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ARTICLE TYPE

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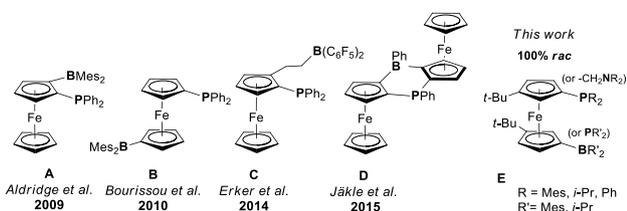
Emmanuel Lerayer,^a Patrice Renault,^a Julien Roger,^a Nadine Piriou,^a H el ene Cattey,^a Charles H. Devillers,^{*a} Dominique Lucas^a and Jean-Cyrille Hierso^{*a,b}

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A general synthesis of highly functionalized ferrocenes, which includes (P, B)- and (N, B)-ambiphiles has been developed at multigram scale. Diastereoselective stepwise modification of di-*tert*-butylated ferrocene included the unprecedented separation of electroactive species. Bulky alkyl groups on ferrocene insure planar chirality of ambiphiles and enforce closer proximity of antagonist Lewis functions.

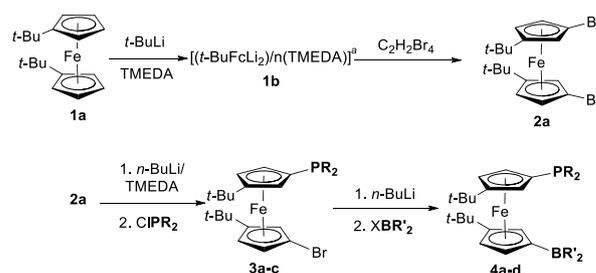
15 Ambiphilic derivatives are molecular systems that combine electron donor and acceptor groups on a common platform. These compounds have prompted much recent interest and their study represents a very active field in main-group chemistry.¹ Applications include their use as ligands for transition metals towards uncommon coordination modes,² and the activation and transfer of small molecules including CO₂ and H₂,³ a reactivity which is usually associated to transition metals. The synthesis of a growing variety of (P, B)- and (N, B)-ambiphiles is relating to modifications in the substitution pattern at Lewis functions,⁴ and in the structure of supporting platform.⁵ With respect to spacers, organic linkers are generally preferred and only a few metallocene-bridged phosphine-borane derivatives have been reported (representative examples are depicted in Figure 1).



³⁰ Figure 1 Representative ferrocene-bridged phosphine-borane ambiphiles.

Aldridge and Bourissou groups reported the preparation of Ph₂P–(1,2-ferrocenyl)–BMe₂ **A** (Mes = 2,4,6-trimethylphenyl),⁶ and the position isomer Ph₂P–(1,6-ferrocenyl)–BMe₂ **B**, respectively.⁷ Based on the ferrocene platform other cousin structures were also reported (**C** and **D**).^{8–9} The flexible phosphine-borane **B** and the related *o*-phenylene bridged system have been evaluated in rhodium-catalysed hydroformylation.⁷ This pioneering work highlighted the structuring potential of 1,1'-ferrocene platform for (P, B)-pairs. Marinetti and Cantat used afterwards ferrocene **B** as catalysts for the hydroboration of CO₂.¹⁰ Diaconescu *et al.* additionally exploited the ferrocene

platform to yield heteroscorpionate ferrocenylphosphine borate compounds made from the synthesis of the ambiphilic precursor Fc(PPh₂)(BOMe₂) and Li chelated derivatives.¹¹ In this context, further extension of this class of ambiphiles is highly desirable. We address herein this challenging issue by introducing a greater modularity in substitution pattern at P and B atoms. Further functionalization at ferrocene introduces novel properties such as planar chirality and backbone steric control. Steric control permits the P...B distance and the rotational rigidity of the platform to be tuned. Our group had designed highly functionalized ferrocenyl polyphosphines incorporating di-*tert*-butylated and *gem*-dimethylated substitution. Such sterically controlled ligands were exploited in palladium-catalysed C–H bonds functionalization.¹² We envisioned that ferrocenyl ambiphilic analogues could be developed by the incorporation of *tert*-butyl groups to the metallocene backbone (**E**, Figure 1). A general approach would allow extending the synthesis to new bifunctional analogues (N/B),¹³ (P/N),¹⁴ and (P/P').¹⁵ We report herein this method that we scaled-up at multigram scale by the electrochemical purification of the essential intermediate di-*tert*-butyl-dibromoferrocene. Ambiphiles of type **E** were prepared by sequential lithiation/electrophilic trapping from 1,1'-dibromo-3,3'-di-*tert*-butyl-ferrocene **2a** (Scheme 1). We found this synthetic pathway to be more efficient than assembling from *tert*-butylated boryl cyclopentadienides, which is also feasible.^{16,17}



⁷⁰ Scheme 1 Synthesis of *tert*-butylated ambiphiles **4a-d**. ^a In THF-d₈ **1b** appeared from ¹H NMR as *ca.* 1:1 adduct (see ESI), under other conditions it was described as a 1:1.5 organolithium/TMEDA adduct.^{18b}

We patented the diastereoselective road for synthesizing **2a** (Scheme 1) in yields up to 93% at the 1 mmol scale.¹⁸ Planar chiral (*rac*) 1,1'-di-*tert*-butyl-ferrocene **2a** had been obtained by using an excess of 1,1,4,4-tetrabromoethane in Et₂O. We then sought at establishing efficient procedures for the preparation of

hybrid bifunctional ferrocenes **E** on a much larger scale. While the general method was found to be convenient at 1 mmol scale, synthesis of **2a** via the bromination of *ca.* 30 mmol of dilithiated-TMEDA complex **1b** showed repeatability troubles. We mainly observed the presence in detrimental amounts of unreacted 1,1'-di-*tert*-butyl-ferrocene **1a** (up to 25 mol%) and monobrominated 1-bromo-3,3'-di-*tert*-butyl-ferrocene **2b** (up to 28 mol%). The separation by chromatography of **1a**, **2b** and **2a** was found to be tedious because of similar retention times on the silica and alumina we tested. We turned our attention to an oxidative purification of **2a** from its mixture with **1a** and **2b**. The purification of ferrocene derivatives mixture by chemical redox processes has been described.¹⁹ Chemical oxidative separation has been exploited with haloferrocenes FcX_n ($X = \text{I, Br, Cl}$ and F , $n = 0-2$) using aqueous FeCl_3 . The aqueous phase contains then ferrocenium species whereas nonoxidized haloferrocenes remains in the organic phase. Several washings procedures are necessary, and the solvent volume used and the concentration of FeCl_3 must be finely adjusted to avoid overoxidation of the targeted haloferrocene and contamination by undesired ferrocene products. In our hands, chemical oxidation applied on large-scale amounts of ferrocenes (10-20 mmol) was unproductive because of the formation of persistent emulsion phases hampering facile phase separation. We thus imagined the development of a large-scale oxidative purification by electrocatalysis,²⁰ to overcome the drawbacks associated with the use of chemical oxidant. An additional benefit is the control of the applied potential for tuning the accuracy of oxidative reactions. We achieved electrochemical oxidative purification of **2a** by a selective oxidation of the undesired **1a** and **2b** in the reaction mixture. These ferrocene side-products exhibit less positive oxidation potential due to their deficit in electron-withdrawing bromine atoms in comparison to **2a**. Accordingly for **1a**, **2b** and **2a**, we found $E_{1/2} = 0.346$, 0.524 and 0.682 V vs. SCE, respectively (Fig. 2, see also in ESI, Fig. S5 and Table S2). Under these conditions ones add -0.400 V for $E_{1/2}$ values vs. Fc^+/Fc . As expected, the resulting oxidized ferrocenium species **1a**⁺ and **2b**⁺ have low solubility in organic solvents compared to **2a**.

A typical initial crude solid (CS_0 , $m = 22.40$ g) resulting from large-scale synthesis of **2a** starting with 29.9 mmol of the dilithiated-TMEDA complex **1b** contained **1**, **2b** and **2a** in 24, 28 and 48 mol% ratio, respectively (Fig. S1, Table S1, in ESI). CS_0 was also contaminated with residual 1,1,4,4-tetrabromoethane (^1H NMR in C_6D_6 , $\delta = 5.08$) and other side-products ($\delta = 6.30$) assigned to *trans*-1,2-dibromoethene (Figure S2). These impurities are present in low amount and did not perturb the electrolytic process. Electrochemical purification of **2** was achieved on small scale of CS_0 (*ca.* $m = 150$ mg, 0.2 mmol) with CH_3CN and 0.1 M of tetraethylammonium tetrafluoroborate (TEABF_4). To reach a satisfactory purity of **2a**, E_{app} was applied at an intermediate value between the $E_{1/2}$ of **2b** and **2a** and allowed a complete transformation of remaining **1a** and side-product **2b** into **1**⁺ and **2b**⁺ (Scheme 2). We first adjusted E_{app} at 0.600 V for electrolysis. After reaction completion and solvent removal from anodic compartment, *n*-pentane extraction allowed eliminating the insoluble **1a**⁺ and **2b**⁺ by filtration. Purity of **2a** reached 90.6% with a contamination of **2b** (9.4%, molar ratio of ferrocenes); we did not detect **1a** or supporting electrolyte.

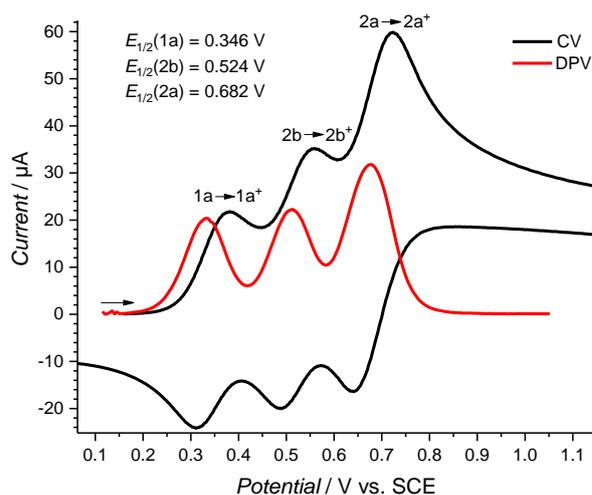
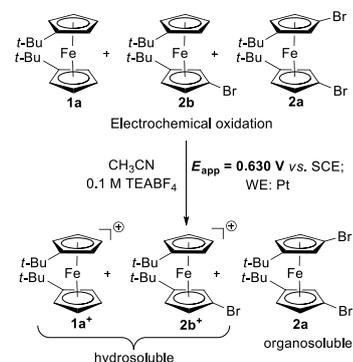


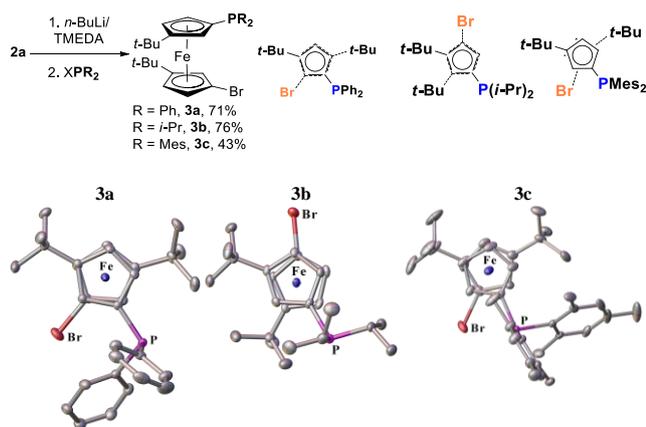
Figure 2 Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of a solution of CS_0 ($m = 150$ mg), $[\mathbf{2}] = 4.8 \times 10^{-3}$ M in CH_3CN 0.1 M TEABF_4 ; $v = 100$ mV/s and 10 mV/s for CV and DPV, respectively, WE: Pt.



Scheme 2 Electrochemical purification for **2a**.

We thus raised E_{app} at 0.630 V to reach purity of **2a** above 97% (**2b** was present in less than 3%, see Figure S2-S4, ESI). Electrolysis on 21.70 g of CS_0 at 0.630 V ($[\mathbf{2a}] = 1.17 \times 10^{-1}$ M) was worked-up similarly and the extract in *n*-pentane was crystallized in MeOH. 5 g of **2a** were recovered with high purity (99 %+). Compounds **2b** and **1** were absent (Fig. S6-S8, ESI). We obtained a 75% yield for the global purification process considering the initial molar content of **2a** in CS_0 . Our electrochemical oxidative process allowed obtaining **2a** on a multigram scale without tedious chromatography step. This general electrochemical purification is conceptually extendable to other mixtures of redox active compounds (*metallocenes* and *others*) with smart tuning of E_{app} after careful CV analysis.

Formation of **2a** in multigram amount with high purity was critical to implement the modular synthesis of amphiphiles **4a-d** via the synthesis of bromophosphinoferrocenes **3a-c** (Scheme 3). These arylphosphino and alkylphosphino compounds are crystalline solids for which we report here X-ray structures. Various eclipsed and staggered conformations have been obtained, in which the distance between the halogen and phosphine functions ranges from 4.4441(6) Å in **3c** to 6.9484(15) Å in **3b** (vs 4.8723(5) Å for **3a**, see Table S3). The presence of the *tert*-butyl groups hampers a *trans*-arrangement of the functions (P-Ct-Br *ca.* 180°) in agreement with the predicted conformational properties of substituted ferrocenes.²¹



Scheme 3 Synthesis and conformation of monobromoferrocenes **3a-c**.

We achieved the introduction of boryl functions on compounds **3a-c** after Br/Li exchange (Scheme 1), to give **4a-d** in excellent yields (81-99%) except for the hindered **4d** (35%). We characterized these ambiphiles in the solid state by X-ray diffraction studies (Figure 3) and in solution by NMR (Table 1).

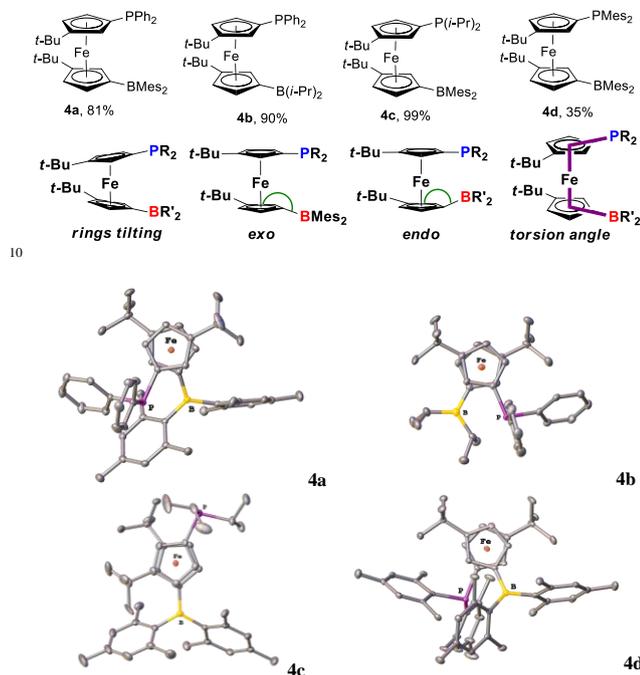


Figure 3 Ambiphiles **4a-d** with typical ferrocene deformation and molecular structures according to XRD analysis.

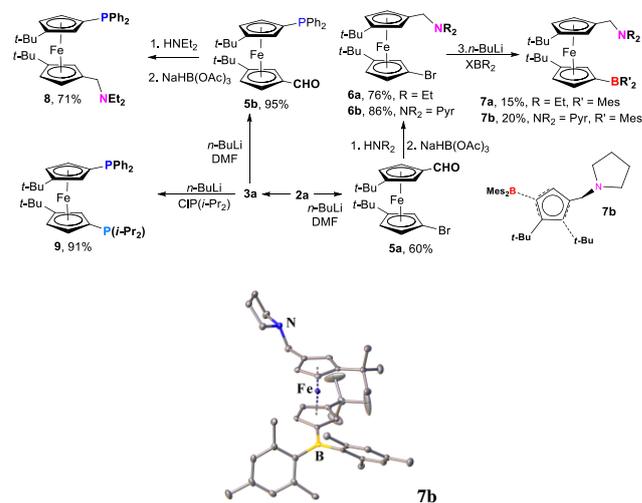
This set of new planar chiral ambiphiles allows the comparative analysis of the geometric features provided by the ferrocene platform to the antagonist functions. We reported in Table 1 the P...B distances in relation with typical deformation of functionalized ferrocenes. Bulky *tert*-butyl groups introduction in general favoured a closer proximity between the phosphine/borane pairs (comparatively the nonalkylated ambiphile **B** synthesized in Bourissou group showed dP...B = 4.876 Å and dihedral angle P...Ct(1)...Ct(2)...B = 57.80 °). However, this was not the case for **4c** in which is conserved the

cisoid vicinal arrangement of *t*-Bu groups found for its bromide precursor **3b** (Scheme 3). X-ray and solution NMR did not indicate P→B pairs closing for **4a-d**.²² Mesityl groups on boron are clearly responsible for *exo* deviation of the Cp–B bond. Less sterically hindering isopropyl groups placed on boron atom conversely induces an *endo* deviation of the Cp–BR₂ bond of 6.6(4)°. It prompted also the shortest P...B distance observed for this class of compounds, up to now, with a d P...B = 4.106 (3) Å. Pyramidalisation of the boron atom was not observed, since the sum of the three angle around the boron atom exceed 359 °, excluding net Fe→B interactions.²³

Table 1 NMR and X-ray features of **4a-d** (P, B) ambiphiles.

	4a	4b	4c	4d
³¹ P NMR δ (ppm)	−18.0	−17.0	−1.8	−34.4
¹¹ B NMR d (ppm)	80.1	79.0	80.0	80.0
d P...B (Å)	4.6018(17)	4.106(3)	6.731(3)	4.453(4)
ring tilting Cp//Cp (°)	7.75(6)	1.98(9)	2.58(13)	5.3(2)
Cp–BR ₂ <i>exo/endo</i> (°)	13.65(14)	6.6(4)	5.8(3)	11.9(7)
	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>exo</i>
P...Ct(1)...Ct(2)...B (°) ^c	42.37(5)	52.99(8)	150.20(5)	46.04(10)

To further illustrate the potential of this synthetic methodology we synthesized from **2a** the bifunctional ferrocene hybrids (N, B) **7a-b**, (P, N) **8**, and (P, P') **9** (Scheme 4). ¹¹B (δ 87-88) in solution indicates open Lewis pairs configuration for **7a-b** that is consistent with the solid state XRD refined for **7b** in which dN...B = 7.506(2) Å with an angle C^N...Ct(1)...Ct(2)...B = −145.19 (6°) similar to the configuration found for **4c**. However, we could determine rarely examined ¹⁵N NMR for both **6a** (δ−327.1) and **7a** (δ−329.8), this resulted in a notable Δδ +2.7 ppm low field shift that is consistent with net electron deshielding at N nuclei. This shift is remarkable since previously Δδ lesser than −0.7 ppm have been found after the *ortho*-phosphination of the cousin *tert*-butylated bis-(diethylamino)methylferrocene (δ−327.8) leading to 1,2-(P, N)-ferrocene derivatives (δ−327.2).²⁴



Scheme 4 Synthesis of *tert*-butylated 1,1'-planar chiral hybrids **7a-b**, **8**, **9**.

Overall, we have delivered a robust, fully diastereoselective, method to provide new 1,1'-planar chiral (P, B)-ferrocene ambiphiles, for which scale up in multigram amount was secured by a smart electrochemical purification mode taking into profit

ferrocene backbone redox properties. The extension to a new class of (N, B)-ferrocene amphiphiles, and (P, P)- and (P, N)-hybrids (potentially hemilabile compounds) illustrates the general interest of this synthetic chemistry. We currently investigate this constrained new class of compounds, as well as other analogues, for their coordination as Lewis pair and intramolecular cooperative chemical reactivity.

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† CCDC numbers: **3a**: 1532854, **3b**: 1532855, **3c**: 1532856, **4a**: 1532857, **4b**: 1532859, **4c**: 1532860, **4d**: 1532861, **7b**: 1532862.

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- 24 F. Allouch, N. Dwadnia, N. V. Vologdin, Y. V. Svyaschenko, H. Cattey, M.-J. Penouilh, J. Roger, D. Naoufal, R. Ben Salem, N. Pirio and J.-C. Hierso, *Organometallics* 2015, **34**, 5015.