–C(11)–C(1)	109.95(15)	O(1)–C(11)–C(12)	108.4(2)
C(2)–C(1)–C(11)	124.69(18)	C(1)–C(11)–C(12)	111.82(18)
C(5)–C(1)–C(11)	128.09(19)	O(1)–C(11)–C(111)	106.88(16)
C(1)–C(11)–C(111)	109.4(2)	C(12)–C(11)–C(111)	110.19(16)
C(11)–C(111)–C(112)	119.43(18)	C(11)–C(111)–C(116)	122.67(19)
C(11)–O(1)–H(1)	107.3(22)	Fe(1)–H(1)–O(1)	123.2(26)

alkylferrocenes. This new method is a mild and efficient alternative to the existing methods [6,7,18]. Further, the procedure has been extended successfully to new substrates (carboxylic acids, esters, ethers, acetals, etc.). On the contrary, equivalent nitrogen containing molecules (nitriles, amines, ammoniums, etc.) do not react with borane. Only, amides have been partially reduced (up to 18%) to methylferrocene.

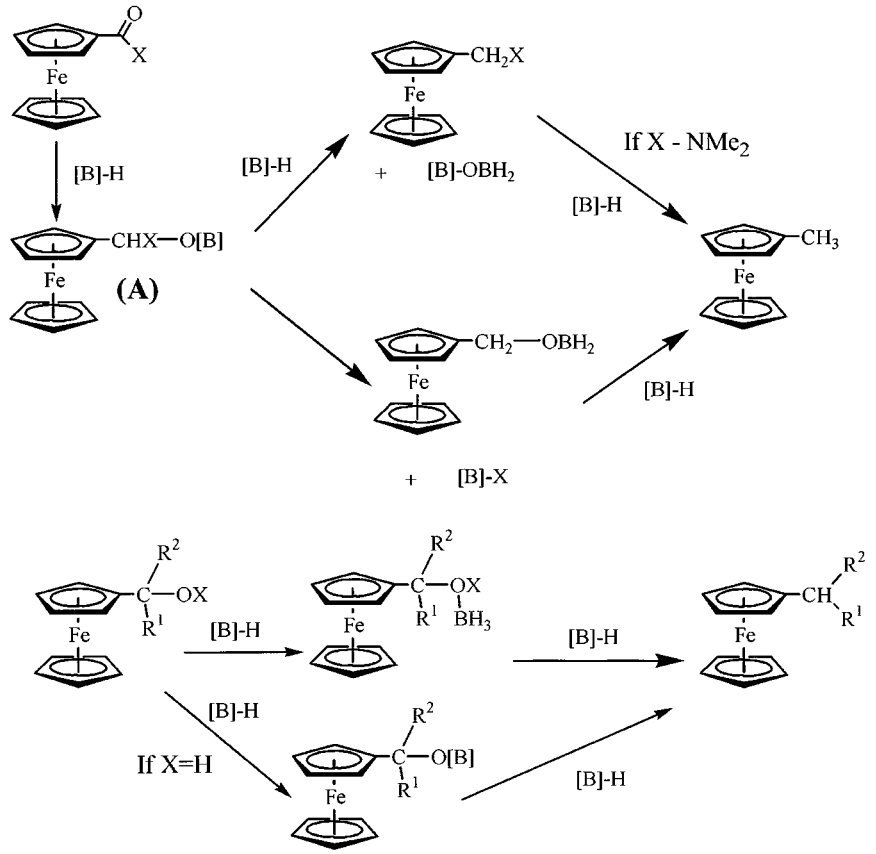
In the reduction of aldehydes, ketones, carboxylic acids or esters, borates are the probable intermediates which can be reduced to alkylferrocenes. In the case of alcohols, borates can also be reactive intermediates (see Scheme 2) but the complexation of borane on the oxygen of the alcohols could be responsible for the activation of the C–O bond towards reduction. These type of intermediates are, for us, the most probable for the molecules lacking an hydroxy group, namely ethers and acetals. For *N*,*N*-dimethylferrocenecarboxamide, we proved that methylferrocene did not come from a reduction of *N*,*N*-dimethylaminomethylferrocene so we proposed that a common intermediate (A) can be reduced to methylferrocene or *N*,*N*-dimethylaminomethyl ferrocene in 18:74 ratio (see Scheme 2).

3. Experimental

Ferrocenecarboxaldehyde (**1a**), 1,1′-dimethylferrocene (**16**), acetylferrocene (**1e**), ethylferrocene (**17**), 1,1′-diacetylferrocene (**1f**), butyrylferrocene (**1g**), butylferrocene (**19**), benzoylferrocene (**1h**), ferrocenecarboxylic acid (**7**), ferrocenylmethanol (**2a**), dimethylamino-methylferrocene (**11**), ferrocenylmethyltrimethylammonium iodide (**12**) are commercially available and have been used without further purification. 2-Tris(*n*-butyltin)ferrocenecarboxaldehyde (**1b**), 2-(diphenylphoshino)-ferrocenecarboxaldehyde (**1c**), 1,1′-ferrocenedicarboxaldehyde (**1d**), 1-phenyl-1-ferrocenylethanol (**2f**), ferrocenyl-1,2-ethane-diol (**2h**), 2-ferrocenyl-1,3-dioxane (**4**), 2-ferrocenyl-1,3-dioxolane (**5**), 4-(methoxymethyl)-2-ferrocenyl)-1,3-dioxane (**6**), ferrocenylnitrile (**10**) have been synthesised following well-known procedures outlined in Refs. [19–24]. (Phenyl)ferrocenylmethanol (**2b**), (4-methoxyphenyl)ferrocenylmethanol (**2c**), (*n*-butyl)ferrocenylmethanol (**2e**) and (*t*-butyl)ferrocenylmethanol (**2d**) have been synthesised with an almost quantitative yield by the action of an alkyl or aryllithium on ferrocenecarboxaldehyde. Their physical data are identical with the published data or given below [25–27]. Methylferrocenecarboxylate (**8**) and *N*,*N*-dimethylferrocenecarboxamide (**9**) have been, respectively, synthesised by the action of FcC(O)Cl on methanol (Yield: 98%) or Me_2NH_2Cl (Yield: 95%). The NMR data are identical with those from the literature [28,29]. Methylferrocene (**13**), benzylferrocene (**20**), *i*-propylferrocene (**25**), 4-methoxyphenylmethylferrocene (**21**), 2-ferrocenylethanol (**26**), 1-ferrocenylstyrene (**24**) have been identified by comparing with the published data [30–33].

3.1. (S)-2-(Tributylstannyl)methylferrocene (14)

^{1}H-NMR ($CDCl_3$): δ 4.22 (m, 1H, subst Cp), 4.20 (t, $J = 2.2$ Hz, 1H, subst Cp), 4.04 (s, 5H, Cp), 3.89 (dd, 1H, $J = 2.2$ Hz and $J = 0.8$ Hz, subst Cp), 1.96 (s, 3H,



Scheme 2.

CH_3), 1.65–0.75 (m, 29H, *n*-Bu). ^{13}C-NMR ($CDCl_3$): δ 89.5 ($J_{Sn-C} = 40.5$ Hz, quat Cp), 73.9 ($J_{Sn-C} = 44$ Hz, subst Cp), 71.5 ($J_{Sn-C} = 32.3$ Hz, subst Cp), 70.3 ($J_{Sn-C} = 140$ Hz, quat Cp), 69.5 ($J_{Sn-C} = 36.6$ Hz, subst Cp), 68.5 (Cp), 29.3 ($J_{Sn-C} = 19.0$ Hz, CH_2), 27.5 ($J_{Sn-C} = 59.4$ Hz, CH_2), 16.4 (CH_3), 13.7 (CH_3 (*n*-Bu)), 10.3 ($J_{119Sn-C} = 345.5$ Hz and $J_{117Sn-C} = 330.3$ Hz, CH_2). $[\alpha]_D$ + 29.0° (*c* 0.5, $CHCl_3$). MS; *m*/*e* (DCI, NH_3): 490 (M + 1, 13%), 433(M − *n*-Bu, 29%), 291 ($SnBu_3$, 100%).

3.2. (S)-2-(Diphenyl(trihydridoboryl)phosphino)-methylferrocene (**15**)

^{1}H-NMR ($CDCl_3$): δ 7.7–7.6 (m, 2H, Ph), 7.5–7.4 (m, 8H, Ph), 4.43 (m, 1H, subst Cp), 4.29 (t, $J = 2.4$ Hz, 1H, subst Cp), 4.24 (s, 5H, Cp), 3.77 (br dd, 1H, $J = 2.4$ Hz and $J = 1.5$ Hz, subst Cp), 2.04 (s, 3H, CH_3).^{13}C-NMR ($CDCl_3$): δ 133.5 ($J_{P-C} = 9.4$ Hz, Ph),133.0 ($J_{P-C} = 9.4$ Hz, Ph), 131.4 ($J_{P-C} = 57.8$ Hz, quat Ph), 131.3 ($J_{P-C} = 2.3$ Hz, Ph), 131.2 ($J_{P-C} = 2.2$ Hz, Ph), 131.1 ($J_{P-C} = 59.4$ Hz, quat Ph), 128.9 ($J_{P-C} = 10.0$ Hz, Ph), 128.7 ($J_{P-C} = 10.0$ Hz, Ph), 89.3 ($J_{P-C} = 13.5$ Hz, quat Cp), 74.6 ($J_{P-C} = 7.6$ Hz, subst Cp), 73.4 ($J_{P-C} = 6.3$ Hz, subst Cp), 70.8 (Cp), 69.6 ($J_{P-C} = 6.8$ Hz, subst Cp), 69.0 ($J_{P-C} = 66.0$ Hz, quat Cp), 15.2 (CH_3). ^{31}P-NMR ($CDCl_3$): δ 18.8. ^{11}B-NMR ($CDCl_3$): δ − 36.5. $[\alpha]_D$ − 23.2° (*c* 0.5, $CHCl_3$). MS; *m*/*e* (DCI, NH_3): 416 ([M + 18], 100%).

3.3. (n-Butyl)ferrocenylmethanol (**2e**)

^{1}H-NMR ($CDCl_3$): δ 4.30 (ddd, $J = 7.2$ Hz, 5.3 Hz and $J = 3.2$ Hz, 1H, subst Cp), 4.23 (dd, $J = 3.3$ Hz and $J = 1.5$ Hz, 1H, subst Cp), 4.19 (s, 5H, Cp), 4.16 (m, 3H, subst Cp + CHOH), 1.93 (d, $J = 3.2$ Hz, 1H, OH), 1.7–1.5 (m, 2H, CH_2), 1.5–1.25 (m, 4H, CH_2), 0.88 (t, $J = 3.2$ Hz, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 93.9 (quat Cp), 69.2 (subst Cp), 67.9 (Cp), 67.5 (subst Cp), 67.3 (subst Cp), 65.1 (subst Cp), 67.5 (subst Cp), 37.5 (CH_2), 27.9 (CH_2), 22.3 (CH_2), 13.9 (CH_3). MS; *m*/*e* (DCI, NH_3): 255 ([M − 17], 100%).

3.4. Pentylferrocene (**23**)

^{1}H-NMR ($CDCl_3$): δ 4.08 (s, 5H, Cp), 4.03 (m, 4H, subst Cp), 2.30 (t, $J = 7.3$ Hz, 2H, CH_2), 1.55–1.4 (m, 2H, CH_2), 1.35–1.25 (m, 4H, CH_2), 0.88 (t, $J = 6.7$ Hz, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 89.5 (quat Cp), 68.4 (Cp), 68.0 (subst Cp), 66.9 (subst Cp), 31.8 (CH_2), 30.8 (CH_2), 29.5 (CH_2), 22.5 (CH_2), 14.1 (CH_3). MS; *m*/*e* (DCI, NH_3): 257 ([M + 1], 100%).

Table 5
Crystal data

	20	**15**	**2f**
Formula	$C_{17}H_{16}Fe$	$C_{22}H_{24}BFeP$	$C_{18}H_{18}FeO$
Formula weight	276.15	398.08	306.19
Shape (color)	Box (orange)	Box (orange)	Flattened (yellow)
Size (mm)	$0.76\times0.62\times0.40$	$0.50\times0.34\times0.22$	$0.50\times0.45\times0.15$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	$P2_12_12_1$	$Pna2_1$
Unit cell dimensions			
a (Å)	7.5357(5)	8.8597(8)	19.267(4)
b (Å)	10.7831(7)	14.885(2)	5.882(1)
c (Å)	32.079(3)	15.614(2)	12.127(2)
V (Å^3)	2606.7(3)	2059.1(4)	1374.3(4)
Z	8	4	4
ρ_{calc} (g cm^{-3})	1.407	1.284	1.480
$F(000)$	1154	833	641
μ (Mo–K$_\alpha$) (cm^{-1})	11.341	8.132	10.891
2θ Range (°)	$4.6<2\theta<52.0$	$5.9<2\theta<61.1$	$5.4<2\theta<52.1$
Reflections collected	14 314	30 989	8489
Unique reflections	2512	6005	2645
Merging factor (R_{int})	0.0384	0.068	0.0467
Reflections observed ($I>2\sigma(I)$)	2163	3029	2333
R indices	0.0330	0.0283	0.0301
R_w	0.0414	0.0311	0.0310
Weighting scheme	Chebyshev	Chebyshev	Chebyshev
Coefficient A_r	1.70, 0.37, 1.31	1.24, −0.49, 0.76	2.28, 0.49, 2.06
(Δ/σ)max	0.045	0.056	0.02
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.46/0.35	−0.38/0.34	−0.66/0.74
Flack's parameter		0.00(2)	0.00(1)
Goodness-of-fit on F^2	0.976	1.052	0.991
Variable parameters	164	237	187

3.5. (2,2-Dimethylpropyl)ferrocene (**22**)

^{1}H-NMR ($CDCl_3$): δ 4.07 (s, 5H, Cp), 4.03 (m, 4H, subst Cp), 2.24 (s, 2H, CH_2), 0.80 (s, 9H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 85.6 (quat Cp), 70.2 (subst Cp), 68.5 (Cp), 67.2 (subst Cp), 45.0(CH_2), 31.7 ($C(CH_3)_3$), 29.3 (CH_3). MS; *m*/*e* (DCI, NH_3) m/e: 257 ([M + 1], 100%).

3.6. 2-Ferrocenyl-1,3-dioxane (**4**)

^{1}H-NMR ($CDCl_3$): δ 5.35 (s, 1H, OCHO), 4.30 (t, $J = 1.9$ Hz, 2H, subst Cp), 4.20(m, 2H, CH_2O), 4.17 (s, 5H, Cp), 4.11 (t, $J = 1.9$ Hz, 2H, subst Cp), 3.90 (td, $J = 2.5$ Hz and 12.3 Hz, 2H, CH_2O), 2.13 (m, 1H, CH_2), 1.37 (m, 1H, CH_2). ^{13}C-NMR ($CDCl_3$): δ 100.5 (OCHO), 86.1 (quat Cp), 68.8 (Cp), 67.9 (subst Cp), 67.3 (subst Cp), 66.4 (OCH_2), 25.8(CH_2). MS; *m*/*e* (DCI, NH_3): 273 ([M + 1], 100%).

3.7. X-ray crystal structure determination

For all the three compounds **20**, **15** and **2f**, the data were collected on a STOE IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 8000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

The three structures were solved by direct methods (SIR97) [34] and refined by least-squares procedures on *F*. All H atoms were located on difference Fourier syntheses. Those attached to carbon were introduced for calculations in idealised positions (d(CH) = 0.96 Å) and their atomic coordinates were recalculated after each cycle with an isotropic thermal parameter 20% higher than those of the carbon to which they are attached. The atomic and isotropic thermal parameters for the H atom attached to oxygen in **2f** were refined. The absolute configuration for **15** and the absolute structure for **2f** were determined by refining Flack's enantiopole parameter [10]. Least-squares refinements were carried out by minimising the function $\Sigma w(|F_o| - |F_c|)$, where F_o and F_c are the observed and calculated structure factors, respectively. The weighting scheme used in the last refinement cycles was $w = w'[1 - \{\Delta F/6\sigma(F_o)\}^2]^2$ where $w' = 1/\Sigma_1^n A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was F_c/F_c (max) [35]. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, having values listed in Table 5.

The calculations were carried out with the CRYSTALS package programs [36]. Molecular view was realised with the help of CAMERON [37].

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 154785, 154786 and 154787. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

5. Note added in proof

During the processing of this paper, another article also describing the reduction of ferrocenyl compounds by borane appeared [38].

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References

[1] A. Togni, T. Hayashi, Ferrocenes, VCH, Weinheim, 1995.
[2] (a) S. Borman, Chem. Eng. News July 22 (1996) 38;
(b) A. Togni, Angew. Chem. Int. Ed. Engl. 35 (1996) 1475.
[3] (a) G. Iftime, C. Moreau-Bossuet, E. Manoury, G.G.A. Balavoine, J. Chem. Soc. Chem. Commun. (1996) 527;
(b) G. Iftime, J.-C. Daran, E. Manoury, G.G.A. Balavoine, Organometallics 15 (1996) 4808.
[4] (a) G. Iftime, J.-C. Daran, E. Manoury, G.G.A. Balavoine, J. Organomet. Chem. 565 (1998) 115;
(b) G. Iftime, J.-C. Daran, E. Manoury, G.G.A. Balavoine, C. Moreau-Bossuet, J. Organomet. Chem. 567 (1998) 191;
(c) G. Iftime, J.-C. Daran, E. Manoury, G.G.A. Balavoine, Angew. Chem. Int. Ed. Engl. 37 (1998) 1698.
[5] H.C. Brown, S. Krishnamurty, Tetrahedron 35 (1979) 567.
[6] S. Bhattacharyya, Synlett (1995) 971.
[7] S. Bhattacharyya, J. Org. Chem. 63 (1998) 7101.
[8] J. Chiffre, G.G.A. Balavoine, J.-C. Daran, E. Manoury, unpublished results.
[9] H.C. Brown, Y.M. Choi, S. Narasimhan, J. Org. Chem. 47 (1982) 3153.
[10] (a) H.D. Flack, Acta Crystallogr. Sect. A 39 (1983) 876;
(b) G. Bernardinelli, H.D. Flack, Acta Crystallogr. Sect. A 41 (1985) 500.
[11] T.-Y. Dong, S.-H. Lee, C.-K. Chang, H.-M. Lin, K.-J. Lin, Organometallics 16 (1997) 2773.
[12] T.-Y. Dong, C.-C. Schei, M.-Y. Hwang, T.-Y. Lee, J. Organomet. Chem. 410 (1991) C39.
[13] H. Tsuruta, T. Imamoto, Tetrahedron: Asymmetry 10 (1999) 877.
[14] F. Maienza, M. Worle, P. Steffanut, A. Mezzetti, F. Spindler, Organometallics 18 (1999) 1041.
[15] K.J. Donaghy, P.J. Carroll, L.G. Sneddon, Inorg. Chem. 36 (1997) 547.
[16] J.J. Curphey, J.O. Santer, M. Rosenblum, J.H. Richards, J. Am. Chem. Soc. 82 (1960) 5249.
[17] R.S. Paley, L.A. Estroff, D.J. McCulley, L.A. Martinez-Cruz, A.J. Sanchez, F.H. Cano, Organometallics 17 (1998) 1841.
[18] (a) H. Patin, R. Dabard, Tetrahedron Lett. (1969) 4971;
(b) S. Bhattacharyya, J. Chem. Soc. Dalton Trans. (1996) 4617;
(c) S. Bhattacharyya, Organometallics 15 (1996) 1065.
[19] O. Riant, O. Samuel, T. Flessner, S. Taudien, H.B. Kagan, J. Org. Chem. 62 (1997) 6733.
[20] G.G.A. Balavoine, G. Doisneau, T. Fillebeen-Khan, J. Organomet. Chem. 412 (1991) 381.
[21] G. Ferguson, J.F. Gallagher, C. Glidewell, C.M. Zakaria, J. Organomet. Chem. 464 (1994) 95.
[22] W.G. Jary, J. Baumgartner, Tetrahedron: Asymmetry 9 (1998) 2081.
[23] G.D. Broadhead, J.M. Osgerby, P.L. Pauson, J. Chem. Soc. (1958) 650.
[24] G.R. Knox, P.L. Pauson, D. Willison, E. Solcaniova, S. Toma, Organometallics 9 (1990) 301.
[25] S. Kovac, V. Rapic, J. Organomet. Chem. 384 (1990) 147.
[26] M. Asahara, S. Natsume, H. Kurihara, T. Yamaguchi, T. Erabi, M. Wada, J. Organomet. Chem. 601 (2000) 246.
[27] G. Neshvad, R.M.G. Roberts, J. Silver, J. Organomet. Chem. 260 (1984) 319.
[28] M. Heberhold, A. Kniesl, J. Organomet. Chem. 334 (1987) 347.
[29] P. Bickert, B. Hildebrandt, K. Hafner, Organometallics 3 (1984) 653.
[30] A.N. Nesmeyanov, N.S. Kotchekova, E.V. Leonova, E.I. Fedin, P.V. Petrovskii, J. Organomet. Chem. 39 (1972) 173.
[31] W.R. Cullen, S.V. Evans, N.F. Han, J. Trotter, Inorg. Chem. 26 (1987) 514.
[32] W. Reeve, E.F. Group Jr., J. Org. Chem. 32 (1967) 122.
[33] G.W. Gokel, J.P. Shepherd, W.P. Weber, H.G. Boettger, J.L Holwick, D.J. Mc Adoo, J. Org. Chem. 38 (1973) 1913.
[34] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[35] E. Prince, Mathematical Techniques in Crystallography, Springer, Berlin, 1982.
[36] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, CRYSTALS Issue 11, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1999.
[37] D.J. Watkin, C.K. Prout, J.R. Carruthers, L.J. Pearce, CAMERON, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1996.
[38] D.-H. Kim, E.-S. Ryu, C.S. Cho, S.C. Shim, H.-S., T.-J. Kim, Organometallics 19 (2000) 5784.